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### A Study of Oxomolybdenum Chelate Compounds of Oxidation States (V) and (IV) When Prepared by Photochemical Reduction of Oxomolybdenum (VI) Complexes in Ethanol Under Inert Atmosphere and by Chemical Reduction

Richard Donald Dendinger

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A STUDY OF OXOMOLYBDENUM CHELATE COMPOUNDS OF OXIDATION  
STATES (V) AND (IV) WHEN PREPARED BY PHOTOCHEMICAL REDUCTION OF  
OXOMOLYBDENUM(VI) COMPLEXES IN ETHANOL UNDER INERT ATMOSPHERE AND  
BY CHEMICAL REDUCTION

BY

RICHARD DONALD DENDINGER

A thesis submitted  
in partial fulfillment of the requirements for the  
degree Doctor of Philosophy, Major in  
Chemistry, South Dakota  
State University

1974



100

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BY CHEMICAL REDUCTION

This thesis is approved as a creditable and independent  
investigation by a candidate for the degree, Doctor of Philosophy,  
and is acceptable for meeting the thesis requirements for this  
degree, but without implying that the conclusions reached by the  
candidate are necessarily the conclusions of the major department.

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To my many friends at South Dakota State University who truly have made Brookings a home away from home to which I shall always look forward to returning;

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I have many reasons to give thanks.

May the many of you who read this consider yourself an integral part of it and accept my gratitude.

RD

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BY CHEMICAL REDUCTION

Abstract

RICHARD DONALD DENDINGER

Under the supervision of Dr. Henry Gehrke, Jr.

A photolysis system was designed for meticulous exclusion of oxygen and moisture. Photolyzed ethanol solutions of dioxobis(acetylacetonato)-molybdenum(VI),  $\text{MoO}_2(\text{acac})_2$ , were studied via preparation of derivatives with several uninegative bidentate ligands (chelH, cysteine was designated  $\text{cystH}_2$ ) and pyridine(py). Infrared spectroscopy was a useful tool in identifying these compounds.

An oxomolybdenum(IV) compound,  $\text{MoO}(\text{dtc})_2$  was isolated from the red photolyzed solution when dtc was the N,N-diethyldithiocarbamate ion. Tropolone, 8-hydroxyquinoline, N,N-diethyldithiocarbamate, and cysteine formed products formulated as the dioxo bridged molybdenum(V) compounds,  $\text{Mo}_2\text{O}_4(\text{chel})_2$ . Acetylacetone, tropolone, 8-Hydroxyquinoline and N,N-diethyldithiocarbamate, formed derivatives formulated as the monooxo bridged molybdenum(V) compounds,  $\text{Mo}_2\text{O}_3(\text{chel})_4$ .

When pyridine was added to the photolyzed solution the product  $\text{Mo}_2\text{O}_4(\text{chel})_2(\text{py})_2$ , where chel was the acetylacetonate ion, was isolated. This product was also prepared by refluxing an ethanol-pyridine solution of dioxobis(acetylacetonato)molybdenum(VI). Both pyridine and 2,2'-bipyridine formed apparent polymeric products with the former

compound formulated as  $\text{MoO}_2(\text{OH})(\text{py})_{0.8}$ . The pyridine product was also obtained from the reflux of an ethanol-pyridine- $\text{MoO}_2(\text{acac})_2$  mixture. Photolysis of an ethanol suspension of the diethyldithiocarbamate compound,  $\text{MoO}_2(\text{dtc})_2$  resulted in an unique, air stable, pressure sensitive green product with the stoichiometry  $3 \text{ Mo}_2\text{O}_3(\text{dtc})_4 \cdot \text{Mo}_2\text{O}_4(\text{dtc})_2$ . Photolysis of an ethanol suspension of a solvated form of  $\text{Na}_2\text{Mo}_2\text{O}_5(\text{cyst})_2(\bullet\text{H})_2$  where cyst is the dinegative cysteinate anion, resulted in a solvated form of the product,  $\text{Na}_2\text{Mo}_2\text{O}_4(\text{cyst})_2$ .

The type and amount of product formed from the red photolyzed solution established that the reduced molybdenum species in ethanol solution had one acetylacetonate ligand attached to each metal atom. The second acetylacetonate unit was proposed to have been oxidized in the photo-oxidation-reduction process. Various other ethanol and aqueous solution and suspension systems were investigated by the photochemical method. Only ethanol solutions resulted in conclusive photochemical reduction.

Chemical methods were utilized to prepare the pyridine products  $\text{Mo}_2\text{O}_5(\text{acac})_2(\text{py})_2$  and  $(\text{pyH})_4 (\text{Mo}_8\text{O}_{26})$ . The tropolonate(trop) compound  $\text{MoO}_2(\text{trop})_2$  was synthesized and the compound  $\text{Mo}_2\text{O}_4(\text{dtc})_2$  was obtained by refluxing aqueous  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ . The many oxygen bridged molybdenum(V) complexes, especially those containing sulfur ligands, were significant to molybdoenzyme chemistry.

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## INTRODUCTION

There have been only limited studies in the general field of transition metal compound photo-oxidation-reduction and a definite void was observed where photo-redox of molybdenum chelates was involved.<sup>1</sup> Although some lower oxidation state molybdenum compounds had been prepared by chemical reduction, reports of preparative procedures based on photochemical reduction were notably absent.

Preliminary work conducted at South Dakota State University indicated that oxobis(acetylacetonato)molybdenum(VI) was photosensitive. Photolysis of ethanol solutions of this compound resulted in a red solution which proved to be a source of a lower oxidation state oxo-molybdenum compound,  $\mu$ -oxo-dioxotetrakis(acetylacetonato)dimolybdenum(V).

The preparation of a molybdenum species in a maximum photoreduced state was the first objective. In order to satisfy the further objective of identifying this molybdenum species in solution, an investigation of their chemical nature was carried out. This was accomplished by preparing derivatives utilizing several chelating agents including acetylacetone, 8-hydroxyquinoline, tropolone, sodium diethyldithiocarbamate, cysteine, pyridine, and bipyridine.

Stimulation to these objectives was furnished by recent proposals<sup>96</sup> which suggest that the oxidation states  $\text{Mo}^{\text{V}}$ ,  $\text{Mo}^{\text{IV}}$ , and  $\text{Mo}^{\text{III}}$  may be involved in biological nitrogen fixation. Since some microorganisms fix dinitrogen in illuminated surroundings,<sup>71</sup> the need for studying model systems which can directly photoenergize the reduction of molybdenum(VI) was also considered a motive for this investigation.

## HISTORICAL

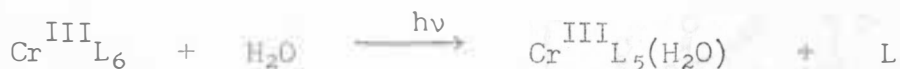
Photochemistry Involving Coordinated Transition Metal Inorganic and Organometallic Compounds.

The field of photochemistry involving transition metal coordination compounds which are sensitive to visible and near-ultraviolet radiation is, by comparison to organic photochemistry, a relatively undeveloped field. Recently, several reviews on the subject have appeared in the literature<sup>1-4</sup>. A photochemical reaction occurs as one alternative, aside from radiative and non-radiative modes, to energy release following the absorption of a photon. Visible light, 800-400 nm, has an energy equivalent of 36-71 kcal mol<sup>-1</sup> while the 400-200 nm near-ultraviolet energy equivalent is 71-143 kcal mol<sup>-1</sup>. Hence, photons in these energy ranges are frequently sufficient, in a photosensitive system, to cause either homolytic or heterolytic bond cleavage. The former typically yields reduced forms of the metal as a result of such cleavage of the metal-ligand bond. Since coordination compounds are noted<sup>1</sup> to form bonds by donation of an electron pair from the ligand to the metal, homolytic cleavage, splitting of the pair, necessarily means a net gain in electron density for the metal. On the contrary, heterolytic cleavage, departure of the electron pair with the ligand, results in no net change in electron density for the metal and is indicative of substitution reactions.

Typical photochemical reactions involving coordination compounds include photosubstitution, photorearrangement, and photo-oxidation-reduction.<sup>1</sup> The type of photo-chemical reaction that a compound

undergoes shows close correlation to the energy absorbed. Photo-substitution and photorearrangement generally occur as a result of low energy absorption while photoredox occurs from high energy absorption. Typically, low energy (visible region) absorption involves electronic d-d transitions while high energy (ultraviolet region) absorption involves a partial shift in electron density or, as it is called, electronic charge transfer. The charge transfer (CT) type transition can then be subcategorized as ligand to metal (CTLM, metal reduction) or metal to ligand (CTML, metal oxidation).

Of the three types of photochemical reactions the type which has received the greatest attention is photosubstitution, a result of heterolytic bond cleavage. A much studied type of photosubstitution is aquation in systems of the type:<sup>2</sup>



where  $\text{L} = \text{NH}_3, \text{NCS}^-, \text{CN}^-$ . However, the complexes of many other metals undergo such reactions as well, e.g.  $\text{Co}^{\text{III}}, \text{Pt}^{\text{III}}, \text{Mo}^{\text{IV}}$ .<sup>2</sup>

Studies involving photorearrangements have also been subject to extensive investigation. This may be subgrouped as ligand rearrangement, racemization, geometrical isomerization, and linkage isomerization. A type of ligand rearrangement is the intramolecular reaction that occurs in mercury(II) bisdithizonates (see Fig. 1-a). Racemization is exemplified<sup>3</sup> by the reaction of the aqueous tris(oxalato)chromate(III) anion,  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$  (see Fig. 1-b). Typical geometrical isomerization is demonstrated by the cis-trans isomerization of platinum(II) bisglycinate (see Fig. 1-c) while linkage isomerization can be

demonstrated by nitro-group isomerization to a nitrito-form as in the case of the nitropentaaminecobalt(III) cation,  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$  (see Fig. 1-d).

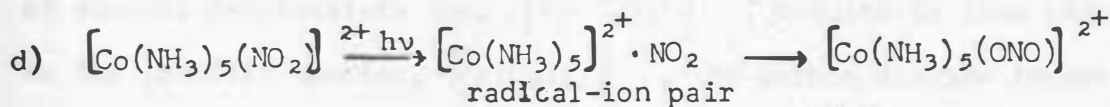
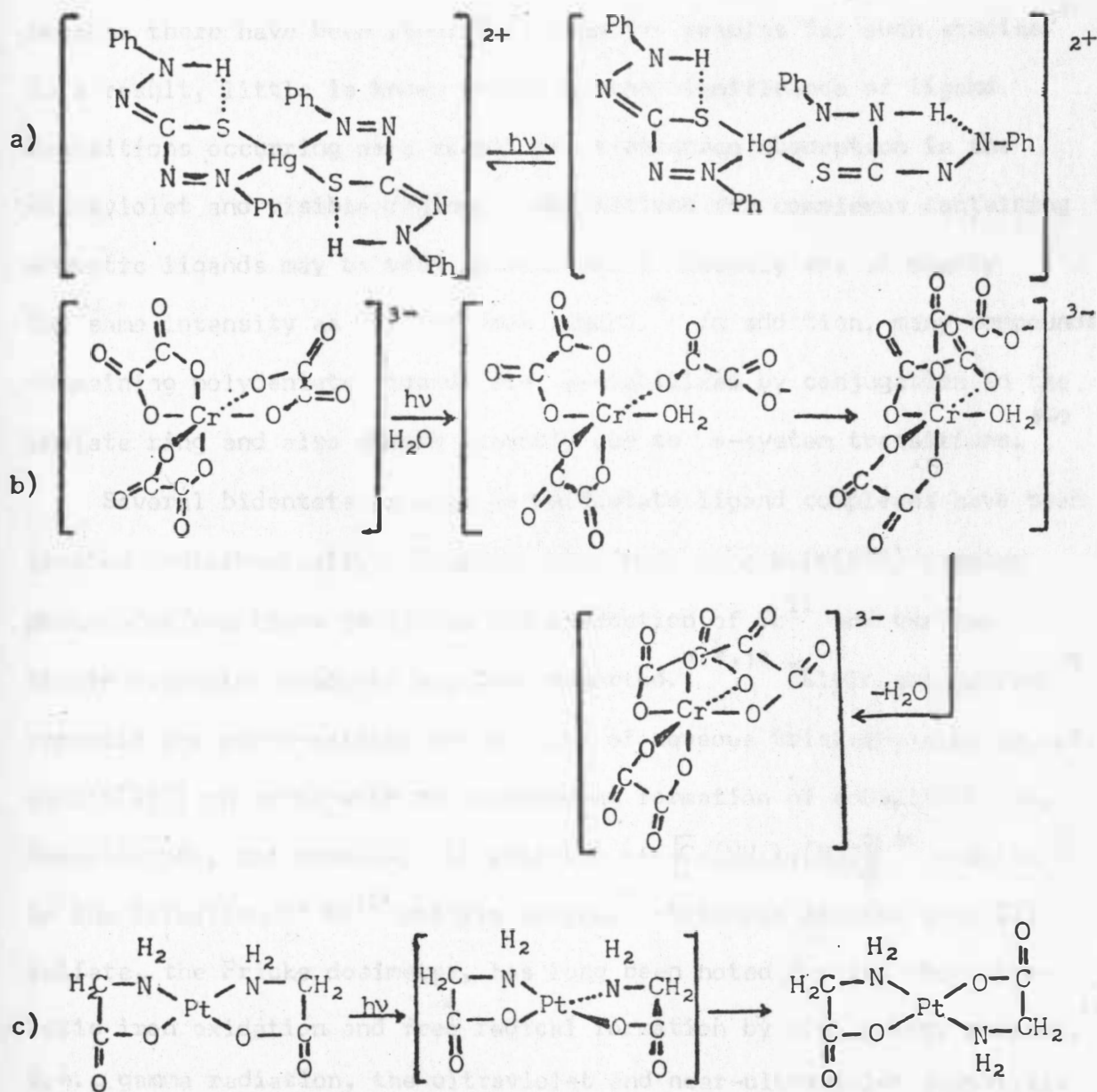


Figure 1. Photorearrangements

On the other hand, photo-redox systems have received only limited attention. Specifically, conjugated chelate compounds of transition metals have not been subjected to photochemical studies<sup>4</sup>, possibly because there have been reports of negative results for such studies.<sup>3</sup> As a result, little is known regarding the significance of ligand transitions occurring as a result of  $\pi$ -electron absorption in the ultraviolet and visible region.<sup>4</sup> Absorptions for complexes containing aromatic ligands may be very intense and frequently are of nearly the same intensity as for the free ligand.<sup>4</sup> In addition, many compounds containing polydentate ligands are  $\pi$ -stabilized by conjugation in the chelate ring and also absorb strongly due to  $\pi$ -system transitions.<sup>5-7</sup>

Several bidentate as well as unidentate ligand complexes have been studied photochemically. Considerable study on cobalt(III) complex photoredox reactions involving the production of  $\text{Co}^{\text{II}}$  and various liquid oxidation products has been reported.<sup>1, 8, 10</sup> Klein and Moeller<sup>10</sup> reported the photo-oxidation-reduction of aqueous tris(ethylenediamine)-cobalt(III) chloride with the subsequent formation of cobalt(II) ion, formaldehyde, and ammonia. Irradiation of  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$  results in the formation of  $\text{Co}^{\text{II}}$  and dinitrogen.<sup>9</sup> Although aqueous iron(II) sulfate, the Fricke dosimeter, has long been noted for its characteristic iron oxidation and free radical formation by high energy photons,<sup>11</sup> i.e., gamma radiation, the ultraviolet and near-ultraviolet photolysis of aqueous ferrioxalate ion,  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ , results in iron reduction to the iron(II) species,  $[\text{Fe}(\text{C}_2\text{O}_4)_2]^{2-}$ , and carbon dioxide formation. The latter system has been extensively studied<sup>12, 13</sup> due to its



popularity for chemical actinometry in the 250-450 nm region and is an example of photocatalyzed metal reduction in the presence of a chelating agent. The photolysis of chelated  $\beta$ -ketoenolates of iron(III) and cobalt(III) have also been reported. In each case the metal is reduced while organic species present are oxidized. Tris(acetylacetonato)cobalt(III),  $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$ , a conjugated metal chelate system, undergoes photo-redox to cobalt(II), biacetyl, and acetic acid in diethyl ether.<sup>5</sup> The photolysis of an alcoholic solution of the iron(III) tris-hexafluoroacetylacetonate,  $\text{Fe}(\text{C}_5\text{F}_6\text{HO}_2)_3$ , results in the isolation of  $\text{Fe}(\text{C}_5\text{F}_6\text{HO}_2)_2 \cdot 2 \text{C}_2\text{H}_5\text{OH}$ , the neutral ligand, and oxidized solvent.<sup>6</sup>

The photochemistry of molybdenum complexes is essentially limited to comprehensive studies of the cyanide ion complexes,  $[\text{Mo}(\text{CN})_8]^{4-}$  and  $[\text{Mo}(\text{CN})_3]^{3-}$ . The stable complex ion,  $[\text{Mo}(\text{CN})_8]^{4-}$ , has received most of the attention and, in fact, has been noted for its photosensitivity for several decades.<sup>14</sup> At its longer wave lengths, i.e., near 370 nm, the complex, excited through its ligand field bands, is noted to produce substitution products.<sup>15-20</sup> Prolonged irradiation in aqueous solution yields a blue product, proposed to be  $[\text{Mo}(\text{O})(\text{OH})(\text{CN})_4]^{3-}$  in solution and  $[\text{Mo}(\text{CN})_4(\text{O})_2]^{4-}$  in the solid state.<sup>15</sup> A red species, the subject of considerable disagreement, is initially formed but disappears quickly when placed in the dark. It is proposed to be  $[\text{Mo}(\text{CN})_8(\text{H}_2\text{O})_2]^{4-}$  by Jakob, et al.,<sup>16-18</sup> but this formulation is disputed by Carassiti and co-workers,<sup>21</sup> who propose that it is eight-coordinate, probably  $[\text{Mo}(\text{CN})_7(\text{H}_2\text{O})]^{3-}$ . At higher energies, i.e., 250 nm, the

reaction is proposed<sup>22</sup> to be triggered by charge transfer excitation since the redox product is determined to be  $[\text{Mo}(\text{CN})_8]^{3-}$ . The exposure of  $[\text{Mo}(\text{CN})_8]^{3-}$  to visible light results in the formation of  $[\text{Mo}(\text{CN})_8]^{4-}$  and the oxidation product oxygen, by an undetermined complex mechanism in various aqueous and/or simple alcohol media.<sup>3, 21</sup>

Reports of molybdenum blue formation from molybdenum(VI) compounds subjected to light are numerous.<sup>7, 23, 24</sup> Molybdenum blue is considered to be a mixture of molybdenum(VI) and molybdenum(V) in compounds whose stoichiometry is not well defined.<sup>25</sup>

Certain metallic acetylacetonates, i.e.,  $\text{Mo}^{\text{VI}}$  and  $\text{Co}^{\text{III}}$ , have been shown to undergo auto-oxidation-reduction when irradiated with visible light.<sup>26</sup> These compounds are useful in initiating polymerization reactions and simultaneously result in reduced metallic species.<sup>1</sup> Bernal<sup>27</sup> observed a slowly developing green coloration for the photosensitive solid oxomolybdenum(VI) acetylacetonate,  $\text{MoO}_2(\text{acac})_2$ , where acac is the acetylacetonate ion,  $\text{C}_5\text{H}_7\text{O}_2^-$ . These observations suggest the formation of free radicals in a redox system sensitized by charge transfer bands.<sup>1, 27</sup>

### Significant Oxomolybdenum Chelate Compounds

Chelating agents have long been recognized for their ability to stabilize otherwise unstable oxidation states of transition metals.<sup>28</sup> This stabilization is looked upon as primarily due to an increased entropy of the system, i.e., one bidentate unit replaces two unidentate units on the metal. This stabilizing effect is demonstrated by the

almost exclusive occurrence of transition metals chelated in natural systems. Thus it is logical to investigate various forms of chelated molybdenum in photochemical systems, especially since the otherwise unstable oxidation states of the metal are relevant to biological systems.

Several preparations of  $\text{MoO}_2(\text{acac})_2$  in varying degrees of purity have been reported<sup>7,29-34</sup> after initial incorrect formulation. These and other preparations of oxomolybdenum acetylacetonates are listed in Table I. Frequently the product was reported as orange-yellow which indicates the presence of a red impurity in the yellow oxomolybdenum(VI) compound.<sup>7</sup> Jones<sup>34</sup> reported that the yellow compound could be prepared without discoloration from acidic solution, i.e., nitric acid. A modification of this procedure was reported by Gehrke and Veal.<sup>7</sup> This pure yellow solid became tinged by small amounts of molybdenum blue when exposed to sunlight.<sup>7</sup> The apparent instability of the molybdenum(VI) acetylacetonate in the presence of trace amounts of acetylacetone was also observed, i.e., yellow  $\text{MoO}_2(\text{acac})_2$  became tinged with red, indicating the reducing ability of acetylacetone.<sup>7</sup>

The stable red-brown compound,  $\text{Mo}_2\text{O}_3(\text{acac})_4$ , prepared by sealed tube reaction, was found to be insoluble in solvents which dissolve the yellow compound, i.e., acetone, ethanol, chloroform, methylene chloride.<sup>7</sup> Like the xanthate analog,<sup>35</sup> the structure of the compound is proposed to be that of a bridging oxygen atom between two molybdenum atoms each of which are bonded to one terminal oxygen located cis to the bridge. Two bidentate acetylacetonate ligands complete the six


Table I. Selected Preparations of Oxomolybdenum Acetylacetonates.

<u>Reaction</u>	<u>Ref.</u>
1. $\text{MoO}_3 + \text{acacH} \longrightarrow \text{MoO}_2(\text{acac})_2$ (yellow-orange)	30
2. $\text{MoO}_3 + \text{acacH} \xrightarrow{\text{reflux}} \text{MoO}_2(\text{acac})_2$ (yellow-orange)	29-32
3. $\text{MoO}_2\text{Cl}_2 + \text{acacH} \xrightarrow{20^\circ\text{C}} \text{MoO}_2(\text{acac})_2$ (yellow-orange)	33
4. $\text{Mo}_7\text{O}_{24}^{6-} + \text{acacH} \xrightarrow[2.\text{HNO}_3]{1.\text{NH}_3} \text{MoO}_2(\text{acac})_2$ (yellow)	34
5. $\text{MoO}_4^{2-} + \text{acacH} \xrightarrow[\text{pH} = 1]{\text{HCl}} \text{MoO}_2(\text{acac})_2$ (yellow)	7
6. $\text{MoO}_2(\text{acac})_2 + \text{acacH} \xrightarrow[2.\text{ reflux}]{1.\text{ Zn dust}} \text{Mo}_2\text{O}_3(\text{acac})_4$ (red-brown)	36
7. $\text{MoO}_2(\text{acac})_2 + \text{acacH} \xrightarrow[\text{sealed tube}]{210^\circ\text{C}} \text{Mo}_2\text{O}_3(\text{acac})_4$ (red-brown)	7

$\text{acac}^- = \text{acetylacetonate}, \text{C}_5\text{H}_7\text{O}_2^-$

coordination sites on each metal atom.

The yellow 8-hydroxyquinolate of oxomolybdenum(VI),  $\text{MoO}_2(\text{oxine})_2$ , where oxine is the 8-hydroxyquinolate ion,  $\text{C}_9\text{H}_6\text{NO}^-$ , is used as a standard method for quantitative determination of the metal.<sup>37,38</sup> The crystal structure of this compound identified the terminal oxygen atoms at octahedral cis-positions.<sup>39</sup> The preparations and reactions of this and other oxomolybdenum 8-hydroxyquinolates are listed in Table II.

The dinuclear oxomolybdenum(V) 8-hydroxyquinolates, containing a single bridging oxygen with the proposed formulation,  $\text{Mo}_2\text{O}_3(\text{oxine})_4$  have been prepared in color variations from maroon to black.<sup>40-43</sup> These variations in coloration may be at least somewhat related to the many possible isomers with this geometry.<sup>42</sup> A dinuclear oxomolybdenum(V) 8-hydroxyquinolate with two oxygen bridges was prepared when the neutral donor ligands pyridine,  $\beta$ -picoline, or  $\gamma$ -picoline were present.<sup>44</sup> These compounds represent an additional dinuclear category which is proposed to have two bridging oxygen atoms, and one terminal oxygen on each molybdenum atom oriented perpendicular to the "plane" of the dioxo bridge, i.e., a  moiety.

A reported preparation of an oxomolybdenum(IV) 8-hydroxyquinolate in pyridine solution was supported by a pink solution coloration and electronic spectra similar to those obtained for the dithiocarbamate and diethyldithiophosphate analogs.<sup>45</sup>

Since the sulfur-metal bond is proposed<sup>49</sup> to be especially

Table II. Selected Preparations of Oxomolybdenum 8-Hydroxyquinolates.

Reaction	Ref.
1. $\text{MoO}_4^{2-}$ (or $\text{Mo}_7\text{O}_{24}^{6-}$ ) + oxineH $\xrightarrow{\text{pH} = 3-8}$ $\text{MoO}_2(\text{oxine})_2$ 37,38,46-48 (yellow)	
2. $\text{MoCl}_5$ + oxineH $\xrightarrow{\text{pH} = 3}$ $\text{Mo}_2\text{O}_3(\text{oxine})_4$ 40 (deep violet)	
3. $(\text{NH}_4)_2\text{MoOCl}_5$ + oxineH $\xrightarrow[100^\circ\text{C}]{\text{pH} = 4}$ $\text{Mo}_2\text{O}_3(\text{oxine})_4 \cdot \text{H}_2\text{O}$ 41 (black)	
4. $\text{K}_3\text{MoCl}_6$ + oxineH $\xrightarrow{50^\circ\text{C}}$ $\text{Mo}_2\text{O}_3(\text{oxine})_4$ 42 (maroon)	
5. $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ + oxineH $\longrightarrow$ $\text{Mo}_2\text{O}_3(\text{oxine})_4 \cdot \text{H}_2\text{O}$ 43 (dark violet)	
6. $\text{MoCl}_5$ + oxineH + X $\xrightarrow{\text{reflux}}$ $\text{Mo}_2\text{O}_4(\text{oxine})_2(\text{X})_2$ 44 (orange-red) (X = pyridine, $\beta$ -picoline, or $\gamma$ -picoline)	

oxine<sup>-</sup> = 8-hydroxyquinolate,  $\text{C}_9\text{H}_6\text{NO}^-$ .

significant in biological systems containing molybdenum, chelate compounds with sulfur available to the metal have been of great interest. The oxomolybdenum dialkyldithiocarbamates have been prepared in several metal oxidation states. The preparations of these compounds are listed in Table III. The dioxomolybdenum(VI) compound,  $\text{MoO}_2(\text{dtc})_2$ , where dtc is the dialkyldithiocarbamate ion,  $\text{R}_2\text{NCS}_2^-$ ,  $\text{R} = \text{C}_2\text{H}_5$ , was also determined to have the cis-structure.<sup>50</sup> It was initially prepared containing a red impurity but, as in the case of the acetylacetonate analog,<sup>7</sup> pH control eliminated the orange coloration.<sup>51</sup>

The violet oxomolybdenum(V) dinuclear compounds,  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ , with  $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , were prepared from several molybdenum starting materials.<sup>45, 52-54</sup> The X-ray crystal structure of the ethyl xanthate analog of  $\text{Mo}_2\text{O}_3(\text{dtc})_4$  determined the presence of terminal oxygen atoms cis to a linear monooxygen bridge, i.e.,  $\begin{array}{c} \text{O} \\ \parallel \\ \text{Mo} \end{array} - \text{O} - \begin{array}{c} \text{O} \\ \parallel \\ \text{Mo} \end{array}$ .<sup>35</sup> The ethyl xanthate ion,  $\text{C}_2\text{H}_5\text{OCS}_2^-$ , acts as a bidentate sulfur coordinated ligand in the compound.

Where reduction of a molybdenum(VI) reactant species is necessary, the dithionite ion,  $\text{S}_2\text{O}_4^{2-}$ , is an effective reductant.<sup>53</sup> In fact, under a nitrogen atmosphere a pink oxomolybdenum(IV) compound,  $\text{MoO}(\text{dtc})_2$ , with  $\text{R} = \text{C}_2\text{H}_5$  was obtained by dithionite ion reduction.<sup>45</sup> This compound is proposed to contain only a single terminal  $\text{Mo} = \text{O}$  bond.

Cysteine and cysteine related molybdenum complexes show the greatest relationships to nitrogenase and other enzyme systems containing molybdenum since they are protein complexes utilizing both sulfhydryl sulfur and amine nitrogen at the coordination site.<sup>49</sup> The

Table III. Selected Preparations of Oxomolybdenum Dialkyldithio-  
carbamates.

<u>Reaction</u>	<u>Ref.</u>
1. $\text{MoO}_4^{2-} + \text{Nadtc}^* \xrightarrow{\text{H}^+} \text{MoO}_2(\text{dtc})_2$ (orange-yellow)	52-54
2. $\text{MoO}_4^{2-} + \text{Nadtc}^{**} \xrightarrow{\text{pH } 5.5} \text{MoO}_2(\text{dtc})_2$ (yellow)	51
3. $\text{MoO}_4^{2-} + \text{Nadtc}^{**} \xrightarrow{\text{S}_2\text{O}_4^{2-}} \text{Mo}_2\text{O}_3(\text{dtc})_4$ (violet)	53
4. $(\text{NH}_4)_2\text{MoOCl}_5 + \text{Nadtc}^{**} \longrightarrow \text{Mo}_2\text{O}_3(\text{dtc})_4$ (violet)	54
5. $\text{K}_2\text{MoOCl}_5 + \text{Nadtc}^{**} \longrightarrow \text{Mo}_2\text{O}_3(\text{dtc})_4$ (violet)	52
6. $\text{MoO}_4^{2-} + \text{Nadtc}^{**} \xrightarrow[\text{S}_2\text{O}_4^{2-}]{\text{N}_2} \text{MoO}(\text{dtc})_2$ (pink)	45

$\text{dtc}^-$  = dialkyldithiocarbamate,  $\text{R}_2\text{NCS}_2^-$

\*  $\text{R} = \text{CH}_3$  or  $\text{C}_2\text{H}_5$

\*\*  $\text{R} = \text{C}_2\text{H}_5$



preparations of several selected oxomolybdenum cysteine and cysteine related compounds are listed in Table IV. Kay and Mitchell<sup>55</sup> prepared the first cysteine complex of molybdenum. It was formulated as  $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{cyst})_2] \cdot 5\text{H}_2\text{O}$ , a molybdenum(V) compound, which contains the



and five uncoordinated water molecules as determined from its X-ray crystal structure.<sup>56,57</sup> A dithio bridged cysteine analog,

$\text{Na}_2\text{Mo}_2\text{O}_2\text{S}_2(\text{cyst})_2 \cdot 4\text{H}_2\text{O}$  was prepared from the above compound<sup>58</sup> after Spence<sup>59</sup> discussed the possibility of sulfur bridged species in

molybdenum enzymes. Both yellow molybdenum(VI) and orange molybdenum(V) cysteinates were prepared in aqueous solutions.<sup>60</sup> The oxomolybdenum(VI) compound,  $\text{Na}_2\text{MoO}_2(\text{cyst})_2 \cdot \text{DMF}$  was isolated from N,N-dimethyl-formamide(DMF) solution.<sup>61</sup>

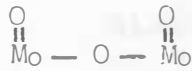


Violet oxomolybdenum(V) cysteine methyl and ethyl esters of formulation  $\text{Mo}_2\text{O}_3(\text{cystR})_4$  were isolated,<sup>61,62</sup> where cystR is the alkylcysteinate. The compound is proposed to contain the  moiety with bidentate cysteine ester ligands. Organic solvents cause these compounds to expel ligands to become the yellow bridged complexes of formulation  $\text{Mo}_2\text{O}_4(\text{cystR})_2$ . The cysteine methyl ester complex was determined by X-ray crystal structure to contain a dioxo bridged moiety, , and bidentate ligand, i.e., molybdenum coordination through ionized sulfhydryl sulfur and amine nitrogen.<sup>63</sup> In addition, the dithio bridged cysteine ester compound,  $\text{Mo}_2\text{O}_2\text{S}_2(\text{cystCH}_3)_2$  was prepared.<sup>61</sup> Again the crystal structure revealed the bidentate nature of the ligand as well as a dithio bridged moiety, .

Table IV. Selected Preparations of Oxomolybdenum Cysteinate and Cysteinate Esters.

<u>Reaction</u>	<u>Ref.</u>
1. $\text{MoO}_4^{2-} + \text{cystH}_2 \cdot \text{HCl} \xrightarrow[\text{N}_2\text{H}_2 \cdot \text{H}_2\text{O}]{\text{S}_2\text{O}_4^{2-} \text{ or}} \text{Na}_2 [\text{Mo}_2\text{O}_4(\text{cyst})_2] \cdot 5\text{H}_2\text{O}$ (orange)	55-57
2. $\text{MoO}_4^{2-} + \text{cystH}_2 \cdot \text{HCl} \xrightarrow{\text{(excess)}} \text{Na}_2 [\text{Mo}_2\text{O}_4(\text{cyst})_2] \cdot 5\text{H}_2\text{O}$ (orange)	55
3. $\text{MoO}_4^{2-} + \text{cystH}_2 \xrightarrow{\text{DMF}} \text{Na}_2 [\text{MoO}_2(\text{cyst})_2] \cdot \text{DMF}$ (yellow)	61
4. $\text{MoCl}_5 + \text{cystRH} \cdot \text{HCl} \xrightarrow{\text{H}_2\text{O}} \text{Mo}_2\text{O}_3(\text{cystR})_4$ (R = CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> ) (violet)	61,62
5. $\text{Mo}_2\text{O}_3(\text{cystR})_4 \xrightarrow[\text{solvents}]{\text{organic}} \text{Mo}_2\text{O}_4(\text{cystR})_2$ (R = CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> ) (yellow)	62
6. $\text{MoO}_4^{2-} + \text{cystRH} \cdot \text{HCl} \xrightarrow{\text{(R = CH}_3, \text{C}_2\text{H}_5)}} \text{MoO}_2(\text{cystR})_2$ (yellow)	61,62
7. $\text{Na}_2 [\text{Mo}_2\text{O}_4(\text{cyst})_2] + \text{H}_2\text{S} \xrightarrow{\text{(red-orange)}} \text{Na}_2 [\text{Mo}_2\text{O}_2\text{S}_2(\text{cyst})_2] \cdot 4\text{H}_2\text{O}$	58
8. $\text{MoO}_4^{2-} + \text{H}_2\text{S} + \text{cystRH} \cdot \text{HCl} \xrightarrow{\text{(R = CH}_3)}} \text{Mo}_2\text{O}_2\text{S}_2(\text{cystR})_2$ (yellow-brown)	61

$\text{cyst}^{2-}$  = cysteinate, C<sub>3</sub>H<sub>5</sub>NO<sub>2</sub>S<sup>2-</sup>

$\text{cystR}^-$  = alkyl cysteinate, C<sub>3</sub>H<sub>5</sub>NO<sub>2</sub>SR<sup>-</sup>

DMF = dimethylformamide

Table IV. Selected Preparations of Oxomolybdenum Cysteinate and Cysteinate Esters.

<u>Reaction</u>	<u>Ref.</u>
1. $\text{MoO}_4^{2-} + \text{cystH}_2 \cdot \text{HCl} \xrightarrow[\text{N}_2\text{H}_2 \cdot \text{H}_2\text{O}]{\text{S}_2\text{O}_4^{2-} \text{ or}} \text{Na}_2 [\text{Mo}_2\text{O}_4(\text{cyst})_2] \cdot 5\text{H}_2\text{O}$ (orange)	55-57
2. $\text{MoO}_4^{2-} + \text{cystH}_2 \cdot \text{HCl} \xrightarrow{(\text{excess})} \text{Na}_2 [\text{Mo}_2\text{O}_4(\text{cyst})_2] \cdot 5\text{H}_2\text{O}$ (orange)	55
3. $\text{MoO}_4^{2-} + \text{cystH}_2 \xrightarrow{\text{DMF}} \text{Na}_2 [\text{MoO}_2(\text{cyst})_2] \cdot \text{DMF}$ (yellow)	61
4. $\text{MoCl}_5 + \text{cystRH} \cdot \text{HCl} \xrightarrow{\text{H}_2\text{O}} \text{Mo}_2\text{O}_3(\text{cystR})_4$ (R = CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> ) (violet)	61,62
5. $\text{Mo}_2\text{O}_3(\text{cystR})_4 \xrightarrow[\text{solvents}]{\text{organic}} \text{Mo}_2\text{O}_4(\text{cystR})_2$ (R = CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> ) (yellow)	62
6. $\text{MoO}_4^{2-} + \text{cystRH} \cdot \text{HCl} \xrightarrow{(\text{R} = \text{CH}_3, \text{C}_2\text{H}_5)} \text{MoO}_2(\text{cystR})_2$ (yellow)	61,62
7. $\text{Na}_2 [\text{Mo}_2\text{O}_4(\text{cyst})_2] + \text{H}_2\text{S} \longrightarrow \text{Na}_2 \text{Mo}_2\text{O}_2\text{S}_2(\text{cyst})_2 \cdot 4\text{H}_2\text{O}$ (red-orange)	58
8. $\text{MoO}_4^{2-} + \text{H}_2\text{S} + \text{cystRH} \cdot \text{HCl} \xrightarrow{(\text{R} = \text{CH}_3)} \text{Mo}_2\text{O}_2\text{S}_2(\text{cystR})_2$ (yellow-brown)	61

$\text{cyst}^{2-}$  = cysteinate,  $\text{C}_3\text{H}_5\text{NO}_2\text{S}^{2-}$

$\text{cystR}^-$  = alkyl cysteinate,  $\text{C}_3\text{H}_5\text{NO}_2\text{SR}^-$

DMF = dimethylformamide

### Nitrogenase Model Systems

Molybdenum chelation in living systems is extremely important. The metal is found in a number of sulfhydryl enzymes including xanthine oxidase,<sup>65</sup> aldehyde oxidase,<sup>66</sup> nitrate reductase,<sup>67</sup> and nitrogenase.<sup>68</sup> Especially important are the nitrogen fixing organisms which are proposed to utilize the cysteine linkage in the protein chain of nitrogenase for molybdenum bonding.

Only a few select micro-organisms have the apparent ability to convert elemental nitrogen into usable combined forms.<sup>69</sup> Legumes and certain blue-green algae<sup>70</sup> are examples of plants known to contain micro-organisms capable of such nitrogen fixation. In legumes the genus of *Rhizobium* and in blue-green algae the species *Azotobacter vinlandii* have been found to contain the essential nitrogen-fixing enzyme nitrogenase.<sup>71</sup> Even the anaerobic bacterium *Clostridium pasteurianum* has this nitrification capability.<sup>72</sup>

The nitrogenase enzyme, although not always of exactly the same composition from all sources, is known to be composed of a Mo-Fe protein and a Fe protein probably in the ratio 1:2.<sup>73</sup> The enzyme is in association-dissociation equilibrium with these component proteins.<sup>74</sup> It has been suggested that there are about 1 Mo, 16 Fe; 16 "labile sulfide", and 20 cysteine groups in the *Azotobacter* nitrogenase Fe-Mo protein.<sup>75</sup> Although no homogeneous nitrogenase preparations have been obtained, i.e., the enzyme cannot be separated from cell media, the Mo-Fe protein has been isolated by crystallization.<sup>76</sup> Reconstituted nitrogenase has been prepared from its components in a form having

purity superior to that of any native nitrogenase but with stoichiometries which do not show complete correspondence.<sup>77</sup> Although the Mo-Fe protein component is itself inactive, when recombined with the Fe protein, it is again active even when the proteins originate from somewhat different bacteria. It is this Mo-Fe protein which is thought to contain the active site for nitrogen complexation and reduction. This site is believed to consist of molybdenum, non-heme iron, "labile sulfide" and sulfhydryl groups, or perhaps a "sulfur-sulfur bridge."<sup>59, 78</sup> The presence of more than the usual amounts of sulfur in the Mo-Fe protein suggests metal-sulfur bonding.<sup>49</sup> In addition the site appears to have extreme "class b metal"<sup>79</sup> or "soft base"<sup>80</sup> character. Perhaps the most unique property is the versatility of the enzyme since it reduces acetylene, azide, nitrous oxide, and low molecular weight nitriles as well as dinitrogen. Acetylene is utilized in the standard assay approach to evaluating nitrogen fixation<sup>74</sup> but the reaction may not be analogous in bonding since it is reduced no further than ethylene. By contrast hydrazine inhibits fixation but is not itself reduced to ammonia.<sup>49</sup> The failure of nitrogenase to reduce larger substrates suggests steric limitation at the active site.

It is noted that nitrogen fixing aerobic bacteria consume much greater amounts of oxygen than other bacteria, and indeed, it is found that the Mo-Fe protein is rendered inactive for fixation by exposure to oxygen. It is reactivated only by the strong reducing agent, dithionite ion.<sup>49</sup> This reductant is apparently a universal nonbiological agent which is able to circumvent the usual electron

carriers in the nitrogenase reaction. However, the chemical mechanism for the reduction of nitrogenase still remains a mystery.

This and other circumstantial evidence has led to the investigation of many model compounds containing metals coordinated to dinitrogen<sup>81-87</sup>

as well as those containing the nitrogenase reducible substrates

mentioned above.<sup>88-90</sup> Several mononuclear models utilize molybdenum

as the transition metal,<sup>81,83,87</sup> others contain iron,<sup>85</sup> some are

dinitrogen bridged dinuclear,<sup>91,92</sup> and a few utilize two metals where

even sulfur-bridged molybdenum-iron compounds have been reported.<sup>93,94</sup>

A typical mononuclear molybdenum dinitrogen complex is

trans-Mo(N<sub>2</sub>)<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub> where Ph is the phenyl group, C<sub>6</sub>H<sub>5</sub>.<sup>83</sup>

Phosphine coordinated dinitrogen complexes have been reported<sup>81</sup> for

several other metals, i.e., Re, Co, Ir, Os, Ru, Ni. Generally the

infrared (or Raman) stretching frequency is diminished from 2331 cm<sup>-1</sup>

to 2000-2100 cm<sup>-1</sup> in compound formation.<sup>81</sup> The formation of dinitrogen

bridged dinuclear compounds is considered very important. However,

most such compounds contain two rutheniums or one ruthenium and one

osmium and show absorptions in the same regions as mononuclear compounds.

Since this further coordination of the nitrogen does little to activate

it, it is hopefully proposed that unsymmetrical double coordination of

dinitrogen might lead to activation. Indeed dinitrogen stretching

frequencies below 1900 cm<sup>-1</sup> and as low as 1680 cm<sup>-1</sup> have been reported

for a possible rhenium-molybdenum compound.<sup>95</sup> In all cases thus far

reported the nitrogen-to-metal bond has a monohapto (end on)

configuration, although some researchers<sup>49</sup> feel that dihapto (side on)

complexes may soon be prepared.

Two types of aqueous systems are known to reduce dinitrogen. One, producing hydrazine in good yield, is a solution of sodium molybdate or molybdenum oxytrichloride, titanium(III) chloride (the reductant), and substantial divalent cation, i.e., magnesium ion, essential even in nitrogenase systems.<sup>96</sup> Reduction is proposed to occur through a  $\text{Mo}^{\text{III}} \cdots \text{N} \equiv \text{N} \cdots \text{Mo}^{\text{III}}$  intermediate. Another, referred to as the Schrauzer system<sup>97</sup> utilizes sodium molybdate, ferrous sulfate, sodium dithionite, and organic thiols to prepare small amounts of ammonia at high pressure. The objective has always been to develop a model system where dinitrogen is reduced to ammonia under mild conditions, other than extreme ones, with non-selectivity of substrate and reversibility much like those in natural systems. Model components thus far developed tend to show only certain of these characteristics.

Concurrent with the study of nitrogen-molybdenum compounds have come attempts to develop and understand the formation of low oxidation state molybdenum chelates. Although the redox pair was earlier thought to be  $\text{Mo}^{\text{V}} \text{--} \text{Mo}^{\text{VI}}$ , it is now believed that molybdenum(IV) or perhaps even molybdenum(III), may be involved.<sup>49,96</sup> The resultant emphasis on stable forms of low oxidation state molybdenum chelates has been observed in the most recent literature.<sup>98,99</sup> Chelates have been prepared from electrolytically reduced systems, as well as by utilization of strong chemical reductants.

It is improbable that chemical model systems will duplicate the characteristics of complex protein systems. At best, simple systems,

by their sheer number, will one day serve to elucidate the more complex protein systems, and in this way lead to a more complete understanding of their function in nitrogen fixation. Thus it is reasonable to assume that contributions by those studying model systems will complement the work accomplished by those working exclusively on the natural systems to accomplish an end where man will be better able to meet the protein needs of the world for future generations.

#### Oxomolybdenum Chelate Compound Structure as Related to Infrared Spectra

In as much as the literature utilizes infrared spectroscopy as the primary means of distinguishing between the several metal-oxygen moieties found in oxomolybdenum compounds, considerable emphasis must be placed upon this diagnostic tool. The relative strengths and frequencies of absorptions below  $1100\text{ cm}^{-1}$  are used to infer the oxidation states and predict the ligand involvement in these compounds.

In addition to the frequently encountered cis-dioxo moiety,  $\text{MoO}_2^{2+}$ , of chelated organomolybdenum systems, there have been reports of a trans-dioxo moiety,  $\text{MoO}_2^{2+}$ , and an all cis-trioxo group,  $\text{MoO}_3$ . All of these structural geometries occur as part of octahedral oxomolybdenum(VI) compounds. A dinuclear oxomolybdenum(VI) compound is proposed to contain the  $\text{Mo}_2\text{O}_5^{2+}$  moiety with one bridging and four terminal oxygen atoms located such that two are bonded cis to each other on each molybdenum atom as well as cis to the linear  $\text{Mo} - \text{O} - \text{Mo}$  bridge. These and other oxomolybdenum structure deviations are listed with the corresponding infrared absorptions of specific compounds in Tables V through X.



Oxomolybdenum(V) compounds are noted for bridging structures containing either the single oxygen bridged  $\text{Mo}_2\text{O}_3^{4+}$  moiety or the double oxygen bridged  $\text{Mo}_2\text{O}_4^{2+}$  moiety. A reported oxomolybdenum(IV) complex is proposed to contain the  $\text{MoO}^{2+}$  moiety which possesses only a single terminal oxygen. Lower oxidation state oxomolybdenum compounds have not been isolated.

The infrared spectra of a number of metal complexes containing terminal  $\text{M}=\text{O}$  bonds as well as bridging  $\text{M}-\text{O}-\text{M}$  bonds were discussed by Barraclough, et. al.<sup>100</sup> In general the presence of a  $\text{M}=\text{O}$  bond was correlated with an absorption in the range  $900-1100\text{ cm}^{-1}$ . The monooxo complexes have been reported<sup>101</sup> to have a single terminal metal-oxygen stretch in the range  $900-1050\text{ cm}^{-1}$  depending upon the transition metal, the metal oxidation state, and the ligands. Most often the frequency for such compounds is observed<sup>102, 103</sup> to be near  $950\text{ cm}^{-1}$ .

Griffith and Wickins<sup>104</sup> have utilized the infrared coupled with Raman spectroscopy to distinguish between cis-dioxo and trans-dioxo species. They have found, utilizing X-ray crystal structure data as a reference, that cis-dioxo species have both symmetrical and asymmetrical stretching frequencies as well as a deformation frequency all active in both the Raman and infrared. On the other hand, trans-dioxo species have only a symmetrical stretching frequency active in the Raman but inactive in the infrared while the asymmetrical stretch and the deformation frequency is active in the infrared only.


It was further observed<sup>104</sup> that for metal cis-dioxo species the stretch frequencies are found near  $950$  and  $900\text{ cm}^{-1}$ , the symmetrical

and asymmetrical frequencies, respectively, while the deformation is found near  $370\text{ cm}^{-1}$ . The metal trans-dioxo species were observed<sup>104</sup> to have an asymmetrical stretch frequency near  $820\text{ cm}^{-1}$  and a deformation frequency near  $300\text{ cm}^{-1}$  in the infrared. It was proposed<sup>101, 102</sup> that for mononuclear tri-oxo species<sup>105</sup> there are two infrared active stretching frequencies, i.e., symmetric at  $880\text{ cm}^{-1}$  and asymmetric at  $830\text{ cm}^{-1}$ , as well as two infrared active deformation frequencies near  $370\text{ cm}^{-1}$ , i.e., symmetric and asymmetric.

Griffith and Hewkin<sup>106</sup> reported that dinuclear transition metal compounds with one linear oxygen bridge possess a single infrared absorption, an asymmetric stretch, near  $860\text{ cm}^{-1}$ . In nonlinear or bent dinuclear complexes, absorptions near  $550$ ,  $750$ , and  $220\text{ cm}^{-1}$  were assigned to symmetric, asymmetric, and deformation modes, respectively.<sup>101, 102</sup> Those containing the  $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{M}-\text{O}-\text{M} \end{array}$  moiety were also shown to possess an infrared absorption in the  $900\text{--}1100\text{ cm}^{-1}$  region attributed to terminal oxygen ( $\text{M}=\text{O}$ ). Infrared correlations on binuclear compounds containing a single oxygen bridge and four terminal oxygens,<sup>107</sup> are limited by the absence of significant data on compounds of this type.

However, some disagreement on infrared oxygen bridge assignments has been noted. Wing and Callahan<sup>108</sup> supported by Baran<sup>109</sup> have reported a theoretical method for correlating the  $\text{M}-\text{O}-\text{M}$  bond angle ( $\phi$ ) to both asymmetric ( $\nu^{\text{as}}$ ) and symmetric ( $\nu^{\text{s}}$ ) frequencies in the  $200\text{--}900\text{ cm}^{-1}$  range. Utilizing predicted force constants in secular equations for metal-oxygen systems, curves of expected frequencies are obtained for both single and double oxygen bridged compounds. Sample calculations

utilizing a specific metal(molybdenum) were given. The asymmetric  $M-O-M$  stretch is predicted to be at least  $215\text{ cm}^{-1}$  higher than the symmetric stretch since the  $M-O-M$  bond angle is frequently  $180^\circ$  and has not been reported less than  $115^\circ$ . Typical predicted values with bond angles in parenthesis are  $800$  and  $570\text{ cm}^{-1}$  ( $115^\circ$ ),  $860$  and  $470\text{ cm}^{-1}$  ( $130^\circ$ ),  $900$  and  $360\text{ cm}^{-1}$  ( $150^\circ$ ),  $930$  and  $200\text{ cm}^{-1}$  ( $180^\circ$ ) for  $\nu^{as}$  and  $\nu^s$ , respectively. For nearly linear single oxygen bridged compounds, the symmetric frequency is predicted to be very weak and hence is expected to be difficult to detect. It is noted that calculated frequency values tend to be least valid at higher values of  $\phi$ .

Dinuclear compounds with two oxygen bridges were assigned an infrared active asymmetric stretch frequency in the  $500-600\text{ cm}^{-1}$  region by Griffith.<sup>102</sup> In addition, those containing the  moiety were also reported to possess an infrared band in the  $900-1000\text{ cm}^{-1}$  region<sup>102</sup> assigned to  $M=O$ .

Again utilizing molybdenum as the example metal in the double oxygen bridged systems,  $M \begin{smallmatrix} \diagup O \diagdown \\ \diagdown O \diagup \end{smallmatrix} M$ , Wing and Callahan<sup>108</sup> report that the  $M-O-M$  bond angles are less than  $90^\circ$  but are not expected to decrease much below  $80^\circ$ . The additional oxygen bridge gives rise to four predicted stretch frequencies which are linear combinations of symmetric and asymmetric vibrations of the isolated monooxygen bridged species and are highly symmetry sensitive. Near an  $M-O-M$  bond angle of  $80^\circ$ , the repredicted stretch frequencies are  $780\text{ cm}^{-1}(\nu_1)$ ,  $750\text{ cm}^{-1}(\nu_3)$ ,  $640\text{ cm}^{-1}(\nu_4)$ , and  $620\text{ cm}^{-1}(\nu_2)$ . Since symmetric and asymmetric stretch assignments for the dioxo bridged species are not proposed, no such significance is attached to numerical subscripts on

the various frequency assignments. Centrosymmetric molecules containing the double oxygen bridge are predicted to lose one infrared active stretch, i.e.,  $\nu_1$  is inactive.

Many highly polymeric compounds containing both metal bridging and terminal oxygen atoms are also known. However, most of these compounds do not contain ligands, i.e., molybdenum trioxide<sup>110</sup> and the isopoly anions of vanadium(V), niobium(V), tungsten(VI), and molybdenum(VI).<sup>111</sup> The infrared spectra for bridging oxygen are typically broad and found in the 800-900  $\text{cm}^{-1}$  region<sup>112</sup> while terminal oxygen absorption is observed at higher energies for these compounds.<sup>110</sup>

Based on the reported spectra of the many chelated oxomolybdenum oxo bridged compounds (see Tables V-XI) related to this work, there appears to be considerable question about the applicability of the proposed (calculated) absorptions of Wing and Callahan.<sup>108</sup> In spite of some disparity involving oxobridging compounds, infrared spectroscopy has become a very useful tool for identification of various oxometal conformations.

There remains a need to more precisely compare general infrared spectral assignments to those of oxomolybdenum complexes of known structure. The metals vanadium, and rhenium show much similarity to the +4, +5, and +6 oxidation state chemistry of oxomolybdenum complexes. Even tungsten and niobium seem to share much of the tendency of these metals to form stable complexes only when oxygen is present at bridging or terminal sites.<sup>113</sup> For example, molybdenum(VI) and rhenium(VII) seem to almost exclusively form the cis-dioxo complexes while

molybdenum(IV) and rhenium(V) tend to form the trans-dioxo complexes.

Few monooxo complexes of molybdenum chelates have been prepared unless the halogen compounds are included. In general, such molybdenum complexes are expected to produce Mo=O stretching frequencies near  $960\text{ cm}^{-1}$  (see Table V). The unstable complex, oxobis(diethyldithiocarbamato)molybdenum(IV), absorbs with a very strong bond at  $962\text{ cm}^{-1}$ . Monooxo compounds containing halogen absorb at considerably higher frequencies.

cis-Dioxo complexes of molybdenum chelates are exclusively molybdenum(VI) compounds. The unstable bisacetylacetonate and the stable bischelate compounds: 8-hydroxyquinolines, cysteinate esters and dithiocarbamates, absorb with doublets near  $900\text{ cm}^{-1}$  (see Table VI). The higher frequency, assigned to the symmetric stretch of the MoO<sub>2</sub> group, differs by 25 to  $35\text{ cm}^{-1}$  from that of the asymmetric stretch frequency. Deformation modes are generally more difficult to assign and have infrequently been utilized as a diagnostic tool.

Very few oxomolybdenum compounds with the trans-dioxo configuration are known. The molybdenum(IV) tetracyanide complex (see Table VII) has a strong asymmetric absorption at  $826\text{ cm}^{-1}$  and shows a deformation absorption at  $317\text{ cm}^{-1}$ . The absence of the doublet absorption near  $900\text{ cm}^{-1}$  distinguishes this configuration from that of the cis-dioxo compounds.

The dinuclear chelate compounds of oxomolybdenum are almost exclusively molybdenum(V). However, two types of such compounds are observed, those with single and those with double oxygen bridges. The presence of terminal oxygens on each metal atom is always observed.<sup>102</sup>

Table V. Infrared Spectra for Oxomolybdenum(IV) Complexes.

<u>Compound</u>	<u><math>\nu(\text{Mo}=\text{O})^*</math></u>	<u>Ref.</u>
$\text{MoO}(\text{dtc})_2$	962vs	45

$\text{dtc}^-$  = diethyldithiocarbamate,  $(\text{C}_2\text{H}_5)_2\text{NCS}_2^-$ .

\* Frequency in  $\text{cm}^{-1}$  from KBr disc spectra.

Table VI. Infrared Spectra for cis-Dioxomolybdenum(VI) Complexes.

<u>Compound</u>	<u><math>\overset{s}{\nu} \text{ (Mo=O)}^*</math></u>	<u><math>\overset{as}{\nu} \text{ (Mo=O)}^*</math></u>	<u>Ref.</u>
$\text{MoO}_2(\text{acac})_2$	935vs	904vs	33,114-116
$\text{MoO}_2(\text{pacac})_2^{**}$	939vs	909vs	115
$\text{MoO}_2(\text{dpacac})_2$	931vs	909vs	115
$\text{MoO}_2(\text{oxine})_2$	924vs	898vs	48,115,116
$\text{MoO}_2(\text{dtc})_2$ (R = $\text{CH}_3$ )	912vs	876vs	54,115,117
$\text{MoO}_2(\text{dtc})_2$ (R = $\text{C}_2\text{H}_5$ )	915vs	883vs	51,52,54,115
$\text{MoO}_2(\text{dtc})_2$ (R = $n\text{-C}_3\text{H}_7$ )	909vs	875vs	54,115
$\text{MoO}_2(\text{dtc})_2$ (R = $n\text{-C}_4\text{H}_9$ )	909vs	877vs	54,115
$\text{MoO}_2(\text{cystR})_2$ (R = $\text{CH}_3$ )	910vs,dbt	880vs	61,62
$\text{MoO}_2(\text{cystR})_2$ (R = $\text{C}_2\text{H}_5$ )	900vs	868vs	62
$\text{Na}_2 \text{MoO}_2(\text{cyst})_2 \cdot \text{DMF}$	922vs	892vs	61

$\text{acac}^-$  = acetylacetonate,  $\text{C}_5\text{H}_7\text{O}_2^-$

$\text{pacac}^-$  = 1-phenyl-1,3-butanedionate,  $\text{C}_{10}\text{H}_9\text{O}_2^-$

$\text{dpacac}^-$  = 1,3-diphenyl-1,3-propanedionate,  $\text{C}_{15}\text{H}_{11}\text{O}_2^-$

$\text{oxine}^-$  = 8-hydroxyquinolate,  $\text{C}_9\text{H}_6\text{NO}^-$

$\text{dtc}^-$  = dialkyldithiocarbamate,  $\text{R}_2\text{NCS}_2^-$

$\text{cystR}^-$  = alkyl cysteinate ester,  $\text{RC}_3\text{H}_5\text{NO}_2\text{S}^-$

$\text{cyst}^{2-}$  = cysteinate,  $\text{C}_3\text{H}_5\text{NO}_2\text{S}^{2-}$

DMF = dimethylformamide

\*Frequency in  $\text{cm}^{-1}$  from nujol mull spectra

\*\*Frequency in  $\text{cm}^{-1}$  from KBr disc spectra.

Table VII. Infrared Spectra for trans-Dioxomolybdenum(IV) Complexes.

<u>Compound</u>	<u><math>\nu</math> <sup>as</sup> (Mo=O)*</u>	<u>Ref.</u>
$K_4[MoO_2(CN)_4]$	826s	102

\*Frequency in  $cm^{-1}$  from nujol mull spectra.



The single oxygen bridged molybdenum(V) chelates are proposed to have a near linear Mo-O-Mo linkage with cis-terminal oxygens such that a  $\begin{array}{c} \text{O} \\ \parallel \\ \text{Mo} \end{array} - \text{O} - \begin{array}{c} \text{O} \\ \parallel \\ \text{Mo} \end{array}$  moiety results (see Table VIII). The terminal oxygen stretch is typically a strong absorption in the 930-970  $\text{cm}^{-1}$  region<sup>54</sup> with a shoulder at just slightly shorter frequency.<sup>7</sup> The acetylacetonate,<sup>7</sup> 8-hydroxyquinolate,<sup>43</sup> dithiocarbamate,<sup>52</sup> xanthate,<sup>117</sup> and cystienate ester<sup>62</sup> complexes show these characteristic absorptions. In addition an asymmetric bridge absorption is noted near 780  $\text{cm}^{-1}$  but since it is frequently weak it is limited as a diagnostic tool. The symmetric bridge absorption was assigned to the 500  $\text{cm}^{-1}$  region by Griffith<sup>101, 102</sup> but to somewhat lower frequencies by Wing and Callahan.<sup>108</sup> The deformation mode<sup>101, 102</sup> for the oxygen bridge absorbs more strongly, but the frequency is below minimum absorptions reported by many workers,<sup>101</sup> i.e., 200  $\text{cm}^{-1}$ . Wing and Callahan<sup>108</sup> do not propose the existence of such an absorption on a theoretical basis.

Single oxygen bridged molybdenum(VI) chelates containing the  $\text{Mo}_2\text{O}_5$  moiety have been only infrequently reported (see Table IX). Observed are both symmetric and asymmetric vibrations in the 900-960  $\text{cm}^{-1}$  region.<sup>117</sup> In addition, an absorption observed near 850  $\text{cm}^{-1}$  is attributed to bridging oxygen.

Dinuclear molybdenum(V) chelates with two oxygen bridges show a terminal oxygen stretch near 970  $\text{cm}^{-1}$  and asymmetric and symmetric bridge oxygen stretch near 740  $\text{cm}^{-1}$  and 480  $\text{cm}^{-1}$ , respectively.<sup>62</sup> Typical are the oxalate-aquo, oxalate-pyridine, cysteinate, and cysteinate ester complexes of molybdenum(V) listed in Table X.

Table VIII. Infrared Spectra for Dinuclear  $\mu$ -Oxobis[oxomolybdenum(V)] Complexes.

<u>Compound</u>	<u><math>\nu^{\text{as}}</math> (Mo = O)*</u>	<u><math>\nu(\text{Mo-O-Mo})^*</math></u>	<u>Ref.</u>
$\text{Mo}_2\text{O}_3(\text{acac})_4$	958.s, 949.sh	778m, 435m	7
$\text{Mo}_2\text{O}_3(\text{oxine})_4 \cdot \text{H}_2\text{O}$	940vs		43
$\text{Mo}_2\text{O}_3(\text{dtc})_4$ (R = CH <sub>3</sub> )	930m	433m	54
$\text{Mo}_2\text{O}_3(\text{dtc})_4$ (R = C <sub>2</sub> H <sub>5</sub> )	930s, 912w	778w, 431s	51, 52, 54
$\text{Mo}_2\text{O}_3(\text{cystR})_4$ (R = CH <sub>3</sub> )	925vs, br	425w	61, 62
$\text{Mo}_2\text{O}_3(\text{cystR})_4$ (R = C <sub>2</sub> H <sub>5</sub> )	925s, dbt	425w	62
$\text{Mo}_2\text{O}_3(\text{xanR})_4$ (R = CH <sub>3</sub> )	952s, 945sh	766w, 432s	54
$\text{Mo}_2\text{O}_3(\text{xanR})_4$ (R = C <sub>2</sub> H <sub>5</sub> )	948s	766w, 431s	54, 117
$\text{Na}_2[\text{Mo}_2\text{O}_3(\text{C}_2\text{O}_4)_2(\text{C}_9\text{H}_6\text{NO})_2] \cdot 5 \text{H}_2\text{O}$	970vs		43

$\text{acac}^-$  = acetylacetonate,  $\text{C}_5\text{H}_7\text{O}_2^-$

$\text{oxine}^-$  = 8-hydroxyquinolate,  $\text{C}_9\text{H}_6\text{NO}^-$

$\text{dtc}^-$  = dialkyldithiocarbamate,  $\text{R}_2\text{NCS}_2^-$

$\text{cystR}^-$  = alkyl cysteinate ester,  $\text{RC}_3\text{H}_5\text{NO}_2\text{S}^-$

$\text{xanR}^-$  = alkyl xanthate,  $\text{ROCS}_2^-$

\*Frequency in  $\text{cm}^{-1}$  from nujol mull spectra.

Table IX. Infrared Spectra for Dinuclear  $\mu$ -Oxobis [ cis-dioxo-Molybdenum(VI) ] Complexes.

<u>Compound</u>	<u><math>\nu(\text{Mo}=\text{O})^*</math></u>	<u><math>\nu(\text{Mo}-\text{O}-\text{Mo})^*</math></u>	<u>Ref.</u>
$\text{K}_2[\text{Mo}_2\text{O}_5(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$	962vs, 917vs	851s	102, 117
$\text{Mo}_2\text{O}_5(\text{C}_5\text{H}_5)_2$	930, 920, 898	850	116-118

\*Frequency in  $\text{cm}^{-1}$  from nujol mull spectra.

Table X. Infrared Spectra for Dinuclear Di-μ-oxo-bis[oxomolybdenum(V)] Complexes.

<u>Compound</u>	<u><math>\nu(\text{Mo}=\text{O})^*</math></u>	<u><math>\nu(\text{Mo}-\text{O}-\text{Mo})^*</math></u>	<u>Ref.</u>
$\text{Mo}_2\text{O}_4(\text{cystR})_2$ (R = CH <sub>3</sub> )	978vs	739vs, 478m	62
$\text{Mo}_2\text{O}_4(\text{cystR})_2$ (R = C <sub>2</sub> H <sub>5</sub> )	980vs	735vs, 470s	62
$\text{Na}_2[\text{Mo}_2\text{O}_4(\text{cyst})_2] \cdot 5\text{H}_2\text{O}$	950vs, 930s	730s, 425s	55,58,61,62
$\text{K}_2[\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$	980vs	725s	43
$\text{Ba}[\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$	975vs	745s, 722m	102,108,117,
$(\text{pyH})_2[\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{py})_2]$	960vs	743s	43
$(\text{pyH})_2[\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$	975vs	725s	43

$\text{cystR}^-$  = alkyl cysteinate ester,  $\text{RC}_3\text{H}_5\text{NO}_2\text{S}^-$

$\text{cyst}^{2-}$  = cysteinate,  $\text{C}_3\text{H}_5\text{NO}_2\text{S}^{2-}$

py = pyridine,  $\text{C}_5\text{H}_5\text{N}$

\*Frequency in  $\text{cm}^{-1}$  from nujol mull spectra.

No trioxo mononuclear complexes of molybdenum bidentate chelates have been reported. The tridentate diethylenetriamine complex of trioxomolybdenum(VI) shows broad strong symmetric and asymmetric stretch frequencies at 876 and 825  $\text{cm}^{-1}$ , respectively (see Table XI).<sup>104</sup>

Table XI. Infrared Spectra for cis-Trioxomolybdenum(VI) Complexes.

<u>Compound</u>	<u><math>\nu</math> (MoO<sub>2</sub>)*</u>	<u>as <math>\nu</math> (MoO<sub>2</sub>)*</u>	<u><math>\nu</math> (MoO<sub>3</sub>)*</u>	<u>Ref.</u>
MoO <sub>3</sub> (dien)	876s,br	825vs,br	380s	104,120

dien = diethylenetriamine

\*Frequency in cm<sup>-1</sup> from nujol spectra.

## EXPERIMENTAL

A. Instrumental1. Infrared Spectra

The infrared spectra of all compounds were obtained from potassium bromide wafers in the region  $4000$  to  $250\text{ cm}^{-1}$ , using one percent of sample in 120 mg of potassium bromide or from nujol mulls on potassium bromide plates in the region  $4000$  to  $400\text{ cm}^{-1}$ . The spectra were obtained on a Perkin-Elmer model 521 grating spectrophotometer. Settings utilized were: slit program, in -1000; gain, 5; attenuator speed, 1100; scan time, 10 ; suppression, 5; source current, 0.8 amp.

2. Electronic Spectra

Electronic spectra were obtained in solution, on either a Beckman model DK-2A or a Varian Techtron model 635 spectrophotometer, using one centimeter silica cells.

3. X-ray Powder Diffraction Patterns

X-ray powder diffraction patterns were obtained on a Picker instrument fitted with a 180 mm Debye-Scherrer powder camera.

4. Photochemical Reaction Apparatus

The photochemical reaction apparatus used was obtained from Ace Glasz Incorporated. The power supply and photochemical immersion lamp were manufactured by the Hanovia Lamp Division of Engelhard Hanovia, Inc. The lamp was a 450 watt Hanovia high pressure quartz mercury-vapor source with 48%

of its radiated energy in the ultraviolet region, 43% in the visible region, and the remainder in the infrared region. The quartz photochemical immersion well was double-walled (completely jacketed) and designed with inlet and outlet tubes for cooling. It had a standard taper 60/50 inner joint which fit the outer joint on the single-walled borosilicate glass photochemical reaction vessel. The reaction vessel also had three standard taper 19/22 outer joints used for assembly to the specialized controlled atmosphere-solvent system used in this work (see Figure 2).

## B. Analyses

### 1. Elemental

The carbon and hydrogen analyses were performed by analysts at South Dakota State University and Galbraith Laboratories in Knoxville, Tennessee. Nitrogen analyses were performed by analysts at Galbraith Laboratories. Sodium analyses were performed by Dr. James McMullen at St. Cloud State College, utilizing a Varian Techtron model 1000 atomic absorption spectrophotometer. Molybdenum analyses were obtained by the Jones Reductor method<sup>121</sup> using ceric sulfate back titration of reduced ferric ammonium sulfate.

### 2. Oxidation State

Oxidation state determination for molybdenum was attempted by the method of Przywarska-Boniecka.<sup>122</sup> Results were not reproducible and repeatedly indicated that the organic chelates



were at least slowly oxidized by 0.1 N ceric ion. The use of chloroform or benzene to extract the organic phase did not give noticeably better results. The utilization of more dilute ceric ion, i.e., 0.025 N, 0.01 N, was also unsuccessful. As a result, considerable doubt is raised regarding the usefulness of the cerimetric method in determining molybdenum oxidation state in the presence of organic chelates.<sup>33, 197</sup>

As an example of organic chelate oxidation, the products of oxidized acetylacetone and several other oxygen-containing organic compounds have been reported<sup>123</sup> for ceric oxidation in acid solution.

A qualitative test, used to determine the presence of molybdenum(V), requires the use of two to three drops of 12 M hydrochloric acid applied directly to a few milligrams of a sample containing molybdenum.<sup>44</sup> A positive test yields a green liquid phase, probably due<sup>55</sup> to the formation of the oxopentachloromolybdate(V) anion,  $\text{MoOCl}_5^{2-}$ .

### C. Commercial Chemicals

The following list of commercial solvents were used as received:

1. Acetone from Matheson, Coleman and Bell in reagent A. C. S. grade.
2. Acetonitrile from Fisher Scientific Company in Certified A. C. S. grade.
3. Benzene from Fisher Scientific Company in Certified A. C. S. grade.

4. Carbon tetrachloride from Fisher Scientific Company in Certified A. C. S. grade.
5. Chloroform from Fisher Scientific Company in Certified A. C. S. grade.
6. Dichloromethane from J. T. Baker Chemical Company in Bakers Analyzed Reagent grade.
7. Diethyl ether (anhydrous) stored over sodium metal, from Matheson, Coleman and Bell in reagent A. C. S. grade.
8. Dimethylformamide from Aldrich Chemical Company in reagent grade.
9. Dimethyl sulfoxide from Matheson, Coleman and Bell in practical A. C. S. grade.
10. Ethanol "absolute," was utilized as received for routine experimental work. Further purification was necessary in certain photolysis systems requiring rigorous exclusion of moisture and oxygen. No 95% ethanol was used in the experimental work. Absolute ethanol was obtained from U. S. Industrial Chemicals in USP reagent grade.
11. Hexane, stored over sodium metal, from Matheson, Coleman and Bell in reagent A. C. S. grade.
12. Methanol from Mallinckrodt Chemical Works in Analytical Reagent grade.
13. Tetrachloroethane from Fisher Scientific Company in Certified A. C. S. grade.

The following list of commercial chemicals used as ligands were used as received:

14. Acetylacetone from Eastman Organic Chemicals in practical grade.
15. Benzoin-anti-oxime from Eastman Organic Chemicals.
16. Bipyridine from Eastman Organic Chemicals.
17. Cysteine free base from Sigma Chemical Company.
18. Cysteine hydrochloride from Eastman Organic Chemicals.
19. 8-hydroxyquinoline from Mallinckrodt Chemical works in Analytical Reagent grade.
20. Pyridine from Matheson, Coleman and Bell in Analyzed Reagent, A. C. S. grade.
21. Sodium N,N-diethyl dithiocarbamate from Eastman Organic Chemicals.
22. Tropolone from Aldrich Chemical Company.

The following list of commercial chemicals received general use as received:

23. Ammonium paramolybdate from Matheson, Coleman and Bell in reagent A. C. S. grade.
24. Arsenic trioxide, primary standard, from Matheson, Coleman and Bell in reagent A. C. S. grade.
25. Calcium sulfate, anhydrous 8 mesh, from Matheson, Coleman and Bell in reagent A. C. S. grade.
26. Catalyst R 3-11, BTS, copper oxide pellet catalyst for removing small amounts of oxygen from nitrogen, from Badische Anilin- and Soda-Fabrik.

27. Ceric sulfate from Fisher Chemical Company in purified grade.
28. Diethylphthalate from J. T. Baker Company in Baker grade.
29. Iron(III) ammonium sulfate from Matheson, Coleman and Bell in A. C. S. grade.
30. Iron(III) chloride from Mallinckrodt Chemical Works in Analytical Reagent grade.
31. Mercury metal from Fisher Scientific Company in Certified Reagent A. C. S. grade.
32. Mercury(II) chloride from Fisher Scientific Company in Certified A. C. S. grade.
33. Molybdenum dioxydichloride from Climax Molybdenum Company.
34. Molybdenum oxytetrachloride from Climax Molybdenum Company.
35. Molybdenum trioxide from Mallinckrodt Chemical Works in Analytical Reagent grade.
36. Phosphorus pentoxide from Matheson, Coleman and Bell in reagent A. C. S. grade.
37. Potassium oxalate from Fisher Scientific Company in Certified A. C. S. grade.
38. Sodium metal from Matheson, Coleman and Bell in reagent A. C. S. grade.
39. Sodium dithionite from Eastman Organic Chemicals in practical grade.
40. Sodium molybdate from J. T. Baker Chemical Company in Bakers Analyzed Reagent grade.

41. Zinc metal, number 30 mesh, from Matheson, Coleman and Bell in reagent A. C. S. grade.
42. Nitrogen, oil pumped, treated to remove small amounts of oxygen for some uses with the hydrogen-reduced copper oxide pellet catalyst, BTS Catalyst R3-11, from the Lindy Division of Union Carbide Corporation and supplied by Dakota Welding Supply Co., Inc., Sioux Falls, South Dakota.

D. Preparation of Compounds by Chemical Methods.

1. Potassium ferrioxalate

Potassium ferrioxalate was prepared by the method of Hatchard and Parker,<sup>13</sup> utilizing potassium oxalate and iron(III) chloride.

2. cis-Dioxobis(acetylacetonato)molybdenum(VI),  $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$

The yellow compound formulated as  $\text{MoO}_2(\text{acac})_2$  was prepared utilizing a modification of the Jones<sup>34</sup> method developed by Gehrke and Veal.<sup>7</sup> Great care was necessary in precisely controlling the pH at 1.0. Utilizing a pH meter, approximately thirteen milliliters of 6 M hydrochloric acid was required for pH adjustment of one hundred milliliters of water containing 9.70 g(0.0401 mol) of sodium molybdate,  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ . Twelve milliliters (11.7 g, 0.117 mol) of acetylacetone was allowed to react for five minutes. The fine yellow product was collected on sintered glass and immediately washed twice

with an equal volume of cold (0°C) ethanol, followed by one volume of cold (0°C) acetone. Since the compound was soluble in both solvents, especially in acetone, a large portion of the crude product was lost. However, an acetone wash was necessary in order to remove acetylacetone; i.e., the presence of unreacted acetylacetone, denoted by its odor, resulted in a blue-green discoloration of the compound. The yellow compound (4.50 g, 34.4%) was stored in foil-covered brown bottles which were vented to the air. The infrared spectrum (see Appendix Figure 5) suggested that the compound was the same as previously reported.<sup>124</sup>

Anal. Calcd. for  $C_{10}H_{14}MoO_6$ : C, 36.83; H, 4.33; Mo, 29.42.

Found: C, 36.70; H, 4.67; Mo, 30.30.

The fine yellow compound turned red-brown on standing in sealed containers under either nitrogen or air. Elimination of stray light by foil covering the sealed sample, resulted in the formation of the same red-brown product. The color change may be attributed to reducing properties of the ligand. Regardless, the continued presence of a component of air, probably oxygen, was required to prevent reduction of  $MoO_2(acac)_2$ .

After standing several hours, the mother liquor and wash from above developed well-formed yellow crystals (2.45 g, 18.7%). This compound was washed as above but with little apparent loss. The infrared spectrum verified that the crystalline solid was the same as the first compound collected above.

3. cis-Dioxobis(8-hydroxyquinolinato)molybdenum(VI),  $\text{MoO}_2(\text{C}_9\text{H}_6\text{NO})_2$ .

cis-Dioxobis(8-hydroxyquinolinato)molybdenum(VI) was prepared by modification of the method of Magee and Witwit.<sup>48</sup>

One hundred milliliters of ethanol solution containing 1.30 g (0.00896 mol) of 8-hydroxyquinoline was added to 0.75 g (0.00061 mol) of ammonium paramolybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , dissolved in twenty one milliliters of water and four milliliters of 12 M ammonia. Eight milliliters of 6 M acetic acid was added to the resulting yellow solution. A heavy yellow precipitate formed and, after isolation by filtration, washing with ethanol, and vacuum drying over phosphorus pentoxide, a yellow compound (1.76 g, 99.5%) was obtained. The infrared spectrum (see Appendix Figure 7) suggested that the yellow compound was the same as that reported previously.<sup>48</sup>

Anal. Calcd. for  $\text{C}_{18}\text{H}_{12}\text{MoN}_2\text{O}_4$  = C, 51.94; H, 2.91; Mo, 23.05. Found: C, 52.04; H, 3.05; Mo, 23.09.

4. cis-Dioxobis(tropolonato)molybdenum(VI),  $\text{MoO}_2(\text{C}_7\text{H}_5\text{O}_2)_2$ .

A yellow solid was prepared by adding 0.50 g (0.00409 mol) of tropolone in five milliliters of ethanol to 0.50 g (0.00207 mol) of sodium molybdate,  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , in five milliliters of water. The heavy yellow precipitate was washed with water and ethanol but much of the product (0.16g) was removed due to solubility in water. The infrared spectrum (see Appendix Figure 17) of the product indicates it is a mixture.

Anal Calcd. for  $C_{14}H_{10}MoO_6$ : C, 45.43; H, 2.72. Found: C, 32.94; H, 2.59.

Addition of an equal volume of ethanol to the filtrate resulted in the reprecipitation of a yellow solid. The yellow compound (0.14 g, 18%) was isolated by filtration, washed with ethanol, and allowed to dry in air. Consult the Appendix (Figure 18) for the infrared spectrum of the compound.

Comparisons of the infrared spectra of both yellow products to those of tropolone and its yellow sodium salt did not reveal conclusive evidence that the initial mixture contained ligand impurity. However, the presence of small amounts of sodium in the first product may be attributed to contamination by the yellow sodium salt,  $NaC_7H_5O_2$ .

Anal. Calcd. for  $C_{14}H_{10}MoO_6$ : C, 45.43; H, 2.72. Found: C, 43.86; H, 2.76. A duplicate reaction gave the same results.

5. cis-Dioxobis(N,N-diethyldithiocarbamato)molybdenum(VI),  
 $MoO_2(C_5H_{10}NS_2)_2$ .

cis-Dioxobis(N,N-diethyldithiocarbamato)molybdenum(VI) was prepared by the method of Jowitt and Mitchell.<sup>51</sup> Sodium molybdate,  $Na_2MoO_4 \cdot 2 H_2O$  (2.50 g, 0.0103 mol), sodium N,N-diethyldithiocarbamate,  $NaS_2CN(C_2H_5)_2 \cdot 3 H_2O$  (2.33 g, 0.0103 mol), and sodium acetate (buffer),  $NaC_2H_3O_2$  (5.55 g, 0.0408 mol), were dissolved in twenty five milliliters of water. Adjustment of the pH to 5.5 with 2 M hydrochloric acid resulted in the formation of a yellow product. A yellow compound (2.14g, 99.7%)



was isolated by filtration, washed with ethanol, washed with diethyl ether, and allowed to air dry. The infrared spectrum (see Appendix Figure 19) suggested that the compound was the same as that previously reported.<sup>51</sup>

Anal. Calcd. for  $C_{10}H_{20}MoN_2O_2S_4$ : C, 28.30; H, 4.75; Mo, 22.60.

Found: C, 28.27; H, 4.54; Mo, 22.97.

A duplicate reaction gave the same results.

6. Mixtures Containing  $\mu$ -Oxo-dioxotetrakis(N,N-diethyldithiocarbamate) dimolybdenum(V),  $Mo_2O_3(C_5H_{10}NS_2)_4$

Attempts were made to prepare  $Mo_2O_3(C_5H_{10}NS_2)_4$  by the method of Jowitt and Mitchell.<sup>51</sup> Ten grams (0.0574 mol) of sodium dithionite,  $Na_2S_2O_4$ , in fifty milliliters of water was added dropwise with stirring to a solution containing 4.84 g (0.0200 mol) of sodium molybdate,  $Na_2MoO_4 \cdot 2 H_2O$ , and 9.00 g (0.0400 mol) of sodium N,N-diethyldithiocarbamate,  $NaS_2CN(C_2H_5)_2 \cdot 3 H_2O$ , in one hundred milliliters of water. It was necessary to allow the dithionite ion reduction to proceed in the presence of air to avoid the formation of a rose product, probably  $MoO(dtc)_2$ , observed as an absorption at  $960\text{ cm}^{-1}$  in the infrared spectrum.<sup>45</sup> However, exposure of the reaction mixture to air resulted in weak absorptions at 881 and  $912\text{ cm}^{-1}$  which suggest the formation of some  $MoO_2(dtc)_2$ . A violet product (6.80 g, 81.6%) was isolated by filtration, washed with water, and vacuum dried over phosphorus pentoxide. Consult the Appendix (Figure 24) for the infrared spectrum of the

compound.

Anal. Calcd. for  $C_{20}H_{40}Mo_2N_4O_3S_8$ : Mo, 23.04. Found: Mo, 23.19.

The violet product was unstable upon prolonged air exposure, slowly turning brown (four days) and finally yellow (thirty days). No decomposition was noted, however, when the violet solid was stored in capped vials.

Modification in the amount of sodium dithionite used did not improve the purity of products collected. Using the same reactants in different ratios, in a procedure utilized by Moore and Larson,<sup>54</sup> impure products were also collected.

7. Oxobis(N,N-diethyldithiocarbamato)molybdenum(IV),  $MoO(C_5H_{10}NS_2)_2$ .

A modification of the method of Jowitt and Mitchell<sup>45</sup> was used to prepare oxobis(N,N-diethyldithiocarbamato)molybdenum(IV). The same reactants utilized in the preparation of  $Mo_2O_3(dtc)_4$  (Experimental section D part 6) were used to prepare  $MoO(dtc)_2$ . Five grams (0.0287 mol) of sodium dithionite,  $Na_2S_2O_4$ , in twenty-five milliliters of water was added quickly to a solution containing 2.42 g (0.0100 mol) of sodium molybdate,  $Na_2MoO_4 \cdot 2 H_2O$ , and 4.50 g (0.0200 mol) of sodium N,N-diethyldithiocarbamate,  $NaS_2CN(C_2H_5)_2 \cdot 3 H_2O$ , in fifty milliliters of water. In order to avoid air oxidation of  $MoO(dtc)_2$ , the container was flushed with nitrogen and sealed to exclude air during the six-day reaction. A pink compound (2.47 g, 60.5%) was isolated by filtration under nitrogen; washed successively under nitrogen with water, ethanol, and diethyl ether; and dried in a

nitrogen stream. An infrared spectrum (see Appendix Figure 21) was obtained immediately. The compound was stored in sealed glass ampoules under nitrogen.

Anal. Calcd. for  $C_{10}H_{20}MoN_2OS_4$ : C, 29.40; H, 4.94; Mo, 23.49; N, 6.86. Found: C, 28.85; 4.84; Mo, 24.60; N, 6.75.

Upon exposure to air for a few minutes, the pink compound became violet and, as observed for impure  $Mo_2O_3(dtc)_4$ , the violet product then turned brown and finally yellow after several days. This color change sequence was followed by infrared spectroscopy. The band at  $960\text{ cm}^{-1}$  diminished in strength as the pink compound became violet. A band at  $928\text{ cm}^{-1}$  with increasing strength, was observed as the violet coloration became predominant. Then as the violet product became brown the band at  $960\text{ cm}^{-1}$  was absent, the  $928\text{ cm}^{-1}$  absorption was very weak, and a doublet at  $881$  and  $912\text{ cm}^{-1}$  was the predominant absorption. After the brown product became yellow only the later doublet was observed in the infrared spectrum. The necessity of air for the above sequential reactions was verified. The pink compound was stable only under nitrogen in sealed glass ampoules.

8. Di- $\mu$ -oxobis[oxo-N,N-diethyldithiocarbamatomolybdenum(V)],  
 $Mo_2O_4(C_5H_{10}NS_2)_2$ .

One gram (0.00120 mol) of the impure violet compound,  $Mo_2O_3(C_5H_{10}NS_2)_4$ , prepared by dithionite ion reduction (Experimental section D part 6), was used as the reactant in this preparation. The insoluble violet solid was suspended in

fifty milliliters of water and refluxed open to the air. Although no noticeable color change was observed in the first few hours, the slurry slowly turned brown. After eleven hours the observed color of the suspended solid was gold. A yellow solid (0.15 g, 23%) was isolated by filtration after fifteen hours, immediately washed successively with boiling water, ethanol, and then diethyl ether, and dried under vacuum over phosphorus pentoxide. The infrared spectrum (see Appendix Figure 38) was obtained immediately. When the yellow product was allowed to stand in air it slowly turned brown, but washing with either ethanol or diethyl ether removed the dark coloration and resulted in a violet wash solution in each case. In order to avoid decomposition, the compound was sealed in glass ampoules until an elemental analysis could be obtained. Anal. Calcd. for  $C_{10}H_{20}Mo_2N_2O_4S_4$ : C, 21.74; H, 3.65; N, 5.07. Found: C, 22.43; H, 3.71; N, 5.22.

The compound was soluble in acetone and methylene chloride but was not noticeably soluble in ethanol or diethyl ether. A duplicate reaction gave the same product as evidenced by infrared spectroscopy.

9. Tetrasodium  $\mu$ -Oxobis[*cis*-dioxocysteinatohydroxomolybdate(VI)] tetrahydrate,  $Na_4[Mo_2O_5(C_3H_5NO_2S)_2(OH)_2] \cdot 4 H_2O$ .

A modification of the procedure<sup>61</sup> for the preparation of  $Na_2[MoO_2(C_3H_5NO_2S)_2] \cdot DMF$  was used to prepare  $Na_4[Mo_2O_5(C_3H_5NO_2S)_2(OH)_2] \cdot 4 H_2O$ . To 2.40 g (0.0185 mol) of

L-cysteine free base,  $C_3H_7NO_2S \cdot \frac{1}{2} H_2O$ , in thirty five milliliters of water was added 2.40 g (0.00992 mol) of sodium molybdate dihydrate,  $Na_2MoO_4 \cdot 2 H_2O$ , in six milliliters of water. Four hundred fifty milliliters of ethanol were added to the yellow-orange solution. A finely divided yellow solid formed but did not settle. The stirred mixture was acidified with two milliliters of 6 M hydrochloric acid. A fine yellow-gold solid (3.13g, 89.0%) was isolated by decantation and filtration. It was washed successively with ethanol and diethyl ether and then allowed to air dry. Consult the Appendix(Figure 28) for the infrared spectrum of the compound.

Anal. Calcd. for  $C_6H_{20}Mo_2N_2Na_4O_{15}S_2$ : C, 10.18; H, 2.85; N, 3.96; Na, 12.99. Found: C, 9.95; H, 2.60; N, 3.74; Na, 11.15.

Excessive acid in the coagulation process darkened the product appreciably. The gold product above was stable for several hours, but upon standing in a capped vial for several days slowly darkened until, in ninety days, it was brown. The gold product was water soluble but was insoluble in nonpolar organic solvents. A yellow aqueous solution of the gold product was determined qualitatively to be a conductor.

A duplicate run resulted in a gold product of similar yield. The infrared spectrum suggested that the product was the same as that prepared above.

Anal. Calcd. for  $C_6H_{20}Mo_2N_2Na_4O_{15}S_2$ : Mo, 27.09. Found: Mo, 28.68.

10. The Compound  $\text{MoO}_2(\text{OH})(\text{C}_5\text{H}_5\text{N})_{0.8}$  and Di- $\mu$ -oxobis[oxoacetyl-acetonatopyridinemolybdenum(V)],  $\text{Mo}_2\text{O}_4(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_5\text{H}_5\text{N})_2$ , Prepared by Ethanol-Pyridine Reflux of  $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$ .

One gram of (0.00307 mol) of dioxobis(acetylacetonato)molybdenum(VI) was placed in a 200 ml flask with 100 ml ethanol. The solution was stirred for a few minutes to obtain complete solution. Then fifteen milliliters (14.75 g, 0.186 mol) of pyridine were added. The white mixture was refluxed and, although no immediate reaction was noted, after one hour the solution turned dark gold. The suspension turned brown after two hours and finally red-brown in six hours. After thirty two hours the reflux was terminated and the mixture was allowed to cool. A brown solid (0.43 g, 67 %) was then collected. Consult the Appendix (Figure 33) for the infrared spectrum of the compound.

Anal. Calcd. for  $\text{C}_4\text{H}_5\text{MoN}_{0.8}\text{O}_3$ : C, 23.07; H, 2.42; Mo, 46.07; N, 5.38. Found: C, 23.97; H, 2.06; Mo, 45.97; N, 5.40.

The pure mother liquor from the reaction above was allowed to stand in a stoppered flask for twelve days during which time red crystals formed. The well formed red crystalline solid (0.22 g, 23 %) was isolated by filtration, washed with ethanol, and air dried. Consult the Appendix (Figure 31) for the infrared spectrum of the compound.

Anal. Calcd. for  $\text{C}_{20}\text{H}_{24}\text{Mo}_2\text{N}_2\text{O}_8$ : C, 39.23; H, 3.95; Mo, 31.34; N, 4.58. Found: C, 39.38; H, 3.94; Mo, 32.56, N, 4.38.

A duplicate reaction with a twelve-hour reflux also yielded  $\text{MoO}_2(\text{OH})(\text{C}_5\text{H}_5\text{N})_{0.8}$  (0.40 g, 63%) for the first product. A nearly identical molybdenum analysis (45.63%) and the same infrared spectrum confirmed that the compound is again the same. After ninety days the mother liquor again yielded a small amount of well-formed red crystalline product (0.084 g, 8.9%). The infrared spectrum suggests the compound is again  $\text{Mo}_2\text{O}_4(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_5\text{H}_5\text{N})_2$ .

A forty-six hour reflux time resulted in a reduced yield, i.e., one half, for the first product collected, when the red solid was allowed to stand in solution several days after cooling. The infrared spectrum of the product suggested it was the same as those initially formed in the reactions discussed above. No attempt was made to collect additional products from the mother liquor after it had been standing.

11. A Pyridinium Polymolybdate Prepared by Benzene-Pyridine Reflux of  $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$ .

A suspension containing 1.00 g (0.00307 mol) of  $\text{MoO}_2(\text{acac})_2$  in fifty milliliters of benzene was refluxed with stirring for two hours. Ten milliliters (9.83 g, 0.124 mol) of pyridine were then added (syringe) to the hot gold-yellow slurry, and in a few seconds a curdy white precipitate formed with disappearance of the yellow coloration. Heating and stirring were continued for three minutes after which stirring was continued for one hour. A white solid tinged by blue (0.62 g) was then collected

immediately. Consult the Appendix(Figure 34) for the infrared spectrum of the product.

Anal. Calcd. for  $C_{20}H_{24}Mo_8N_4O_{26}$ : C, 15.97; H, 1.61; Mo, 51.03.

Found: C, 18.76; H, 2.01; Mo, 48.66.

A second duplicate reaction produced a white product after a fifteen minute initial slurry reflux. The molybdenum analysis was found to be 47.81%. There was no substantial difference in the infrared spectrum from that prepared above.

12.  $\mu$ -Oxo-bis[ cis-dioxoacetylacetonatopyridinemolybdenum(VI) ].

$Mo_2O_5(C_5H_7O_2)_2(C_5H_5N)_2$ . Prepared by the Room Temperature Reaction of  $MoO_2(C_5H_7O_2)_2$  in Pyridine.

One gram (0.00307 mol) of dioxobis(acetylacetonato)-molybdenum(VI) was added to twenty-five milliliters (24.0 g, 0.310 mol) of pyridine in a fifty milliliter flask which was then stoppered to exclude additional air. Within the first hour, a fine off-white solid formed slowly in the yellow solution. The suspension in the stoppered flask was stirred initially for two hours at room temperature and was then stirred periodically for short intervals for eleven days. The pale yellow solid (0.86 g, 89%) was then isolated by filtration, washed with ethanol, and allowed to air dry. Consult the Appendix(Figure 35) for the infrared spectrum of the compound.

Anal. Calcd. for  $C_{20}H_{24}Mo_2N_2O_9$ : C, 38.23; H, 3.85; Mo, 30.54.

Found: C, 38.28; H, 3.62; Mo, 31.68.



E. Preliminary Photolysis of an Ethanol Solution of Dioxobis-(acetylacetonato)molybdenum(VI) in a Closed System with an Air Atmosphere.

For this preliminary photochemical reaction, no attempts were made to remove air from the solution. "Absolute" ethanol was used as obtained as the solvent.

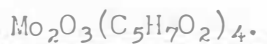
Ten grams (0.0307 mol) of dioxobis(acetylacetonato)molybdenum(VI) were placed in the photolysis reaction vessel containing a Teflon coated magnetic stir bar. Eight hundred milliliters of "absolute ethanol" were then added while stirring and the quartz immersion well was placed in position. The yellow solid dissolved readily in the stirred ethanol forming a yellow solution. After stoppering the remaining reaction flask openings and inserting the Hanovia high pressure lamp into the immersion well, the flask was covered completely with aluminum foil.

The pale yellow solution became orange within a few minutes after photolysis commenced and slowly darkened to red over a four-hour period. In order to ensure complete reaction the photolysis was continued for twelve hours. Upon termination of irradiation, the deep-red solution was observed to contain no solid product. The photolyzed solution, hereafter called the "red hv I" solution was removed from the reaction vessel and used immediately to prepare several derivatives. However, no attempt was made to exclude air from the reaction mixtures before isolation of solid derivatives.

All derivatives were isolated on sintered glass, washed with

ethanol, and air dried unless otherwise described.

1.  $\mu$ -Oxo-dioxotetrakis(acetylacetonate)dimolybdenum(V),



Fifty milliliters of the "red hv I" solution (0.000958 dinuclear mol) were added to ten milliliters (9.76 g, 0.0976 mol) of acetylacetone in a flask which was immediately stoppered. The solution became a darker red immediately, and after standing four hours a fine brown compound (0.52 g, 85%) was isolated from the pale yellow mother liquor. Consult the Appendix (Figure 6) for the infrared spectrum of the compound.

Anal. Calcd. for  $\text{C}_{20}\text{H}_{28}\text{Mo}_2\text{O}_{11}$ : C, 37.75; H, 4.44; Mo, 30.16.

Found: C, 37.22; H, 4.34; Mo, 30.30.

Upon dissolving in 12 M hydrochloric acid the brown solid yielded a green solution. The solid was insoluble in all common organic solvents except that it was slightly soluble in dimethyl sulfoxide, dimethylformamide, acetonitrile, dichloromethane, and tetrachloroethane.

In order to exclude stray light, a foil wrapping was used on the stoppered reaction flask of a duplicate run. The brown compound isolated from this reaction had an infrared spectrum identical to the above.

2. A Mixture of Di- $\mu$ -oxo-bis[oxo-8-hydroxyquinolinatomolybdenum(V)],  
 $\text{Mo}_2\text{O}_4(\text{C}_9\text{H}_6\text{NO})_2$ , and  $\mu$ -Oxodioxotetrakis(8-hydroxyquininato)  
dimolybdenum(V),  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ .

Fifty milliliters of the "red hv I" solution

(0.000958 dinuclear mol) were added to thirty milliliters of ethanol containing 0.50 g (0.00345 mol) of 8-hydroxyquinoline in a flask which was immediately stoppered. The solution became very dark red and some precipitation occurred immediately. After thirty hours a black solid (0.68 g, 87%) was isolated from the orange solution. Consult the Appendix (Figure 8) for the infrared spectrum of the product.

Anal Calcd. for  $C_{36}H_{24}Mo_2N_4O_7$ : C, 52.96; H, 2.96; Mo, 23.50.  
Found: C, 51.70; H, 3.27; Mo, 25.07.

The black product formed a green solution when dissolved in 12 M hydrochloric acid. The solid was insoluble in common organic solvents except that it was slightly soluble in tetrachloroethane, dichloromethane, chloroform, acetonitrile, and dimethyl sulfoxide. The product was somewhat unstable upon prolonged exposure to air.

The infrared spectrum did not indicate that the product was a mixture. However, the elemental analysis indicated approximately 90%  $Mo_2O_3(C_9H_6NO)_4$  when the remainder was assumed to be  $Mo_2O_4(C_9H_6NO)_2$ .

A duplicate run which utilized a foil wrap on the stoppered reaction flask, gave similar results. The infrared spectrum of the product suggested that it was the same as prepared above. The ultraviolet-visible spectrum of the product was the same as that reported<sup>41</sup> for  $Mo_2O_3(C_9H_6NO)_4$ .

3. A Mixture of Di- $\mu$ -oxo-bis [oxotropolonatomolybdenum(V)],  $\text{Mo}_2\text{O}_4(\text{C}_7\text{H}_5\text{O}_2)_2$ , and  $\mu$ -Oxo-dioxotetrakis(tropolonato)-dimolybdenum(V),  $\text{Mo}_2\text{O}_3(\text{C}_7\text{H}_5\text{O}_2)_4$ .

Fifty milliliters of the "red hv I" solution (0.000958 dinuclear mol) was added to 0.50 g (0.0041 mol) of tropolone in fifteen milliliters of ethanol in a flask which was immediately stoppered. A fine brown solid immediately formed in the solution and darkening continued as a black precipitate formed. After twelve hours the black solid (0.72 g) was isolated from the orange filtrate. It was dried six hours under vacuum at  $78^\circ\text{C}$  with no weight loss.

Anal. Calcd. for  $\text{C}_{28}\text{H}_{20}\text{Mo}_2\text{O}_{11}$ : C, 46.43; H, 2.78; Mo, 26.49.

Found: C, 42.44; H, 2.83; Mo, 28.65.

The black solid became green upon dissolving in 12 M hydrochloric acid. It was insoluble in all common organic solvents except that it was slightly soluble in dimethylformamide, acetonitrile, dimethyl sulfoxide, dichloromethane, and tetrachloroethane. The insolubility of black solid did not permit obtaining molecular weight data or a satisfactory ultraviolet-visible spectrum.

The infrared spectrum suggests a mixture, and the elemental analysis indicates approximately 70%  $\text{Mo}_2\text{O}_3(\text{C}_7\text{H}_5\text{O}_2)_4$  when the remainder was assumed to be  $\text{Mo}_2\text{O}_4(\text{C}_7\text{H}_5\text{O}_2)_2$ .

Another reaction gave an initial tan product (0.43 g) when the volume of the "red hv I" solution was first reduced to one

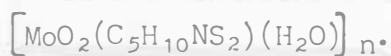
half before addition to the tropolone solution. The infrared spectrum of this product suggested it was primarily  $\text{MoO}_2(\text{C}_7\text{H}_5\text{O}_2)_2$  (section D part 4). After the mother liquor was allowed to stand for twelve hours, a black solid (0.11g) was isolated.

Anal. Calcd. for  $\text{C}_{28}\text{H}_{20}\text{Mo}_2\text{O}_{11}$ : C, 46.43; H, 2.78; Mo, 26.49.

Found: C, 43.90; H, 2.75; Mo, 29.97.

The elemental analysis indicated that the product was a mixture containing about 80%  $\text{Mo}_2\text{O}_3(\text{C}_7\text{H}_5\text{O}_2)_4$  and 20%  $\text{Mo}_2\text{O}_4(\text{C}_7\text{H}_5\text{O}_2)_2$ . The infrared spectrum supported the contention that this mixture contained less  $\text{Mo}_2\text{O}_4(\text{C}_7\text{H}_5\text{O}_2)_2$  than the black mixture above by the observed decrease in intensity of the terminal  $\text{Mo}=\text{O}$  absorption at  $958\text{ cm}^{-1}$ .

4. The N,N-Diethyldithiocarbamate Polymer Derivative,



To 0.90 g (0.0040 mol) of sodium N,N-diethyldithiocarbamate trihydrate in fifteen milliliters of ethanol were added 50 ml (0.000958 dinuclear mol) of the "red hv I" solution in a flask which was immediately stoppered. The solution immediately turned violet coloration and after about three minutes some precipitation had occurred. After standing, the solid became very dark, and after eight hours a black solid (0.46 g) was isolated. Consult the Appendix(Figure 2) for the infrared spectrum of the product.

Anal. Calcd. for  $\text{C}_5\text{H}_{12}\text{Mo N O}_3\text{S}_2$ : Mo, 32.61. Found: Mo, 32.09.

The black solid dissolved slowly in 12 M hydrochloric acid, yielding a green solution. It was insoluble in all common organic solvents except that it was slightly soluble in dimethylformamide, dichloromethane, tetrachloroethane, and acetonitrile.

After two weeks a light tan residue (0.10 g) was isolated from the mother liquor. The infrared spectrum of the solid suggested a hydroxyoxide of molybdenum with no dithiocarbamate ligand present.

5. Di-μ-oxo-bis [oxocysteinatomolybdenum(V)] ethanolpentahydrate.  
 $[\text{Mo}_2\text{O}_4(\text{C}_3\text{H}_6\text{NO}_2\text{S})_2] \cdot \text{C}_2\text{H}_5\text{OH} \cdot 5 \text{H}_2\text{O}.$

To 0.70 g (0.0040 mol) of L-(+)-cysteine hydrochloride monohydrate in twenty-five milliliters of ethanol were added fifty milliliters of the "red hv I" solution (0.000958 dinuclear mol) in a flask which was immediately stoppered. After ten minutes, cloudiness occurred with subsequent settling of yellow solid after another ten minutes. The fine yellow product (0.25 g, 41%) was collected after nine hours.

Anal. Calcd. for  $\text{C}_8\text{H}_{28}\text{Mo}_2\text{N}_2\text{O}_{14}\text{S}_2$ : Mo, 30.35. Found: Mo, 30.85.

Upon dissolving in 12 M hydrochloric acid the yellow product became dark green. The yellow solid was insoluble in all common organic solvents except it was slightly soluble in dimethyl sulfoxide, dimethylformamide, dichloromethane, and acetonitrile. Only faint chloride tests were obtained using either the Beilstein method or the silver nitrate test after

sodium fusion.<sup>124</sup> The mother liquor yielded additional yellow product (0.04 g, 7%) after standing two weeks. The infrared spectrum suggested that the product was the same as that prepared above.

6. Di- $\mu$ -oxobis[oxoacetylacetonatopyridinemolybdenum(V)],  
 $\text{Mo}_2\text{O}_4(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_5\text{H}_5\text{N})_2$ .

Fifty milliliters of the "red hv I" solution (0.00958 dinuclear mol) were added with stirring to ten milliliters (9.83 g, 0.124 mol) of pyridine in a flask which was immediately stoppered. The solution became slightly cloudy, but no precipitate formed in the stoppered flask for several days. After nine days a red crystalline solid (0.345 g, 58.8%) was isolated from the yellow-orange mother liquor. The infrared spectrum of the compound suggested that the compound was  $\text{Mo}_2\text{O}_4(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_5\text{H}_5\text{N})_2$ , also prepared by the reflux method in section D part 10.

Anal. Calcd. for  $\text{C}_{20}\text{H}_{24}\text{Mo}_2\text{N}_2\text{O}_8$ : C, 39.23; H, 3.95; Mo, 31.34; N, 4.58. Found: C, 38.31; H, 3.89; Mo, 32.73; N, 4.38.

The red solid became green upon dissolving in 12 M hydrochloric acid. It was insoluble in all common organic solvents, except it was slightly soluble in tetrachloroethane, dichloromethane, acetonitrile, dimethylformamide, and dimethyl sulfoxide.

No additional product formed when the mother liquor was allowed to stand another thirty days in the stoppered flask.

7. The Compound  $\text{MoO}_2(\text{OH})(\text{C}_5\text{H}_5\text{N})_{0.8}$

The procedure was the same as that used in section E part 6 above, except that the "red hv I" solution-pyridine mixture was first allowed to stand twenty hours in a stoppered flask. Then its volume was reduced to one half in a beaker over a two-hour period, utilizing a water bath at  $80^\circ\text{C}$ . The red crystalline product (0.14 g, 35 %) was immediately isolated and observed to be somewhat darker than the product discussed in section E part 6 above. Consult the Appendix (Figure 32) for the infrared spectrum of the compound.

Anal. Calcd. for  $\text{C}_4\text{H}_5\text{MoN}_{0.8}\text{O}_3$ : C, 23.07; H, 2.42; Mo, 46.07; N, 5.38. Found: C, 23.08; H, 2.13; Mo, 45.85; N, 5.02.

The red product was very insoluble and, hence, did not discolor 12 M hydrochloric acid. It was also insoluble in all common organic solvents, except that it was very slightly soluble in dimethyl sulfoxide.

8. Dioxobis(benzoin-anti-oximate)molybdenum(VI),  $\text{MoO}_2(\text{C}_{14}\text{H}_{12}\text{NO}_2)_2$

Fifty milliliters of the "red hv I" solution (0.000958 dinuclear mol) were added to 0.50 g (0.0022 mol) of benzoin-anti-oxime in thirty milliliters of ethanol in a flask which was immediately stoppered. After a few minutes the solution slowly became cloudy, and after thirty minutes curds of light colored solid appeared in the brown solution. After one hour a finely divided off-white precipitate (0.44 g, 68 %) was isolated from the orange filtrate. The light-colored solid did



not dissolve or react noticeably in 12 M hydrochloric acid and was insoluble in all common organic solvents. Consult the Appendix(Figure 13) for the infra-red spectrum of the compound.

Anal Calcd. for  $C_{28}H_{24}MoN_2O_6$ : C, 57.94; H, 4.17; Mo, 16.53.

Found: C, 57.51; H, 4.64; Mo, 17.15.

A duplicate reaction gave almost identical results; and, by doubling the amount (1.00 g) of benzoin-anti-oxime, white  $MoO_2(C_{14}H_{12}NO_2)_2$  was obtained in nearly quantitative yields.

F. General Procedure for the Purification of Nitrogen.

Since this work required study of several photochemical reactions under dry, oxygen-free conditions, a system was designed for this purpose. The system developed is shown in detail in Figure 2 where oil-pumped nitrogen was utilized in a train designed to remove traces of oxygen via reduced commercial copper oxide catalyst.

In order to activate (reduce) the BTS Catalyst R 3-11 packed in column A, a stream of hydrogen, entering at stopcock 3C-1, was passed through the column at  $140^{\circ}C$  and vented through stopcock 3C-2 and bubbler B-1. All bubblers were mercury-filled in such a way that vented gases were required to displace approximately two millimeters of mercury. When water condensation and accumulation ceased above the heated column A, stopcock 3C-1 was reversed to allow nitrogen to enter and to sweep hydrogen and water vapor from the column and system. An

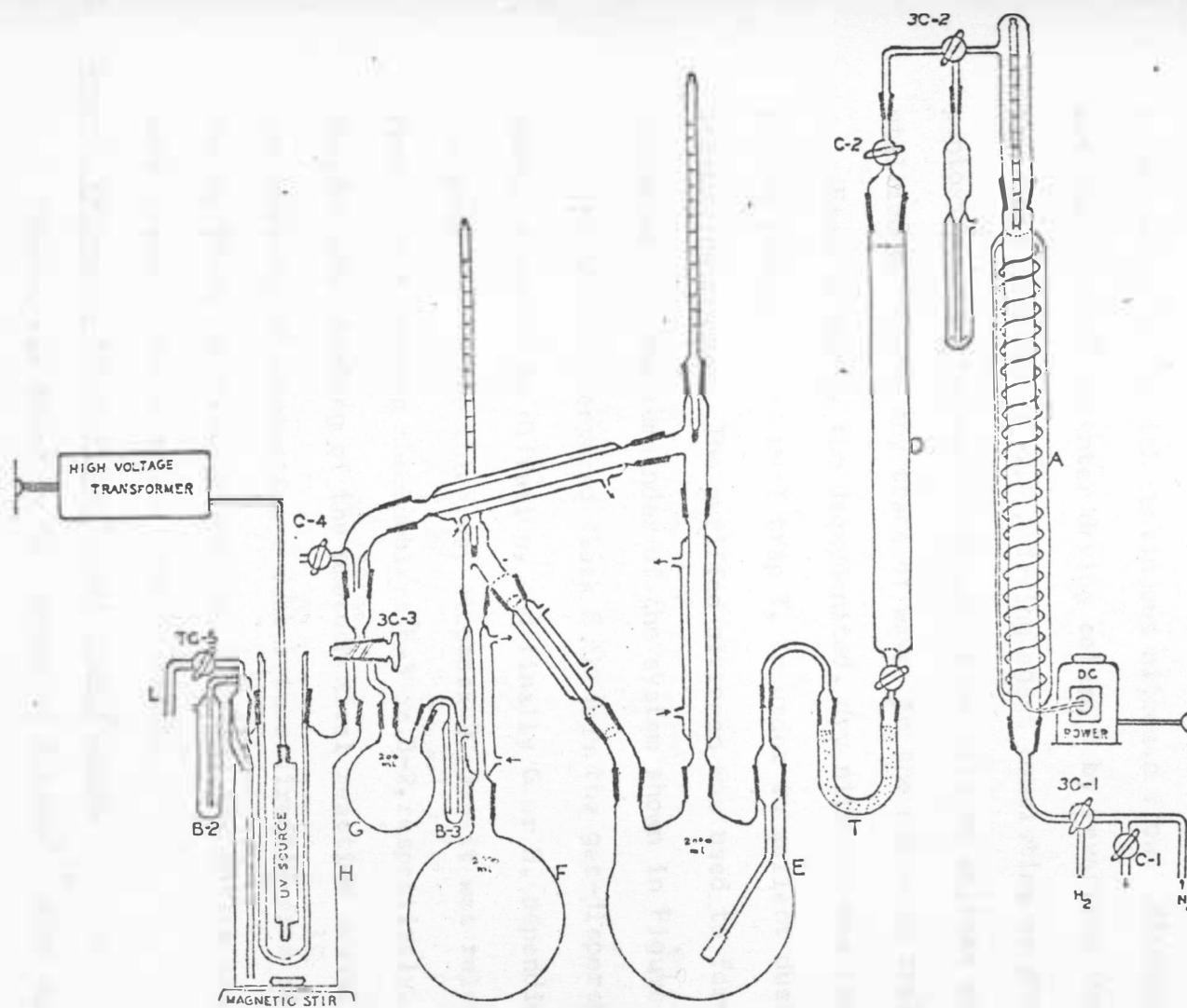


Figure 2. Controlled Atmosphere System with Photochemical Reactor.

infrared lamp was used to hasten vaporization of condensed water (above column A) into the nitrogen stream. The temperature on column A containing the reduced form of BTS catalyst was increased to  $190^{\circ}\text{C}$  with continuous nitrogen flow. Nitrogen was then allowed to enter drying column D by reversing the three-way stopcock 3C-2. A drying agent consisting of phosphorus pentoxide supported on 8-mesh anhydrous calcium sulfate was utilized to remove any trace of water in the nitrogen train.

From Column D, the deoxygenated, dry nitrogen was then passed through glass wool trap T, in order to collect dust from the drying column. The purified nitrogen was used to form the atmosphere in the remainder of the system shown in Figure 2.

The nitrogen entered flask E through the gas-dispersion tube, entered F by diffusion, and finally G or H, depending on the position of the three way stopcock 3C-3. It was released from G or H through the bubblers B-3 or B-2, respectively. Preliminary flushing of the photochemical reaction vessel H was accomplished by connecting a rubber tube directly from stopcock C-1 to TC-5, while simultaneously flushing the entire system with a small amount of purified nitrogen.

#### G. General Procedure for the Purification of Ethanol

Ethanol was dried by the method of Wiberg<sup>125</sup> with certain modifications. Preliminary treatment of ethanol was accomplished by adding approximately two hundred grams of oven dried ( $600^{\circ}\text{C}$ ) calcium oxide lumps to 1500 ml of "absolute ethanol" in a

tightly capped bottle agitated by magnetic stirring. This technique results in ethanol containing no more than one-half of one percent water, if the initial content was no more than five percent water prior to treatment.<sup>125</sup>

Further purification of the ethanol was accomplished by treating the solvent under purified nitrogen as follows in the system shown in Figure 2. Approximately 1200 ml of the calcium oxide dried ethanol were quickly decanted into flask F, which contained an additional 50-100 g of dry CaO. This mixture was refluxed under a sweeping nitrogen atmosphere for at least four hours. All except the last 100-150 ml was then distilled, at a rate of one to two drops per second, into flask E. After the distillation apparatus of flask F had been quickly removed, seven grams of sodium metal were added to the ethanol in flask E. Prior to use the sodium had been cut into small pieces and washed with diethyl ether to remove hydrocarbon residue. After all of the sodium had reacted (three to four hours), 27.5 g (24.5 ml) of diethyl phthalate were quickly added to the flask E with a syringe. The solution was allowed to reflux under nitrogen purge for a minimum of six hours before distillation. Rotation of the three-way stopcock 3C-3 allowed selection of flask G or photochemical reaction vessel H for receiving twice-distilled ethanol from flask E. Since distillation follows sample introduction, this phase of the procedure will be discussed in the following section (H).

#### H. Sample Introduction and Photolysis.

As the ethanol solution was refluxing in flask E, nitrogen was passing through flask G and out of the system through bubbler B-3. At the same time the photochemical reaction vessel H was fitted with bubbler B-2 and a liquid removal assembly L, as shown in Figure 2. The liquid removal assembly L consisted of a glass tube reaching to the bottom of the vessel H and an outlet tube controlled with a Teflon stopcock (TC-5). After the solid sample to be photolyzed was introduced into the bottom of the reaction vessel with a long paper funnel, a one and one-half inch Teflon coated stir bar was also introduced. The water-cooled quartz immersion well was then placed in position, and the photochemical reaction vessel H was then ready for nitrogen flushing.

After rapid preliminary flushing (using small amounts of purified nitrogen from the purification train and large amounts of unpurified nitrogen directly from stopcock C-2 through stopcock TC-5) and final flushing (using only purified nitrogen) of the photochemical reaction vessel H, stopcock 3C-3 was reversed and flask G was flushed with purified nitrogen. Under the nitrogen stream approximately seventy five milliliters of ethanol were then distilled from flask E into flask G. This served to prevent low-boiling impurities from entering the photochemical reaction vessel H. The three-way stopcock 3C-3 was then reversed, and purified ethanol was distilled into vessel H under the purified nitrogen stream. After eight hundred milliliters (fill mark) of the purified ethanol

had been added, with stirring, to the vessel at a rate of one to two drops per second, stopcock 3C-3 was again reversed, as flask E was allowed to cool. The last small amount of distilling ethanol was collected in flask G, as purified nitrogen flushing continued. Once distillation had stopped and the system was at constant temperature, the stopcock 3C-3 was reversed to allow continuous nitrogen flow through vessel H.

For greatest eye safety, the vessel H was completely covered with aluminum foil when the stirred solution was photolyzed with the high pressure Hanovia ultraviolet source. During the twelve-hour photolysis period the lamp was periodically turned off to observe color changes in the irradiated solution.

Upon completion of photolysis the solution was removed from the reaction vessel H through the liquid removal assembly and the open Teflon stopcock TC-5. In order to accomplish this the vent from bubbler B-2 was closed as nitrogen slowly continued to flow into the reaction vessel H. This increased internal nitrogen pressure could then be used to force the photolyzed solution from the vessel H through stopcock TC-5. In this manner the photolyzed solution in the vessel H could be removed, as required for investigation, while the unused portion could be kept under nitrogen flush or static nitrogen atmosphere.

I. Photolysis of an Ethanol Solution of *cis*-Dioxobis(acetylacetonato)-molybdenum(VI) in the Absence of Oxygen and Water.

A yellow solution containing ten grams (0.0307 mol) of *cis*-

dioxobis(acetylacetonato)molybdenum(VI) in eight hundred milliliters of purified ethanol was photolyzed under purified nitrogen in the controlled atmosphere system described previously in sections F-H. The yellow solution turned dark red almost immediately as photolysis was initiated. After a twelve-hour irradiation, several derivatives were prepared from the red ethanolic photolyzed solution, hereafter called the "red hv II" solution. All derivatives were isolated by filtration on sintered glass, immediately washed with ethanol, washed with diethyl ether, and air dried, unless otherwise described.

1.  $\mu$ -Oxo-dioxotetrakis(acetylacetonato)dimolybdenum(V),  $\text{Mo}_2\text{O}_3(\text{C}_5\text{H}_7\text{O}_2)_4$ .

One hundred milliliters (0.001916 dinuclear mol) of the "red hv II" solution were added to twenty milliliters (19.52 g, 0.1952 mol) of acetylacetone under nitrogen. A brown precipitate formed very slowly in the stoppered flask and after twenty four hours, a finely divided brown solid (1.19 g, 98%) was isolated from the yellow mother liquor.

Anal. Calcd. for  $\text{C}_{20}\text{H}_{28}\text{Mo}_2\text{O}_{11}$ : Mo, 30.16. Found: Mo, 29.94.

The infrared spectrum was obtained immediately and, coupled with the molybdenum analysis, suggested that this compound was the same as that prepared in section E part 1.

2.  $\mu$ -Oxo-dioxotetrakis(8-hydroxyquinolinato)dimolybdenum(V),  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ , and a Mixture of Di- $\mu$ -oxo-bis[oxo-8-hydroxy-quinolinatomolybdenum(V)] ,  $\text{Mo}_2\text{O}_4(\text{C}_9\text{H}_6\text{NO})_2$ , and  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ .

One hundred milliliters of the "red hv II" solution

(0.001916 dinuclear mol) were added under a continuous stream of nitrogen to 1.20 g (0.00827 mol) of 8-hydroxyquinoline in fifteen milliliters of ethanol in a flask which was immediately stoppered. The stirred solution in the nitrogen-filled flask immediately darkened and after forty-five minutes a brown solid (0.35 g) was collected under a nitrogen atmosphere. The infrared spectrum (see Appendix Figure 9) was obtained immediately and the mixture was then sealed under nitrogen in glass ampoules. Consult the Appendix (Tables XXV and XXVI) for two X-ray powder diffraction patterns, i.e., obtained by sealing samples in nitrogen and air, respectively.

Anal. Calcd. for  $C_{18}H_{12}Mo_2N_2O_6$ : C, 39.73; H, 2.22; Mo, 35.26; N, 5.15. Found: C, 43.31; H, 2.92; Mo, 23.31; N, 5.28.

The brown solid formed a green solution when dissolved in 12 M hydrochloric acid and was insoluble in common organic solvents except it was slightly soluble, forming deep violet solutions, in dichloromethane, chloroform, acetonitrile, and dimethyl sulfoxide.

The infrared spectrum shows two terminal  $Mo=O$  absorptions at 935 and 965  $cm^{-1}$  indicative of  $Mo_2O_3^{4+}$  and  $Mo_2O_4^{2+}$  moieties, respectively. The elemental analysis indicated approximately 75%  $Mo_2O_4(C_9H_6NO)_2$  when the remainder was assumed to be  $Mo_2O_3(C_9H_6NO)_4$ . The X-ray powder diffraction pattern obtained from a sample sealed in air was different from that obtained from a sample sealed in nitrogen, demonstrating the instability



of the brown solid. Both X-ray powder patterns were unlike those reported previously for  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ .<sup>126</sup>

After sixty minutes, the mother liquor was again filtered; and a black solid (0.28 g) was collected under nitrogen atmosphere. The infrared spectrum (see Appendix Figure 10) suggested that the product was the same as that isolated in section D part 2 from "red hv I". Only the terminal  $\text{Mo}=\text{O}$  absorption at  $935\text{ cm}^{-1}$  was prominent for this product.

Another run, with somewhat less rigor in excluding air during the derivative preparation, resulted in an initial deep violet product with an infrared spectrum (see Appendix Figure 11) nearly the same as that obtained from the brown initial product isolated above (Appendix Figure 9). Consult the Appendix (Table XXIII) for the X-ray powder diffraction pattern, a simple pattern different from those reported previously for  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ .<sup>126</sup>

Anal. Calcd. for  $\text{C}_{18}\text{H}_{12}\text{Mo}_2\text{N}_2\text{O}_6$ : C, 39.73; H, 2.22; Mo, 35.26.  
Found: C, 46.32; H, 2.91; Mo, 27.04.

The infrared spectrum was again observed with two terminal  $\text{Mo}=\text{O}$  absorptions at 965 and  $935\text{ cm}^{-1}$ . The elemental analysis suggested a mixture composed of 50%  $\text{Mo}_2\text{O}_4(\text{C}_9\text{H}_6\text{NO})_2$  when the remainder was assumed to be  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ .

The mother liquor produced a black solid (0.13 g, 17%) with an infrared spectrum (see Appendix Figure 12) similar to that obtained for the black solid isolated from the mother liquor

above (Appendix Figure 10). However, the X-ray powder diffraction pattern (see Appendix Table XXIV) was found to be distinctly different from those obtained for the products above but identical to that reported<sup>126</sup> as an isomer of  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ .

Anal. Calcd. for  $\text{C}_{36}\text{H}_{24}\text{Mo}_2\text{N}_4\text{O}_7$ : C, 52.9%; H, 2.9%; Mo, 23.50.  
Found: C, 51.87%; H, 3.05%; Mo, 23.9%.

Only the sharp terminal  $\text{Mo}=\text{O}$  absorption at  $935\text{ cm}^{-1}$  was observed in the infrared spectrum for this compound. This observation, coupled with other spectra comparisons and the X-ray powder diffraction pattern, suggests a compound of high purity.

3.  $\mu$ -Oxo-dioxotetrakis(tropolonato)dimolybdenum(V),  $\text{Mo}_2\text{O}_3(\text{C}_7\text{H}_5\text{O}_2)_4$   
and the Mixture Containing Di- $\mu$ -oxobis[oxotropolonato-  
molybdenum(V)],  $\text{Mo}_2\text{O}_4(\text{C}_7\text{H}_5\text{O}_2)_2$ , and  $\text{Mo}_2\text{O}_3(\text{C}_7\text{H}_5\text{O}_2)_4$ .

Fifty milliliters of the "red hv II" solution (0.000958 dinuclear mol) were added to an ethanol solution containing 0.50 g (0.0041 mol) of tropolone in a flask which was immediately stoppered. The solution in the flask immediately darkened as a brown precipitate formed. The brown solid (0.42 g) was isolated after 20 minutes, and the infrared spectrum was obtained immediately.

Anal. Calcd. for  $\text{C}_{14}\text{H}_{10}\text{Mo}_2\text{O}_8$ : C, 33.76%; H, 2.02%; Mo, 38.52.  
Found: C, 36.14%; H, 3.04%; Mo, 34.98.

The infrared spectrum suggests that the product is a mixture,

and the elemental analysis indicates the product is composed of about 80%  $\text{Mo}_2\text{O}_4(\text{C}_7\text{H}_5\text{O}_2)_2$  when the remainder is assumed to be  $\text{Mo}_2\text{O}_3(\text{C}_7\text{H}_5\text{O}_2)_4$ .

The mother liquor yielded a black product (0.17 g, 24 %) after seven days. Consult the Appendix (Figure 15) for the infrared spectrum of the compound.

Anal. Calcd. for  $\text{C}_{28}\text{H}_{20}\text{Mo}_2\text{O}_{11}$ : C, 46.43; H, 2.78; Mo, 26.49. Found: C, 46.57; H, 2.92; Mo, 26.48.

The infrared spectrum shows only one strong terminal  $\text{Mo}=\text{O}$  absorption, a sharp band at  $946\text{ cm}^{-1}$ . The isolation of the compound is confirmed by the elemental analysis.

Another run under more rigorous exclusion of oxygen during preparation of the derivative resulted in the formation of a brown solid (0.55 g) which was isolated after ten minutes of reaction time under a nitrogen atmosphere. An infrared spectrum (see Appendix Figure 14) was obtained immediately. The product was sealed in glass ampoules in a nitrogen atmosphere until analysis could be obtained.

Anal. Calcd. for  $\text{C}_{14}\text{H}_{10}\text{Mo}_2\text{O}_8$ : C, 33.76; H, 2.02. Found: C, 35.14; H, 2.95.

The infrared spectrum suggested that the product consisted of one predominant component as indicated by the observation of only one terminal  $\text{Mo}=\text{O}$  band at  $958\text{ cm}^{-1}$ . The elemental analysis indicated that the mixture contained approximately 90%  $\text{Mo}_2\text{O}_4(\text{C}_7\text{H}_5\text{O}_2)_2$  when the remainder was assumed to be  $\text{Mo}_2\text{O}_3(\text{C}_7\text{H}_5\text{O}_2)_4$ .

The mother liquor yielded a black solid (0.05 g, 7%) after another hour of reaction time. The infrared spectrum of this product was the same as that obtained for the black compound obtained from the mother liquor of the run above (Appendix Figure 15).

Still another run resulted in a brown-violet solid whose molybdenum analysis (31.13%) suggested about 50%  $\text{Mo}_2\text{O}_4(\text{C}_7\text{H}_5\text{O}_2)_2$  when the remainder was assumed to be  $\text{Mo}_2\text{O}_3(\text{C}_7\text{H}_5\text{O}_2)_4$ . The infrared spectrum was observed to absorb strongly at both 958 and  $946\text{ cm}^{-1}$ , further supporting the likelihood of an equally mixed two-component product.

4. A Mixture Containing Oxobis(N,N-diethyldithiocarbamato)-molybdenum(IV),  $\text{MoO}(\text{C}_5\text{H}_{10}\text{NS}_2)_2$ .

One hundred milliliters of the "red hv II" solution (0.001915 dinuclear mol) were added to a solution composed of 1.80 g (0.00798 mol) of sodium N,N-diethyldithiocarbamate trihydrate in fifteen milliliters of ethanol in a flask which was immediately stoppered. The stoppered reaction flask was nitrogen flushed prior to addition of the photolyzed solution, and the contents were continuously under nitrogen as the reaction progressed. The solution became pink after two minutes reaction, and after six minutes prismatic crystals appeared. The dark pink crystals (0.30 g, 19%) were isolated under nitrogen after eight minutes. The infrared spectrum was obtained immediately with minimum exposure to air, while the

remainder of the solid was stored under nitrogen in sealed glass ampoules. Consult the Appendix(Figure 20) for the infrared spectrum and the X-ray powder diffraction pattern (Table XXIX) of the product.

Anal. Calcd. for  $C_{10}H_{20}MoN_2OS_4$ : C, 29.40; H, 4.94; Mo, 23.49; N, 6.86. Found: C, 26.48; H, 4.43; Mo, 24.31; N, 5.99.

Much of the fine pink solid passed through the sintered glass disc. After one hour efforts to again filter the flocculent solid in the mother liquor, resulted in a clogged sintered glass disc. The remaining air-sensitive pink product turned dark red and then violet when further collection attempts failed to exclude air. Upon standing in air, the violet solid slowly turned brown and finally yellow after several days.

A duplicate run using the same collection technique resulted in a similar pink product, as determined by molybdenum analysis (24.86%) and infrared spectroscopy.

In additional runs, where air was not rigorously excluded during preparation and isolation, a violet solid was obtained. The infrared spectra of these products were similar to violet products (Figure 24) prepared by dithionite ion reduction (section D part 6). Derivatives left to stand in solution for several hours before isolation became black. The infrared spectra were similar to that obtained (Figure 22) for the product from the "red hv I" solution (section E part 4).

5. Di- $\mu$ -oxo-bis[oxocysteinatomolybdenum(V)]ethanolpentahydrate,  
 $[\text{Mo}_2\text{O}_4(\text{C}_3\text{H}_6\text{NO}_2\text{S})_2] \cdot \text{C}_2\text{H}_5\text{OH} \cdot 5 \text{H}_2\text{O}$  Obtained from Cysteine Hydro-  
chloride.

Fifty milliliters of the "red hv II" solution (0.000958 dinuclear mol) were added with stirring to 0.70 g (0.0040 mol) of L-(+)-cysteine hydrochloride monohydrate in a flask which was immediately stoppered. After a few minutes a yellow solid began forming, and after six hours it was isolated (0.41 g, 68%). The water insoluble product had an infrared spectrum similar to that obtained from the derivative (section E part 5) of the "red hv I" solution. A faint chloride test was obtained using the methods of Beilstein and silver nitrate after sodium fusion.<sup>127</sup> Consult the Appendix (Figure 26) for the infrared spectrum of the compound.

Anal. Calcd. for  $\text{C}_8\text{H}_{28}\text{Mo}_2\text{N}_2\text{O}_{14}\text{S}_2$ : C, 15.20; H, 4.46; Mo, 30.35; N, 4.43. Found: C, 15.32; H, 3.04; Mo, 30.06; N, 4.36.

Another run utilizing one hundred milliliters of photolyzed solution and 1.40 g of the ligand produced a yellowish-gold solid (0.75 g, 62%). The infrared spectrum of the product suggested that it was the same as that prepared above.

Anal. Calcd. for  $\text{C}_8\text{H}_{28}\text{Mo}_2\text{N}_2\text{O}_{14}\text{S}_2$ : C, 15.20; H, 4.46; Mo, 30.35; Found: C, 15.92; H, 3.51; Mo, 31.30.

A nitrogen atmosphere was used during collection of the product from still another run. The infrared spectrum suggested

that the product was again the same as those prepared above.

6. Di-μ-oxo-bis[oxocysteinato-molybdenum(V)]-1.2-ethanol.

Mo<sub>2</sub>O<sub>4</sub>(C<sub>3</sub>H<sub>6</sub>NO<sub>2</sub>S)<sub>2</sub> · 1.2 C<sub>2</sub>H<sub>5</sub>OH Obtained from Cysteine Free Base.

Fifty milliliter of the "red hv II" solution (0.000958 dinuclear mol) were added to 0.60 g (0.0050 mol) of cysteine free base, C<sub>3</sub>H<sub>7</sub>NO<sub>2</sub>S ·  $\frac{1}{2}$  H<sub>2</sub>O in a nitrogen flushed flask which was immediately stoppered. The stirred solution in the nitrogen filled stoppered flask immediately became yellow-brown and cloudy. After five hours a fine gold solid (0.40 g) was obtained. However, much solid passed through the sintered glass filtering assembly. The infrared spectra suggested that the product was primarily unreacted cysteine.

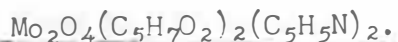
The mother liquor containing some unfiltered solid was allowed to stand ninety days. A fine yellow solid developed slowly in the solution. The fine suspension was centrifuged, isolated on sintered glass, and washed. An infrared spectrum (Figure 27) of the gold product (0.28 g, 53%) did not indicate the presence of unreacted cysteine.

Anal. Calcd. for C<sub>8.4</sub>H<sub>19.2</sub>Mo<sub>2</sub>N<sub>2</sub>O<sub>9.2</sub>S<sub>2</sub>: C, 18.30; H, 3.51; N, 5.08. Found: C, 18.35; H, 3.62; N, 5.13.

Another run gave an initial product similar to that above when the stoppered reaction flask contained air during the derivative preparation. After several months, the mother liquor also yielded a product which was similar to that obtained from the mother liquor above. These comparisons

were based on infrared spectroscopy.

7. D1-u-oxobis[oxoacetylacetonatopyridinemolybdenum(V)].



One hundred milliliters of the "red hv II" solution (0.001916 dinuclear mol) were added to twenty milliliters (19.66 g, 0.248 mol) of pyridine in a flask which was immediately stoppered. No immediate reaction was noted but upon standing five days in the stoppered flask, well-formed red crystals (0.97 g, 83%) were isolated from the orange mother liquor. The infrared spectrum suggested that the product was the same as that prepared from the "red hv I" solution (section E part 6) and the reflux method (section D part 10). Consult the Appendix (Figure 30) for the infrared spectrum of the compound. Anal. Calcd. for  $\text{C}_{20}\text{H}_{24}\text{Mo}_2\text{N}_2\text{O}_8$ : C, 39.23; H, 3.95; Mo, 31.34. Found: C, 39.48; H, 4.25; Mo, 31.46.

After ten days the mother liquor yielded additional red crystals (0.10 g, 8%). The infrared spectrum suggested that this product was the same as that isolated earlier from the reaction mixture.

Another run yielded a red crystalline product (0.99 g, 84%) which was isolated after twelve days. The infrared spectrum suggested that the product was the same as that prepared above. Anal. Calcd. for  $\text{C}_{20}\text{H}_{24}\text{Mo}_2\text{N}_2\text{O}_8$ : C, 39.23; H, 3.95; Mo, 31.34. Found: C, 38.90; H, 3.93; Mo, 31.16.



8. The 2,2'-Bipyridine Derivative Mixture.

Fifty milliliters (0.000958 dinuclear mol) of the "red hv II" solution were added to 0.90 g (0.0058 mol) of 2,2'-bipyridine in a nitrogen-flushed flask which was immediately stoppered. The solution immediately turned orange-brown and cloudy, as a fine solid slowly formed. After six hours, an orange-gold solid (0.35 g) was collected. The infrared spectrum (see Appendix Figure 36) was obtained immediately.

Anal. Calcd. for  $C_{10}H_{12}Mo_2N_2O_7$ : Mo, 41.34; Found: Mo, 38.59.

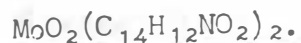
The infrared spectrum of the product indicated that it was a mixture, as evidenced by the band at  $955\text{ cm}^{-1}$  with a shoulder at  $970\text{ cm}^{-1}$ .

After an additional ninety days of reaction in the nitrogen-flushed flask, more orange-gold solid (0.15 g) was isolated from the mother liquor. The infrared spectrum suggested that this product was the major component, i.e., identified by the  $970\text{ cm}^{-1}$  band, of the first product collected above. In addition, the infrared spectrum was the same as that obtained from the product isolated from the mother liquor originating from the "red hv III" solution (section J part 7).

A duplicate run resulted in an orange-gold solid whose infrared spectrum suggested that the product was very similar to the initial mixture isolated above.

Anal. Calcd. for  $C_{10}H_{12}Mo_2N_2O_7$ : C, 25.88; H, 2.61; Mo, 41.34; N, 6.04. Found: C, 28.99; H, 2.94; Mo, 37.53; N, 5.28.

9. cis-Dioxobis(benzoin-anti-oximato)molybdenum(VI),



One hundred milliliters of the "red hv II" solution (0.001916 dinuclear mol) were added to 2.00 g (0.0088 mol) of benzoin-anti-oxime in a flask which was immediately stoppered. A light-colored precipitate formed slowly from the red-brown solution. After four hours a finely divided off-white solid (1.75 g, 79%) was isolated.

Anal. Calcd. for  $\text{C}_{28}\text{H}_{24}\text{MoN}_2\text{O}_6$ : Mo, 16.53. Found: Mo, 16.64.

The infrared spectrum suggested that this compound was the same as that prepared (Appendix Figure 13) from the "red hv I" solution (section E part 8).

The red-brown mother liquor slowly became yellow as additional off-white precipitate (0.04 g, 2%) formed over a two week period.

J. Photolysis of an Ethanol Solution of cis-Dioxobis(acetylacetonato)-molybdenum(VI) through Borosilicate Glass in the Absence of Oxygen and Water.

A yellow solution containing ten grams (0.0307 mol) of cis-dioxobis(acetylacetonato)molybdenum(VI) in eight hundred milliliters of ethanol was photolyzed under purified nitrogen in the controlled atmosphere system previously described in Sections F-H. All procedures were identical to that used in the previous section I except that a one millimeter thick Pyrex sleeve was positioned around the Hanovia ultraviolet source so

that photons emitted from the source would be filtered by the Pyrex. The yellow solution became dark red in less than two hours during the twelve hour irradiation period. Several derivatives were prepared from the red ethanolic photolyzed solution, hereafter called the "red hv III" solution. All derivatives were isolated by filtration on sintered glass, immediately washed with ethanol, then washed with diethyl ether, and air dried, unless otherwise described.

1.  $\mu$ -Oxo-dioxotetrakis(acetylacetonato)dimolybdenum(V),  
 $\text{Mo}_2\text{O}_3(\text{C}_5\text{H}_7\text{O}_2)_4$ .

Fifty milliliters (0.000958 dinuclear mol) of the photolyzed solution were added to ten milliliters (9.76 g, 0.0976 mol) of acetylacetone in a flask which was immediately stoppered. A brown precipitate formed very slowly and after twenty-nine hours well-formed brown crystals (0.55 g, 90%) were isolated from the yellow mother liquor. Anal. Calcd. for  $\text{C}_{20}\text{H}_{28}\text{Mo}_2\text{O}_{11}$ : Mo, 30.16. Found: Mo, 30.46. The infrared spectrum and the molybdenum analysis indicated that this compound was the same as that prepared from the "red hv I" solution (section E Part 1) and the "red hv II" solution (section I Part 1).

2.  $\mu$ -Oxo-dioxotetrakis(8-hydroxyquinolinato)dimolybdenum(V),  
 $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ , and a Mixture of Di- $\mu$ -oxo-bis[oxo-8-hydroxy-  
quinolinatomolybdenum(V)],  $\text{Mo}_2\text{O}_4(\text{C}_9\text{H}_6\text{NO})_2$ , and  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ .

Fifty milliliters of the "red hv III" solution

(0.000958 dinuclear mol) were added to 0.60 g (0.0041 mol) of 8-hydroxyquinoline in a nitrogen flushed flask which was immediately stoppered. The stirred solution in the flask immediately became dark brown and continued to darken. After two and one half hours the black compound (0.82 g, 98%) was isolated and air dried for two days.

Anal. Calcd. for  $C_{36}H_{24}Mo_2N_4O_7$ : C, 52.96; H, 2.96; Mo, 23.50.

Found: C, 52.39; H, 3.05; Mo, 23.72.

The infrared spectrum of the compound indicated the presence of only one terminal  $Mo=O$  absorption, i.e.,  $935\text{ cm}^{-1}$ . The spectrum was very similar to that of a black product (Appendix Figure 12) obtained from the mother liquor of the "red hv II" solution in Section I Part 2.

Another reaction with an initial product collected after twelve minutes resulted in the isolation of a dark solid (0.43 g). The infrared spectrum was obtained immediately.

Anal. Calcd. for  $C_{18}H_{12}Mo_2N_2O_6$ : C, 39.73; H, 2.22; Mo, 35.26.

Found: C, 48.09; H, 3.00; Mo, 25.71.

The infrared spectrum was very similar to that of the product obtained (Appendix Figure 10) from the mother liquor of the reaction mixture of the "red hv II" solution (section I part 2). Two terminal  $Mo=O$  absorptions were observed at  $965$  and  $935\text{ cm}^{-1}$ . The elemental analysis also suggested that the product was about 30%  $Mo_2O_4(C_9H_6NO)_2$  when the remainder was assumed to be  $Mo_2O_3(C_9H_6NO)_4$ . The dark

mixture formed a green solution when dissolved in 12 M hydrochloric acid.

After one hour, a black solid (0.17 g) was isolated from the mother liquor of the reaction above. An infrared spectrum somewhat different from that of the initial product was obtained.

Anal. Calcd. for  $C_{36}H_{24}Mo_2N_4O_7$ : C, 52.96; H, 2.96; Mo, 23.50. Found: C, 50.68; H, 3.11; Mo, 23.94.

The infrared spectrum of this product also had two terminal Mo=O absorptions but the band at  $965\text{ cm}^{-1}$  was of diminished absorbance when compared to the spectrum of the first product above.

After another eighteen hours more black solid (0.16 g, 19%) was isolated from the colorless mother liquor. Again a variation in the infrared spectrum was noted, as the absorption at  $965\text{ cm}^{-1}$  was completely absent. The molybdenum analysis (23.89%) supported the infrared spectrum observations.

3. A Mixture of Di- $\mu$ -oxobis[oxotropolonatomolybdenum(V)],  $Mo_2O_4(C_7H_5O_2)_2$ , and  $\mu$ -Oxo-dioxotetrakis(tropolonato)-dimolybdenum(V),  $Mo_2O_3(C_7H_5O_2)_4$ .

Fifty milliliters of the "red hv III" solution (0.000958 dinuclear mol) were added to 0.50 g (0.0041 mol) of tropolone in a nitrogen flushed flask which was immediately stoppered. A brown precipitate began forming immediately, and after forty minutes a brown solid (0.60 g) was collected from

the yellow-orange mother liquor.

Anal. Calcd. for  $C_{14}H_{10}Mo_2O_8$ : Mo, 38.52. Found: Mo, 33.08.

The infrared spectrum suggested that the product was a mixture.

The molybdenum analysis indicated that the brown solid was a mixture primarily composed of  $Mo_2O_4(C_7H_5O_2)_2$ .

After seven days a black solid (0.04 g, 6 %) was collected from the then pale yellow mother liquor. The infrared spectrum was similar to that (Appendix Figure 15) from  $Mo_2O_3(C_7H_5O_2)_4$  obtained from the "red hv II" (Section I Part 3).

4. Di- $\mu$ -oxobis[oxo-N,N-diethyldithiocarbamatomolybdenum(V)]<sub>2</sub>,  $Mo_2O_4(C_5H_{10}NS_2)_2$ .

One hundred milliliters of the "red hv III" solution (0.001916 dinuclear mol) were added with stirring to 1.80 g (0.00798 mol) of sodium N, N-diethyldithiocarbamate trihydrate in a nitrogen flushed flask which was immediately stoppered. After ten minutes an orange solid (0.75 g, 71%) was isolated, washed, and dried under nitrogen. The infrared spectrum was obtained immediately with minimum exposure to air. Consult the Appendix (Figure 23) for the infrared spectrum of the product. At the time the molybdenum analysis was determined, the product had become brown on standing under nitrogen in a capped vial.

Anal. Calcd. for  $C_{10}H_{20}Mo_2N_2O_4S_4$ : Mo, 34.73. Found: Mo, 31.02.

The infrared spectrum of the product was very similar to that of  $Mo_2O_4(C_5H_{10}NS_2)_2$  obtained by refluxing  $Mo_2O_3(C_5H_{10}NS_2)_4$  in

water (Section D Part 8).

5. Di-μ-oxo-bis[oxocysteinatomolybdenum(V)] ethanolpentahydrate,  
 $[\text{Mo}_2\text{O}_4(\text{C}_3\text{H}_6\text{NO}_2\text{S})_2] \cdot \text{C}_2\text{H}_5\text{OH} \cdot 5 \text{H}_2\text{O}$ , Obtained from Cysteine  
Hydrochloride.

Fifty milliliters of the "red hv II" solution (0.000958 dinuclear mol) were added with stirring to 0.70 g (0.00399 mol) of L-(+)-cysteine hydrochloride monohydrate in a nitrogen flushed flask which was immediately stoppered. After twenty hours a fine yellow solid (0.28 g, 46%) was isolated. The infrared spectrum of this product suggested that it was the same as that (Appendix Figure 26) prepared from the "red hv II" solution (Section I Part 5).

6. Di-μ-oxobis[oxoacetylacetonatopyridinemolybdenum(V)],  
 $\text{Mo}_2\text{O}_4(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_5\text{H}_5\text{N})_2$ .

Fifty milliliters of the "red hv III" solution (0.000958 dinuclear mol) were added to ten milliliters (9.83 g, 0.124 mol) of pyridine in a flask which was immediately stoppered. No immediate reaction was detected, but, after standing thirty hours, well formed crystals were observed. The red crystals (0.40 g, 67%) were collected after three days from the orange mother liquor.

Anal. Calcd. for  $\text{C}_{20}\text{H}_{24}\text{Mo}_2\text{N}_2\text{O}_8$ : C, 39.23; H, 3.95; Mo, 31.34; N, 4.58. Found: C, 39.19; H, 4.00; Mo, 31.44; N, 4.40.

The infrared spectrum indicated that the product was the same as the product collected from the "red hv II" solution

(Section I Part 7).

7. The 2,2'-Bipyridine Derivative Mixture.

Fifty milliliters (0.000958 dinuclear mol) of the "red hv III" solution were added with stirring to 0.90 g (0.00576 mol) of 2,2'-bipyridine in a flask which was immediately stoppered. After twenty hours a brown-yellow solid (0.33 g) was isolated from the red-brown solution.

Anal. Calcd. for  $C_{10}H_{12}Mo_2N_2O_7$ : C, 25.88; H, 2.61; Mo, 41.34.

Found: C, 30.99; H, 2.83; Mo, 36.26.

The infrared spectrum and elemental analysis suggested that the product was similar to the duplicate run mixture (Appendix Figure 36) collected from the "red hv II" solution (Section I Part 8).

After twelve days of reaction a yellow-brown solid (0.18 g) was collected from the mother liquor. The product was insoluble in all common organic solvents. Consult the Appendix (Figure 37) for the infrared spectrum of the compound.

Anal. Calcd. for  $C_{10}H_{12}Mo_2N_2O_7$ : C, 25.88; H, 2.61; N, 6.04.

Found: C, 31.44; H, 2.77; N, 6.44.

The infrared spectrum suggested the compound was very similar to the product collected from the first run using the "red hv II" derivative solution (Section I Part 8).

8. cis-Dioxobis(benzoin-anti-oximato)molybdenum(VI),  $MoO_2(C_{14}H_{12}NO_2)_2$ .

Fifty milliliters of the "red hv III" solution (0.000958 dinuclear mol) were added to 1.00 g (0.0044 mol) of



benzoin-anti-oxime in a nitrogen flushed flask which was immediately stoppered. A light colored precipitate formed slowly in the red solution. After thirty minutes a fine off-white solid (0.50 g, 45%) was isolated.

The infrared spectrum of the compound indicated it was the same (Appendix Figure 13) as that prepared from the "red hv I" solution (Section E, Part 8) and the "red hv II" solution (Section I Part 9).

Additional collections after one hour, five hours, and eleven days produced additional off-white solid (0.42 g, 38%). Each infrared spectrum and molybdenum analysis indicated that the compound was the same as the first product collected above.

K. Photolysis by Outdoor Illumination of *cis*-Dioxobis(acetylacetonato)-molybdenum(VI) in Ethanol Solution.

A solution containing ten grams (0.0307 mol) of *cis*-dioxobis(acetylacetonato)molybdenum(VI) in eight hundred milliliters of absolute ethanol was first prepared for use in several illumination experiments. Twenty milliliter aliquots of the yellow solution were placed in each of four 150 mm quartz test tubes. Two test tubes were tightly cork stoppered and two were tightly rubber stoppered. One of each type of stoppered quartz test tube with solution was taken to the roof of the chemistry building where the test tubes were mounted in such a way as to receive maximum illumination by sunlight. At the same time one of each quartz test tube of stoppered solution

was placed in an indoor darkroom for comparison as a photolysis blank.

Simultaneously, an identical experiment to the above was accomplished with four 150 mm borosilicate glass test tubes. Again twenty milliliters of the solution were utilized in the cork and rubber stoppered test tubes.

Rubber stoppered solutions in both quartz and borosilicate glass developed a dark amber tinge after two hours of exposure to sunlight. The coloration became amber-orange after four hours and was orange after twelve hours of sunlight exposure. Additional exposure did not appreciably change the color. No significant difference between reactions in quartz and borosilicate glass was observed.

Cork stoppered solutions in both quartz and borosilicate glass developed a pale blue-green colloid after four hours of exposure to sunlight. The blue-green product, probably molybdenum blue, slowly intensified throughout the twelve-hour exposure period.

No significant difference between reactions in quartz and borosilicate glass was observed. Indoor darkroom control reactions underwent no noticeable color changes except that cork stoppered tubes became slightly tinged with green in twelve hours. Again, this emphasized the importance of dry anaerobic conditions during photolysis of oxomolybdenum(VI) complexes. Rubber stoppers are noted for impermeability to vapors, but cork

stoppers are apparently quite permeable to vapors. Moisture is probably instrumental in the formation of the blue-green colloid since it was observed, in a preliminary run, that rain resulted in copious amounts of deep blue colloid in the cork-stoppered samples.

L. Photolysis of an Ethanol Solution-Suspension of  $\text{cis}$ -Dioxobis(8-hydroxyquinolinato)molybdenum(VI),  $\text{MoO}_2(\text{C}_9\text{H}_6\text{NO})_2$ , in the Absence of Oxygen and Water with Resulting Products and Derivatives.

The photolysis of  $\text{cis}$ -dioxobis(8-hydroxyquinolinato)-molybdenum(VI) was accomplished in the same manner as that described previously for the photolysis of an ethanol solution of dioxobis(acetylacetonato)molybdenum(VI) in the absence of oxygen and water (Sections F-I). From preliminary solubility studies it was found that  $\text{MoO}_2(\text{oxine})_2$  had only negligible solubility in ethanol. A yellow suspension resulted when 12.74 g (0.0306 mol) of the bright yellow solid was mixed with the distilling ethanol in the reaction vessel H (Figure 2). During the four-hour distillation of ethanol into the reaction vessel, the stirred yellow suspension did not noticeably discolor.

The continuously stirred yellow suspension was irradiated for twelve hours. The solution became dark red, with some darkening of the solid as well. A light green solid (12.43 g, 97%) was isolated from the mother liquor by filtration, washed with ethanol, then washed with diethyl ether, and air

dried. The infrared spectrum suggested that there was no substantial change from that of the reactant,  $\text{MoO}_2(\text{oxine})_2$ . The molybdenum analysis also indicated that the solid was unchanged from the yellow starting material. When an aliquot of the red photolyzed solution was evaporated to dryness on a rotary evaporator, a brown residue was obtained. The infrared spectrum of the residue indicated that there was essentially no change from the yellow starting material.

Due to the insolubility of  $\text{MoO}_2(\text{oxine})_2$  in ethanol, the level of dissolved photolyzed oxomolybdenum species was very low. When 0.60 g (0.00413 mol) of 8-hydroxyquinoline was added to fifty milliliters (0.00096 dinuclear mol) of the photolyzed solution, a small amount of fine yellow solid was observed in the red solution. However, sufficient product could not be collected for identification. In a similar fashion, a small amount of white product was obtained by reaction with benzoin-anti-oxime. Both acetylacetone and pyridine failed to yield solid product. Traces of solid were formed when the photolyzed solution was reacted with each of the chelates, N,N-diethyldithiocarbamate, cysteine hydrochloride, and bipyridine.

- M. Photolysis of an Ethanol Solution-Suspension of  $\text{cis-Dioxobis N,N-diethyldithiocarbamato}$ molybdenum(VI),  $\text{MoO}_2(\text{C}_5\text{H}_{10}\text{NS}_2)_2$ , in the Absence of Oxygen and Water with the Resulting Product,  
 $3\text{Mo}_2\text{O}_3(\text{C}_5\text{H}_{10}\text{NS}_2)_4 \cdot \text{Mo}_2\text{O}_4(\text{C}_5\text{H}_{10}\text{NS}_2)_2$ .

The photolysis of dioxobis(N,N-diethyldithiocarbamato)-

molybdenum(VI) was accomplished in the same manner as that described previously for the photolysis of an ethanol solution of dioxobis(acetylacetonato)molybdenum(VI) in the absence of oxygen and water (Sections F-I). From preliminary solubility studies it was estimated that approximately two grams of the solid would dissolve in eight hundred milliliters of ethanol. A yellow suspension resulted when 3.43 g (0.00808 mol) of the yellow solid were mixed with the distilling ethanol in the reaction flask H (Figure 2). During the four hour distillation of ethanol into the reaction vessel, it was observed that considerable yellow solid did not dissolve with stirring and that solubility estimates were probably excessive. However, the solution was tinged a greenish-yellow indicating some  $\text{MoO}_2(\text{dtc})_2$  was dissolved.

The continuously stirred greenish-yellow suspension was irradiated for twelve hours. The suspension became dark green in less than one hour of irradiation and considerable solid was observed adhering to the reaction flask wall. The dark green solid (2.61 g, 85.1%) was isolated by filtration from the pale red mother liquor after mechanical removal from the glass surface. It was washed with ethanol, then diethyl ether, and air dried. Consult the Appendix for the infrared spectrum (Figure 25) and the X-ray powder diffraction pattern (Table XXX) of the product.

Anal. Calcd. for  $\text{C}_{17.5}\text{H}_{35}\text{Mo}_2\text{N}_{3.5}\text{O}_3\text{S}_7$ : C, 27.70; H, 4.65; Mo, 25.29, Found: C, 27.65; H, 4.49; Mo, 25.42.

The air stable green solid was slightly soluble in acetone, acetonitrile, dimethyl sulfoxide, dichloromethane, and benzene; in each case yielding a violet solution. When some of the green solid was placed in benzene and allowed to stand forty-eight hours, the initial violet color of the solution slowly faded and the green solid turned brown. However, the infrared spectrum of the brown product indicated that it was the same as the original green compound.

The compound was very sensitive to even small amounts of pressure from which a deep violet product was obtained. The coloration of the green solid did not change when left to stand in capped vials. After two years a duplicate analysis was obtained to verify the stability of the product.

Anal. Calcd. for  $C_{17.5}H_{35}Mo_2N_{3.5}O_3S_7$ : C, 27.70; H, 4.65; N, 6.46.

Found: C, 27.61; H, 4.46; N, 6.37.

Due to the limited solubility of  $MoO_2(dtc)_2$  in ethanol, the level of dissolved photolyzed oxomolybdenum species was very low. When 0.16 g (0.0011 mol) of 8-hydroxyquinoline was added to fifty milliliters of the photolyzed solution, a few small yellow crystals were observed in the reaction flask. However, sufficient product for identification could not be collected. An attempted acetylacetone derivative preparation was unsuccessful.

A duplicate photolysis reaction gave the same results as those reported above. The infrared spectrum of the green

compound suggested that it was the same product as that prepared above.

N. Photolysis of an Ethanol Solution-Suspension of  
 $\text{Na}_4[\text{Mo}_2\text{O}_5(\text{C}_3\text{H}_5\text{NO}_2\text{S})_2(\text{OH})_2] \cdot 4 \text{ H}_2\text{O}$  in the Absence of Oxygen and  
Water with the Resulting Preparation of Disodium  
 $\text{Di-}\mu\text{-oxobis[oxo(cysteinato)molybdate(V)]} \cdot \frac{1}{2}\text{-ethanol-4-water,}$   
 $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{C}_3\text{H}_5\text{NO}_2\text{S})_2] \cdot \frac{1}{2}\text{C}_2\text{H}_5\text{OH} \cdot 4 \text{ H}_2\text{O}.$

The photolysis of the salt,  $\text{Na}_4[\text{Mo}_2\text{O}_5(\text{C}_3\text{H}_5\text{NO}_2\text{S})_2(\text{OH})_2] \cdot 4 \text{ H}_2\text{O}$ , was accomplished in the same manner as that described previously for the photolysis of dioxobis(acetylacetonato)molybdenum(VI) under dry nitrogen atmosphere (Sections F-I). The yellow solid (2.00 g, 0.00282 mol) was added to flask H (Figure 2) and was followed by nitrogen flush just prior to distilling ethanol into the flask. Since ethanol was used to precipitate the yellow solid from water (Section D Part 9), only low solubility in ethanol was expected. During the four-hour distillation of ethanol into flask H, it was found that considerable yellow solid did not dissolve with rapid stirring.

The continuously stirred yellow suspension was irradiated for twelve hours. The suspension first became red-brown in less than thirty minutes, then slowly turned grey over a six hour period. No further darkening of the suspension was observed throughout the remainder of the irradiation period. A brown solid (0.52 g, 29%) was isolated from the yellowish brown solution, but considerable solid was lost in the collection process. The brown solid was

washed with ethanol and then with diethyl ether. It was very soluble in water but insoluble in organic solvents. Consult the Appendix(Figure 29) for the infrared spectrum of the compound.

Anal. Calcd. for  $C_7H_{21}Mo_2N_2Na_2O_{12.5}S_2$ : C, 13.23; H, 3.33; Mo, 30.21; N, 4.41; Na, 7.24. Found: C, 13.76; H, 3.06; Mo, 28.32; N, 4.63, Na, 6.44.

When a one hundred milliliter aliquot of the yellow-brown solution was evaporated by rotary evaporation, a gold solid (0.03 g, 2%) was isolated. The infrared spectrum suggested that the product was the same as that collected above.

An attempt to prepare a derivative of the yellow-brown solution with 8-hydroxyquinoline produced a small amount of yellow-brown solid. The infrared spectrum of the product indicated it was  $MoO_2(oxine)_2$ .

O. Photolysis of an Ethanol Solution of Molybdenum Dioxydichloride in the Absence of Oxygen and Water.

The photolysis of molybdenum dioxydichloride,  $MoO_2Cl_2$ , was accomplished in the same manner as that described previously for the photolysis of dioxobis(acetylacetonato)molybdenum(VI) under dry nitrogen atmosphere (Sections F-I). The scaley yellow solid was opened and weighed (1.40 g, 0.00704 mol) in a nitrogen-filled glove bag and transferred to the photolysis vessel, which was continuously under nitrogen flush. After the system was sealed and flushed with additional nitrogen, ethanol



was distilled into the photolysis vessel H (Figure 2). The first ethanol dissolved the yellow solid, leaving a bluish solution, but as more solvent was added, the solution appeared colorless. During the twelve hour photolysis, the colorless solution turned pale yellow in a few minutes and then dark yellow-brown after seven hours. No further color change was observed during the twelve hour photolysis period.

A derivative of 8-hydroxyquinoline (0.60 g, 0.0041 mol) was prepared from a fifty milliliter aliquot (0.00022 dinuclear mol) of the photolyzed solution. A violet-black solid (0.10 g, 56%) was isolated. The infrared spectrum indicated that the compound was  $\text{Mo}_2\text{O}_3(\text{oxine})_4$ . Derivatives of acetylacetone and sodium diethyldithiocarbamate could not be isolated from solution.

P. Photolysis of an Ethanol Solution of Molybdenum Oxytetrachloride in the Absence of Oxygen and Water.

The photolysis of molybdenum oxytetrachloride,  $\text{MoOCl}_4$ , was accomplished in the same manner as that described previously for the photolysis of dioxobis(acetylacetonato)molybdenum(VI) under dry nitrogen atmosphere (Sections F-I). The green solid was opened and weighed (5.67 g, 0.0223 mol) in a nitrogen-filled glove bag and placed in a screw capped vial until placed in the photolysis vessel H (Figure 2). The sample was then transferred to the photolysis vessel, which was continuously under nitrogen flush. The solid became reddish-brown indicating some decomposition. After the system was sealed

and flushed with additional nitrogen, ethanol was distilled into the photolysis vessel. The brown solid reacted immediately with the first few milliliters of ethanol, yielding a gaseous product and a deep green solution. As additional solvent was added to fill the photolysis vessel, the solution remained medium green. The solution was photolyzed for twelve hours, at the end of which time, the solution was dark yellow-brown.

A derivative of 8-hydroxyquinoline (0.60 g, 0.0041 mol) was prepared from a fifty milliliter aliquot (0.00070 dinuclear mol) of the photolyzed solution. A black product (0.36 g, 63%) was isolated. The infrared spectrum and molybdenum analysis indicated that the compound was  $\text{Mo}_2\text{O}_3(\text{oxine})_4$ . Attempts to prepare the acetylacetonate derivative were unsuccessful.

Q. Photolysis of an Ethanol Solution-Suspension of Ammonium Paramolybdate and Cysteine in the Absence of Oxygen and Water.

The photolysis of ammonium paramolybdate and cysteine free base was accomplished in the same manner as that described previously for the photolysis of dioxobis(acetylacetonato)-molybdenum(VI) under dry nitrogen atmosphere (Sections F-I). The solution of ammonium paramolybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{ H}_2\text{O}$  (0.858 g, 0.00486 mol), and cysteine free base,  $\text{C}_3\text{H}_7\text{NO}_2\text{S} \cdot \frac{1}{2} \text{ H}_2\text{O}$  (1.25 g, 0.00972 mol), became yellow as ethanol was distilled into the photolysis flask H (Figure 2). Some white solid, indicative of incomplete dissolution of

ammonium paramolybdate was also observed suspended in the yellow ethanol solution. The solution with suspended solid was photolyzed for twelve hours. After thirty minutes of irradiation, the suspension appeared brown. Upon completion of photolysis, a black solution containing some light colored solid was obtained.

A brown solid was isolated by filtration, but its infrared spectrum contained no distinct absorptions. When the dark supernatant liquid from the photolysis suspension was rotary evaporated to dryness, a dark product was collected. The infrared spectrum was not greatly different from that of the suspended solid collected above. No further investigation was carried out on this system.

R. Photolysis of Aqueous Ammonium Paramolybdate in the Absence of Oxygen.

The photolysis of ammonium paramolybdate in water was accomplished in the same manner as that described for the photolysis of dioxobis(acetylacetonato)molybdenum(VI) under purified nitrogen atmosphere (Sections F-I), with the exception that nitrogen purged water was distilled into the photolysis flask H (Figure 2). The aqueous solution of ammonium paramolybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$  (5.41 g, 0.00438 mol), was photolyzed for twelve hours during which time the solution turned green.

Rotary evaporation of the green solution yielded a green

solid whose infrared spectrum could not be identified, due to the absence of distinct absorptions. Utilizing 8-hydroxyquinoline (0.60 g, 0.0041 mol) and a fifty milliliter aliquot (0.00192 mol Mo) of the photolyzed solution, a light colored product was isolated by filtration. The yellow-green solid (0.73 g, 91%) was observed to have an infrared spectrum and a molybdenum analysis which indicated it was primarily composed of dioxobis(8-hydroxyquinolinato)molybdenum(VI). Attempts to prepare an acetylacetone derivative were unsuccessful, although trace amounts of a yellow solid were observed.

S. Photolysis of Aqueous Ammonium Paramolybdate and Acetylacetone in the Absence of Oxygen.

The photolysis of ammonium paramolybdate and acetylacetone in water was accomplished in the same manner as that described for the photolysis of aqueous ammonium paramolybdate. The aqueous solution of ammonium paramolybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{ H}_2\text{O}$  (5.41 g, 0.00438 mol), and acetylacetone (6.24 ml, 6.12 g, 0.0612 mol) was photolyzed for twelve hours. After irradiation was complete, a red-orange solution was obtained.

Rotary evaporation of the red-orange solution yielded a brown solid whose infrared spectrum could not be identified, due to the absence of distinct absorptions. Utilizing 8-hydroxyquinoline (0.60 g, 0.0041 mol) and a fifty milliliter aliquot (0.00192 mol Mo) of the photolyzed solution, a solid

was isolated by filtration. The dark green product (0.80 g, 99%) was observed to have an infrared spectrum which was the same as that of dioxobis(8-hydroxyquinolino)-molybdenum(VI).

#### T. Chemical Actinometry

Since broad spectrum irradiation of various ethanol and aqueous solutions and suspensions was utilized, quantum yield data was essentially meaningless. This was especially true since the wave length of the high pressure mercury-vapor lamp spectrum responsible for the photoexcitation in each case was unknown. It was therefore considered futile to attempt comprehensive quantum yield studies. The method of Hatchard and Parker<sup>13</sup> was utilized to prepare the potassium ferrioxalate chemical actinometer.

Broad spectrum exposure of the 0.006 M ferrioxalate ion actinometer resulted in complete conversion of the compound in less time than was necessary for reaching maximum intensity of the Hanovia high pressure mercury-vapor lamp, i.e., one to two minutes. However, the ferrioxalate actinometer is sensitive over the entire range of 200 to 500 nm<sup>128</sup> which was also emitted by the lamp and transmitted by the quartz immersion well. On this basis it was estimated that the broad spectrum quantum yield was less than  $10^{-3}$  for ethanolic dioxobis(acetylacetonato)-molybdenum(VI) photolysis, which assumed that complete photochemical conversion of the oxomolybdenum(VI) compound and

ferrioxalate ion occurred at sixty minutes and ten seconds, respectively. It was recognized, however, that the broad spectrum of photons emitted by the source and detected by the actinometer were probably not the same as those utilized by the photosensitive oxomolybdenum compounds irradiated in any but certain regions of the spectrum.

## DISCUSSION

Introduction

A study of oxomolybdenum complexes in oxidation states 6+, 5+, and 4+ was chosen due to its relevance to certain molybdoredoxenzymes. Nitrogenase was noted for its ability to effect reduction of substrates concurrently with oxidation of the metal at the active sites.<sup>74</sup>

Although much literature exists on photosubstitution and photo-rearrangement, very little investigation has been reported on photo-oxidation-reduction of molybdenum complexes. The tendency to photo-reduce has been observed for certain chelated oxomolybdenum(VI) complexes. This suggested a potentially new and unexplored avenue for preparing new oxomolybdenum chelate compounds of lower oxidation state. In certain cases, nitrogenase has been observed to be active in an illuminated environment. Thus, for these systems, there may be a possibility that reduction of the metal is triggered by photoexcitation.

Since it is well established that nitrogenase consists of chelated molybdenum in the polypeptide chain,<sup>68</sup> several chelated oxomolybdenum(VI) compounds were investigated for photochemical changes. Solutions of the photosensitive compound<sup>7</sup>  $\text{MoO}_2(\text{acac})_2$  were investigated as well as suspensions of  $\text{MoO}_2(\text{oxine})_2$ , noted for its stability.<sup>37</sup> Since molybdenum in molybdoenzymes was proposed to be bonded through sulfur to the protein chain,<sup>49</sup> the compounds  $\text{MoO}_2(\text{dtc})_2$  and  $\text{Na}_2[\text{Mo}_2\text{O}_5(\text{cyst})_2]$ , both containing the Mo-S bond, were also investigated for photosensitivity in ethanol. Because of the high solubility of the photosensitive compound  $\text{MoO}_2(\text{acac})_2$  in ethanol, this solvent was selected for further investigations.

Certain chelating agents were then selected in order to investigate the nature of the species formed in solution by photolysis. The selection of ligands was based upon the following criteria:

- 1) to prepare products relevant to the molybdoenzyme redox systems;
- 2) to prepare previously unreported oxomolybdenum compounds of low oxidation state;
- 3) to prepare and isolate products containing low oxidation state oxomolybdenum moieties, i.e., stabilizing ligands known for their reducing properties such as diethyldithiocarbamates, cysteinates, and acetylacetonates could enhance the chances of isolating these compounds;
- 4) to prepare products containing a second ligand of the neutral donor type, i.e., pyridine and bipyridine, which would allow isolation of otherwise unstable low oxidation state oxomolybdenum moieties;
- 5) to compare photochemical to chemical methods of preparing low oxidation state oxomolybdenum complexes;
- 6) to prepare compounds previously characterized in order to determine oxidation state and structure;
- 7) to establish conditions necessary for formation of lower oxidation state oxomolybdenum compounds;
- 8) to investigate the formation of oxo bridged molybdenum complexes;
- 9) to investigate the oxidation state sequence for oxomolybdenum complexes of specific ligands where confusion exists in the literature.



In addition, various chemical systems were investigated in order to prepare reactants for photolysis, i.e., various chelated oxomolybdenum(VI) complexes. Also chemical methods of preparing lower oxidation state oxomolybdenum complexes with ligands paralleling those used in photochemical systems were studied. These investigations were useful in complementing the photochemical studies so that evidence could be collected regarding the path of interconversion between the oxomolybdenum oxidation states, as well as interchange within each of these oxidation states.

Photosensitivity of Dioxobis(acetylacetonato)molybdenum(VI).

Initial studies supported previous reports<sup>7,27</sup> of photosensitivity for dioxobis(acetylacetonato)molybdenum(VI),  $\text{MoO}_2(\text{acac})_2$ , where acacH is acetylacetone and acac is the acetylacetonate ion,  $\text{C}_5\text{H}_7\text{O}_2^-$ . It was confirmed that the compound became blue-green upon prolonged exposure to stray light. Storage in dark bottles away from light became the general method of storage but, if tightly sealed, the compound became tinged with brown indicative of  $\text{Mo}_2\text{O}_3(\text{acac})_4$ . If the container was left vented to the surrounding air, discoloration was not noticeable and the yellow solid appeared to be stable indefinitely. This suggested the possibility of an internal reductant in the compound, i.e., probably the combined acetylacetonate ion, since both blue-green and brown compounds were indicative of molybdenum(V).<sup>7</sup> A yellow ethanolic solution of  $\text{MoO}_2(\text{acac})_2$ , separated from the photon source by a quartz or borosilicate filter, became deep orange when exposed to sunlight and red when exposed to a high pressure mercury-vapor source, as long as the

solution was not continuously exposed to air. However, when the yellow solutions were exposed to small amounts of moisture from external contamination, i.e., water vapor in air or addition of water, only the formation of molybdenum blue was observed.

In order to establish the usefulness of photolysis as a means of preparing low oxidation state oxomolybdenum complexes, several ligands noted for their chelating ability were added to aliquots of the red solution prepared by photolysis of  $\text{MoO}_2(\text{acac})_2$  in ethanol. Chemical methods of preparing these low oxidation state compounds were also investigated to complement studies utilizing photolysis.

#### Acetylacetonates

Acetylacetone had long been recognized as a standard bidentate chelating agent for many metals. The ligand was symmetrical and, therefore, stereoisomerization cannot occur as it did with unsymmetrical chelating agents. In addition, the ligand was quite compact and, hence, steric hindrance prohibiting the formation of complexes was also minimized. Only two oxomolybdoacetylacetonates had been confirmed by previous work. The molybdenum(VI) compound,  $\text{MoO}_2(\text{acac})_2$ , had been prepared by many workers,<sup>29-34</sup> but isolation was not accomplished until recently.<sup>7</sup> The molybdenum(V) compound,  $\text{Mo}_2\text{O}_3(\text{acac})_2$ , had been isolated from a sealed tube reaction.<sup>7</sup>

#### Acetylacetonate Derivatives of Photolyzed Dioxobis(acetylacetonato)-molybdenum(VI) Solutions.

The addition of acetylacetonate ( $\text{acacH}$ ) to the red ethanolic photo-reduced oxomolybdoacetylacetonate solutions, hereafter called the

"red h<sub>v</sub>" solutions, resulted in the immediate formation of a brown compound. This product was found to be the same compound, regardless of rigor, in excluding oxygen either during photolysis or during the formation of the acetylacetone derivative.

Elemental analysis and infrared spectroscopy indicated that the brown product was the compound  $\text{Mo}_2\text{O}_3(\text{acac})_4$ , previously characterized by Gehrke and Veal.<sup>7</sup> No other acetylacetonate compounds of oxomolybdenum(V) or oxomolybdenum(IV) were observed in repeated attempts to isolate them. Jowitt and Mitchell<sup>45</sup> were also unsuccessful in attempting to prepare the acetylacetonate analog of the oxomolybdenum(IV) dithiocarbamate compound,  $\text{MoO}(\text{dtc})_2$ , by chemical reduction, i.e., dithionite ion. Only  $\text{Mo}_2\text{O}_3(\text{acac})_4$  was obtained.

Infrared absorptions in the region below  $1050\text{ cm}^{-1}$  were of special interest since molybdenum-oxygen vibrations were found in this region (Table XII). In general, higher bond order vibrations occurred at higher frequencies. The strong terminal  $\text{Mo}=\text{O}$  absorption reported<sup>7</sup> at  $958\text{ cm}^{-1}$  was verified, as was a shoulder at  $950\text{ cm}^{-1}$  in all of the brown products (Appendix Figure 6). These bands were observed repeatedly in the  $910\text{--}960\text{ cm}^{-1}$  region for monooxo bridged oxomolybdenum(V) compounds (Table VIII). A medium band at  $780\text{ cm}^{-1}$  was assigned<sup>7,54</sup> to the  $\text{Mo}-\text{O}-\text{Mo}$  bridge stretch, as was a medium band at  $435\text{ cm}^{-1}$ . Two strong but broad ligand bands were observed at  $1560$  and  $1510\text{ cm}^{-1}$  and have been assigned<sup>7</sup> to symmetric and asymmetric carbonyl stretch, respectively. All other ligand bands reported<sup>7</sup> also agreed with those observed for the brown product.

Elemental analysis confirmed the formulation  $\text{Mo}_2\text{O}_3(\text{acac})_4$  for the

Table XII. Selected Infrared Spectra of Prepared OxomolybdenumAcetylacetonates.

<u>Compound</u>	<u>Color</u>	<u><math>\nu(\text{Mo}=\text{O})</math></u>	<u><math>\nu(\text{Mo}-\text{O}-\text{Mo})</math></u>	<u><math>\nu(\text{C}=\text{O})</math></u>
$\text{Mo}_2\text{O}_3(\text{acac})_4$	brown	958 (s)	780 (m)	1560 (s,br)
		950 (sh)	435 (m)	1510 (s,br)
$\text{MoO}_2(\text{acac})_2$	yellow	932 (s)		1580 (s,br)
		903 (s)		1495 (s,br)

Legend: s, strong; m, medium; sh, shoulder; br, broad.

brown compound. A green solution formed when 12 M hydrochloric acid was added to the brown solid, supporting evidence from infrared spectra for the presence of molybdenum(V) species.<sup>129</sup> In order to eliminate the possibility that stray light could be triggering the reaction to form  $\text{Mo}_2\text{O}_3(\text{acac})_4$  from the photolysis solution after acetylacetone was added, the reaction flask was completely wrapped in foil.

Although there was stoichiometrically enough acetylacetone initially present in the reactant,  $\text{MoO}_2(\text{acac})_2$ , to allow formation of any product not exceeding an acac: Mo ratio of 2:1, no  $\text{Mo}_2\text{O}_3(\text{acac})_4$  was precipitated as the yellow solution turned red during irradiation. However, reduction of the metal necessarily required oxidation of another component in the system. Since the brown product discussed below and formulated as the molybdenum(V) compound,  $\text{Mo}_2\text{O}_3(\text{acac})_4$ , was not precipitated directly from the photolysis mixture, there is at least circumstantial evidence that some of the acetylacetone was no longer present in a utilizable form, e.g., was oxidized to carboxylic acids, etc.<sup>5,123</sup>

### 8-Hydroxyquinolines

8-Hydroxyquinoline had received considerable attention as a chelating ligand in oxomolybdenum complexes. Since these reports covered the entire range of oxomolybdenum oxidation states, i.e., 6+, 5+, and 4+, the bidentate chelate was considered potentially useful in identifying the red species formed from photolysis of  $\text{MoO}_2(\text{acac})_2$  in ethanol.

In contrast to its acetylacetonate analog,  $\text{MoO}_2(\text{oxine})_2$ , where oxineH is 8-hydroxyquinoline and oxine is the 8-hydroxyquinolate anion,  $\text{C}_9\text{H}_6\text{NO}^-$ ,  $\text{MoO}_2(\text{oxine})_2$  was known for its stability.<sup>37</sup> Conflicting

reports<sup>40-43</sup> on maroon to black variations of molybdenum(V) compounds containing a monooxo bridge and formulated as  $\text{Mo}_2\text{O}_3(\text{oxine})_4$  suggested there could be at least subtle differences in geometry.<sup>42</sup> Another oxomolybdenum(V) compound,  $\text{Mo}_2\text{O}_4(\text{oxine})_2(\text{py})_2$ , which contained the neutral ligand pyridine(py) was proposed to contain a dioxo bridge.<sup>44</sup> In addition, an oxomolybdenum(IV) compound, possibly an analog of the diethyldithiocarbamate(dtc) compound,  $\text{MoO}(\text{dtc})_2$ , was reported,<sup>45</sup> but could not be isolated from solution.

#### 8-Hydroxyquinolate Derivatives of Photolyzed Dioxobis(acetylacetonato)-molybdenum(VI) Solutions.

The addition of 8-hydroxyquinoline to the "red hv" solutions in each run resulted in the formation of violet-black solids upon standing several hours. However, initial products formed were brown, with these lighter colorations predominating during early collection of the derivative from nitrogen atmosphere photolysis solutions. There were, in addition to color, both spectral and analysis distinctions between these brown products and the darker products formed upon standing. In addition, X-ray powder diffraction patterns of the black and brown products indicated considerable diversity in crystal structure. This may be attributed to the presence of mixtures in some instances although the black products which were isolated still produced greatly different powder patterns. This attests to the possibility of isomers of these compounds which were formulated as  $\text{Mo}_2\text{O}_3(\text{oxine})_4$ . None of these products retained acetylacetone as was evidenced by the absence of the carbonyl doublet in the  $1500\text{--}1600\text{ cm}^{-1}$  region of their infrared spectra.

A brown product, obtained by meticulous exclusion of air during preparation and early collection, had an infrared spectrum (Appendix Figure 9) somewhat similar to that of the dark products discussed below. However, an absorption at  $965\text{ cm}^{-1}$  was observed with greatest intensity while a band at  $935\text{ cm}^{-1}$ , indicative of  $\text{Mo}_2\text{O}_3(\text{oxine})_4$  and the black products, was also present (see Table XIII). An absorption at  $1040\text{ cm}^{-1}$  was evident but an absorption at  $425\text{ cm}^{-1}$ , characteristic of the black products, was negligible. In addition, this brown product gave a distinctly different powder pattern when the powder diffraction capillary was sealed in nitrogen (Appendix Table XXV) than when it was sealed in air (Appendix Table XXVI). This difference was possibly due to the instability of the product in air. It was observed that the  $965\text{ cm}^{-1}$  absorption became diminished in intensity after twenty-four months as bands at  $925$  and  $900\text{ cm}^{-1}$ , indicative of the compound  $\text{MoO}_2(\text{oxine})_2$  (see Appendix Figure 7), were observed. The continued brown coloration suggested that the initial product had a color somewhat the same as the yellow reported<sup>39</sup> for the compound,  $\text{MoO}_2(\text{oxine})_2$ . Since the band at  $935\text{ cm}^{-1}$  was assigned<sup>126</sup> to the terminal  $\text{Mo}=\text{O}$  in the  $\text{Mo}_2\text{O}_3$  moiety, the assignment of the absorption at  $965\text{ cm}^{-1}$  was proposed to be a terminal  $\text{Mo}=\text{O}$  stretch in the  $\text{Mo}_2\text{O}_4$  moiety. This was consistent with a recent report<sup>130</sup> of a yellow diethyldithiocarbamate(dtc) compound,  $\text{Mo}_2\text{O}_4(\text{dtc})_2$ , which also absorbed at high frequency, i.e.,  $970\text{ cm}^{-1}$ . Thus, the brown coloration of the initial product, formed from the "red hv II" solution, was proposed to result from the presence of a considerable amount of  $\text{Mo}_2\text{O}_4(\text{oxine})_2$  in a mixture with  $\text{Mo}_2\text{O}_3(\text{oxine})_4$ .

Since the percent carbon in the analysis for the brown mixtures

Table XIII. Selected Infrared Spectra of Prepared Oxomolybdenum  
8-Hydroxyquinolates.

Compound	Color	$\nu(\text{Mo}=\text{O})$	$\nu(\text{Mo}-\text{O}-\text{Mo})$	$\nu(\text{Mo} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{Mo})$
$\text{Mo}_2\text{O}_3(\text{oxine})_4$	black-violet	935 (s) 918 (sh)	425 (w) *	
$\text{Mo}_2\text{O}_4(\text{oxine})_2$	brown	965 (s) 1040 (w)		*
$\text{MoO}_2(\text{oxine})_2$	yellow	925 (s) 900 (s)		

\* Ligand interference prohibits absolute assignment in the  $700\text{--}800\text{ cm}^{-1}$  region.

**Legend:** s, strong; w, weak; sh, shoulder.



was several percent lower than that of the violet-black compounds, it was clear that the brown product had a diminished oxine:molybdenum ratio. The formulation which best satisfies these analyses appears to be  $\text{Mo}_2\text{O}_4(\text{oxine})_2$  (see Table XIV). Among the reduced oxomolybdenum species reported<sup>101</sup> to combine with organic chelates, only the  $\text{Mo}_2\text{O}_4^{2+}$  moiety had a chelate:molybdenum ratio of less than 2:1.

Since the  $965\text{ cm}^{-1}$  band was very high compared to terminal  $\text{Mo}=\text{O}$  absorptions in  $\text{Mo}_2\text{O}_3(\text{oxine})_4$  and  $\text{MoO}_2(\text{oxine})_2$  (Table XIII), an alternative assignment to the formulation of the compound as  $\text{Mo}_2\text{O}_4(\text{oxine})_2$  was considered. This absorption region corresponded closely to that reported<sup>45</sup> for the  $\text{Mo}=\text{O}$  band in  $\text{MoO}(\text{dtc})_2$  and, therefore, suggested the possibility of  $\text{MoO}(\text{oxine})_2$  in the brown product. The oxidizing nature of the 8-hydroxyquinolate ligand<sup>126</sup> could then definitely signify that the photolyzed solution is the source of molybdenum(IV). A similar conclusion could not be reached for the observed formation of all oxomolybdenum(IV) chelate compounds. The oxomolybdenum(IV) compounds containing ligands which were noted for their reducing power could attain the molybdenum(IV) oxidation state from reduction by ligand reducing agents. However, the slow decomposition but continued presence of the  $965\text{ cm}^{-1}$  absorption, upon exposure of the brown product to air, seemed to make an oxomolybdenum(IV) assignment quite dubious.

The black-violet product which was collected last closely resembled the deep violet hydrate  $\text{Mo}_2\text{O}_3(\text{oxine})_4 \cdot \text{H}_2\text{O}$ , identified by Stevens<sup>40</sup> and isolated by Busev and Fan.<sup>41</sup> However, there was little evidence of an OH stretch in the infrared near  $3400\text{ cm}^{-1}$ , and hence, it was concluded

Table XIV. Theoretical Analysis for Oxomolybdenum 8-Hydroxyquinolates.

<u>Compound</u>	<u>% C</u>	<u>% H</u>	<u>% Mo</u>	<u>% N</u>
1) $\text{MoO}_2(\text{oxine})_2$	51.94	2.91	23.05	6.73
2) $\text{Mo}_2\text{O}_3(\text{oxine})_4$	52.96	2.96	23.50	6.86
3) $\text{Mo}_2\text{O}_4(\text{oxine})_2$	39.73	2.22	35.26	5.15
4) $\text{MoO}(\text{oxine})_2$	54.02	3.02	23.97	7.00
5) 50% 3) and 50% 4)	46.87	2.62	29.62	6.07
6) 75% 3) and 25% 4)	43.30	2.42	32.44	5.61
7) 25% 2) and 75% 3)	43.04	2.41	32.32	5.58
8) 50% 2) and 50% 3)	46.35	2.59	29.38	6.01
9) 90% 2) and 10% 3)	51.64	2.89	24.68	6.69

that the compound could not contain water or the solvent, ethanol. The elemental analyses suggested the formulation  $\text{Mo}_2\text{O}_3(\text{oxine})_4$ , but the slightly high molybdenum analysis and correspondingly low carbon analysis could be due to the presence of small amounts of the initially formed brown product,  $\text{Mo}_2\text{O}_4(\text{oxine})_2$  (see Table XIV).

One of the black photolysis derivatives was determined to have an X-ray powder diffraction pattern (Appendix Table XXIV) very similar to that of one isomer of  $\text{Mo}_2\text{O}_3(\text{oxine})_4$ , as reported by Archer and Andruchow.<sup>126</sup> Minor, but definite, discrepancy with this reported powder pattern indicated possible impurities in both the photolysis and the reported<sup>126</sup> product. It is important to note that, in addition, this stable photolysis product was observed to have an infrared absorption for terminal  $\text{Mo}=\text{O}$  at  $935\text{ cm}^{-1}$  and for bridging oxygen at  $425\text{ cm}^{-1}$ . The former band was in very good agreement with that reported<sup>126</sup> at  $933\text{ cm}^{-1}$  for the compound,  $\text{Mo}_2\text{O}_3(\text{oxine})_4$ , of comparable powder pattern. The latter absorption agreed closely with that reported for several compounds containing the  $\text{Mo}_2\text{O}_3^{4+}$  moiety and had been assigned to oxygen bridge deformation.<sup>7,54,61</sup> Since infrared absorptions near 825, 785, and  $740\text{ cm}^{-1}$  were assigned<sup>43</sup> to coordinated oxine, positive identification of a bridging oxygen band in the  $700\text{--}850\text{ cm}^{-1}$  region was impossible. In addition, infrared absorptions at 1570, 1500, 1465, 1377, 1317, 1265, and  $1105\text{ cm}^{-1}$  were also assigned to ligand vibrations.<sup>43</sup> These ligand bands were also observed in spectra of the brown photolysis derivative and in  $\text{MoO}_2(\text{oxine})_2$ .<sup>48</sup> The visible absorptions reported by Busev and Fan<sup>41</sup> at 398 and 550 nm in chloroform for a black compound, formulated as  $\text{Mo}_2\text{O}_3(\text{oxine})_4\cdot\text{H}_2\text{O}$ , were also observed for the black photolysis

products. Therefore, it was concluded that the black photolysis product is the same as that for an isomer of  $\text{Mo}_2\text{O}_3(\text{oxine})_4$  prepared by Archer and Andruchow.<sup>126</sup>

X-ray powder patterns of considerably greater simplicity than those of any previously reported<sup>126</sup> black to maroon "isomers" were obtained for two black derivatives (Appendix Table XXIII). However, the powder patterns were not obtained until some apparent decomposition of the products had occurred. The first infrared spectra of these products indicated the presence of two products. In addition to bands at 935 and 425  $\text{cm}^{-1}$ , an absorption at 965  $\text{cm}^{-1}$  was especially evident for one of these products. After twenty-four months, at which time the X-ray powder patterns were obtained, the 965  $\text{cm}^{-1}$  band was diminished in strength while two additional bands at 925 and 900  $\text{cm}^{-1}$  were observed (Table XIII). The latter bands correspond to those reported<sup>48, 115</sup> for  $\text{MoO}_2(\text{oxine})_2$  indicating air oxidation of one product. The identification<sup>126</sup> of 8-hydroxyquinoline as a weak oxidizing agent could explain the slight tendency, in the presence of limited air, toward formation of  $\text{MoO}_2(\text{oxine})_2$  in preference to a stable oxomolybdenum(V) compound such as  $\text{Mo}_2\text{O}_3(\text{oxine})_4$ .

A reported<sup>42</sup> color change from red-orange to brown to violet, for an aqueous solution of molybdenum(III) and 8-hydroxyquinoline in the presence of air, could be related to the order of 8-hydroxyquinolate complex formation from photolyzed solutions. If the red coloration was due to an oxomolybdenum(IV) species, the brown may well be due to oxomolybdenum(V) which was undoubtedly different than the only product isolated, a maroon final product formulated as  $\text{Mo}_2\text{O}_3(\text{oxine})_4$ . This

proposal was substantiated by the observation<sup>45</sup> of a pink product, proposed to be  $\text{MoO}(\text{oxine})_2$ , which was prepared in solution but could not be isolated.

Although the compound  $\text{MoO}(\text{oxine})_2$  was not prepared and  $\text{Mo}_2\text{O}_4(\text{oxine})_2$  was not isolated, there is strong evidence that the previously unreported compound,  $\text{Mo}_2\text{O}_4(\text{oxine})_2$ , was present in the initially collected brown derivative from the "red hv" solutions. On the other hand,  $\text{Mo}_2\text{O}_3(\text{oxine})_4$  formed simultaneously from the photolyzed solutions during initial product formation and, when collected in the last stages of precipitation, could be isolated from the solution.

### Tropolonates

The synthesis of tropolone complexes constituted some of the most recent work in coordination chemistry. Like the acetylacetonates, the tropolonate chelate was symmetrical and, thus, eliminated the ligand stereoisomerization possible in unsymmetrical bidentate ligands such as the 8-hydroxyquinolines. Since Mettertides and Wright<sup>131</sup> first expressed the suitability of the tropolonate anion for forming compounds with high coordination number, the compact ligand had been used to form complexes of both high<sup>132-135</sup> and low<sup>132, 135, 136</sup> coordination number. One of the compounds reported<sup>132</sup> was  $\text{MoOCl}(\text{trop})_2$ , where tropH represents tropolone and trop is the tropolonate anion,  $\text{C}_7\text{H}_5\text{O}_2^-$ . Spectral data was not reported for the compound. However, no oxomolybdenum complexes with the  $\text{MoO}^{2+}$ ,  $\text{Mo}_2\text{O}_4^{2+}$ ,  $\text{Mo}_2\text{O}_3^{4+}$ , or  $\text{MoO}_2^{2+}$  moiety had been isolated. This complete void of oxomolybdenum tropolonates was a prime consideration for selection of tropolone as a chelating

ligand.

Tropolonate Derivatives of Photolyzed Dioxobis(acetylacetonato)-molybdenum(VI) Solutions.

Not unlike the 8-hydroxyquinolines, the addition of tropolone to the "red hv II" solutions resulted in the formation of two distinctly different products. When rigorous exclusion of air and moisture was utilized during tropolone derivative preparation, the result was an initial precipitate lighter in color than that formed later upon standing. In addition to differences in color, the initial brown products had distinctly different infrared spectra (Table XV) and elemental analyses (Table XVI) than the black products.

The brown initial product had a strong terminal Mo=O stretch at  $958\text{ cm}^{-1}$  with a shoulder at  $935\text{ cm}^{-1}$  (Appendix Figure 14). A shoulder at  $746\text{ cm}^{-1}$  was assigned to bridging oxygen in the  $\text{Mo}_2\text{O}_4^{2+}$  moiety<sup>43,62</sup> while a medium-weak band at  $1040\text{ cm}^{-1}$  was also observed in spectra of analogous dioxo bridged compound in this work. Notably absent was an absorption in the  $760\text{--}800\text{ cm}^{-1}$  region representative of monooxo bridging oxygen in the  $\text{Mo}_2\text{O}_3$  moiety.<sup>7,54,61</sup> In the region below  $1000\text{ cm}^{-1}$ , ligand bands could be assigned to absorptions at  $550$ ,  $720$ ,  $735$ ,  $760$ , and  $880\text{ cm}^{-1}$ ,<sup>135</sup> In the high frequency region, ligand bands were found at  $1595$ ,  $1520$ ,  $1435$ ,  $1420$ ,  $1360$ ,  $1350$ ,  $1320$ ,  $1270$ ,  $1255$ , and  $1220\text{ cm}^{-1}$ .<sup>135</sup>

The elemental analysis of the initial brown products were somewhat inconsistent suggesting the possibility of a mixture of compounds (Table XVI). In addition, maximum rigor in excluding oxygen during

Table XV. Selected Infrared Spectra of Prepared OxomolybdenumTropolonates.

Compound	Color	$\nu(\text{Mo}=\text{O})$	$\nu(\text{Mo}-\text{O}-\text{Mo})$	$\nu(\text{Mo} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{Mo})$
$\text{Mo}_2\text{O}_4(\text{trop})_2$	brown	1040(w) 958(s) 935(sh)		746(sh)
$\text{Mo}_2\text{O}_3(\text{trop})_4$	black	946(s) 932(sh)	785(m)	
$\text{MoO}_2(\text{trop})_2$	yellow	930(s) 900(s)		

Legend: s, strong; m, medium; w, weak; sh, shoulder.

Table XVI. Theoretical Analysis for Oxomolybdenum Tropolonates.

<u>Compound</u>	<u>% C</u>	<u>% H</u>	<u>% Mo</u>
1) $\text{MoO}(\text{trop})_2$	47.48	2.85	27.09
2) $\text{Mo}_2\text{O}_4(\text{trop})_2$	33.76	2.02	38.52
3) $\text{Mo}_2\text{O}_3(\text{trop})_4$	46.43	2.78	26.49
4) $\text{MoO}_2(\text{trop})_2$	45.43	2.72	25.92
5) $\text{Mo}_2\text{O}_5(\text{trop})_2$	32.71	1.96	37.32



tropolonate derivative preparation consistently resulted in lowest carbon and highest molybdenum analysis for these brown initial products. These elemental analyses dictated the predominance of a compound whose tropolone:molybdenum ratio is 1:1 (see Table XVI). Only the oxo-molybdenum(V) formulation,  $\text{Mo}_2\text{O}_4(\text{trop})_2$ , among compounds containing known oxomolybdenum(V) moieties, satisfied this requirement. Terminal  $\text{Mo}=\text{O}$  absorptions for  $\text{Mo}_2\text{O}_3(\text{trop})_4$ , i.e.,  $946\text{ cm}^{-1}$  with a shoulder at  $932\text{ cm}^{-1}$ , were observed in the infrared spectra of some of the initially collected mixtures (Appendix Figure 16). It was therefore proposed that the high carbon and the low molybdenum analyses were due to the presence of a secondary product in the initially formed  $\text{Mo}_2\text{O}_4(\text{trop})_2$  discussed below. The possibility of the presence of the oxo-molybdenum(IV) compound,  $\text{MoO}(\text{trop})_2$ , could be an alternative explaining the low molybdenum and high carbon analysis of the initial products but no terminal  $\text{Mo}=\text{O}$  stretch was detected at a uniquely high frequency which could be analogous to the  $\text{Mo}=\text{O}$  absorption reported<sup>45</sup> for  $\text{MoO}(\text{dtc})_2$ , i.e.,  $960\text{ cm}^{-1}$ . Another explanation for the analysis proposed the presence of free ligand as an impurity in the brown product. However, this was discounted as unlikely because of the high solubility of tropolone in the ethanol solvent and the lack of evidence for it in the infrared spectra. Both the infrared spectrum (Table XV) and the elemental analysis (Table XVI) indicated the presence of  $\text{Mo}_2\text{O}_4(\text{trop})_2$  as the primary component in the brown initial mixture.

The black compound, collected from the mother liquor, had absorptions for terminal  $\text{Mo}=\text{O}$  at  $946\text{ cm}^{-1}$  with a shoulder at  $932\text{ cm}^{-1}$  (Appendix Figure 15). Thus, the brown and black tropolonate derivatives

were found to show somewhat similar but not identical absorptions in the 900-1000  $\text{cm}^{-1}$  region (Table XV) as was observed for the proposed 8-hydroxyquinolinate analogs. In the 700-800  $\text{cm}^{-1}$  region there was a unique medium band observed at 785  $\text{cm}^{-1}$  but no band at 746  $\text{cm}^{-1}$ , as was observed for the brown mixture above. This absorption was assigned to the Mo-O-Mo bridge.<sup>7,54</sup> Also absent was the band at 1040  $\text{cm}^{-1}$ , noted in the infrared spectrum of the brown product. Ligand absorptions were, however, reproduced closely for tropolone, as discussed above for the brown product.

The elemental analyses of the black products collected after standing were, in general, much higher in carbon and lower in molybdenum than their brown counterparts. When the initial product was not removed from the mother liquor and the mixture was allowed to stand before making the single collection, the dark product was determined to contain considerable of the initial brown solid as indicated by the elemental analysis and observed in the infrared spectrum, (Appendix Figure 16). Utilizing the technique of careful removal of initial products, however, the black compound was isolated and the elemental analysis was in excellent agreement with the values calculated for the formulation,  $\text{Mo}_2\text{O}_3(\text{trop})_4$  (see Table XVI). It is therefore proposed that the compound was the tropolonate analog of the dinuclear molybdenum(V) compounds,  $\text{Mo}_2\text{O}_3(\text{oxine})_4$ <sup>41</sup> and  $\text{Mo}_2\text{O}_3(\text{acac})_4$ <sup>7</sup>, discussed earlier.

Although an oxomolybdenum(IV) compound could not be prepared from the photolyzed solutions, both proposed oxomolybdenum(V) compounds which were prepared have not previously been reported. Thus, it was concluded

that the initially formed product from the "red hv" solutions was predominantly  $\text{Mo}_2\text{O}_4(\text{trop})_2$  and that  $\text{Mo}_2\text{O}_3(\text{trop})_4$  formed more slowly and was isolated only over extended reaction periods. These observations suggested that the two oxomolybdenum(V) compounds do not undergo appreciable interconversion, probably due to their extreme insolubility in ethanol. The reaction of ligand with the "red hv" solutions closely paralleled the observations for the formation of 8-hydroxyquinolates. However, one important difference was that tropolone, a symmetrical ligand, could not form the numerous isomers theoretically feasible with 8-hydroxyquinoline.<sup>42</sup>

#### Oxomolybdenum(VI) tropolonates

Since an oxomolybdenum(VI) tropolonate had not previously been reported, an attempt was made to prepare such a compound. The reaction of aqueous sodium molybdate and tropolone in ethanol resulted in the formation of a copious yellow precipitate. Unlike other oxomolybdenum(VI) chelates, much of the product was dissolved in the water wash. The infrared spectrum of this initial product had multiple absorptions in the  $850\text{--}950\text{ cm}^{-1}$  region (Appendix Figure 17). This region had generally been assigned to terminal  $\text{Mo}=\text{O}$  stretch, with mononuclear oxomolybdenum(VI) compounds containing the  $\text{MoO}_2^{2+}$  moiety being noted for the symmetric and asymmetric doublet. The compound  $\text{MoO}_2(\text{acac})_2$  had a doublet reported<sup>115</sup> at  $935$  and  $904\text{ cm}^{-1}$  while  $\text{MoO}_2(\text{oxine})_2$  was reported<sup>115</sup> to have a similar doublet at  $924$  and  $898\text{ cm}^{-1}$ . The initial ethanol-washed, yellow tropolonate solid, however, had a triplet in the  $900\text{--}950\text{ cm}^{-1}$  region and a doublet in the

850-900  $\text{cm}^{-1}$  region. Sharp, strong bands were observed at 930, 915, 900, 880, and 860  $\text{cm}^{-1}$  as well as a triplet at 720, 745, and 760  $\text{cm}^{-1}$

Reprecipitation of the water soluble product with ethanol resulted in a solid similar in color to that formed initially, but with an infrared spectrum showing only bands at 930, 900, and 880  $\text{cm}^{-1}$  (Appendix Figure 18). Since the 930 and 900  $\text{cm}^{-1}$  sharp doublet was present in about the same relative intensities and similar doublets had been reported for other oxomolybdenum(VI) compounds, these absorptions were assigned to the cis-dioxo moiety,  $\text{MoO}_2^{2+}$  (Table XV). The elemental analysis supported the formulation of the compound as  $\text{MoO}_2(\text{trop})_2$ . The presence of sodium and the low carbon analysis of the initial product suggested that two products were formed or that considerable coprecipitation with reactants had occurred. An infrared spectrum of identical nature to that of the product isolated after reprecipitation (Appendix Figure 18) was obtained for a yellow product formed by ceric oxidation of  $\text{Mo}_2\text{O}_3(\text{trop})_4$ . The same spectrum was also obtained from a tan product obtained from a "red hv" solution which was first rotary evaporated to one-half volume prior to tropolone derivative preparation. These incidental preparations strongly supported the formation of  $\text{MoO}_2(\text{trop})_2$ , and indicated the relationship, via oxidation, of this compound to others prepared in this work.

#### N,N-Diethyldithiocarbamates

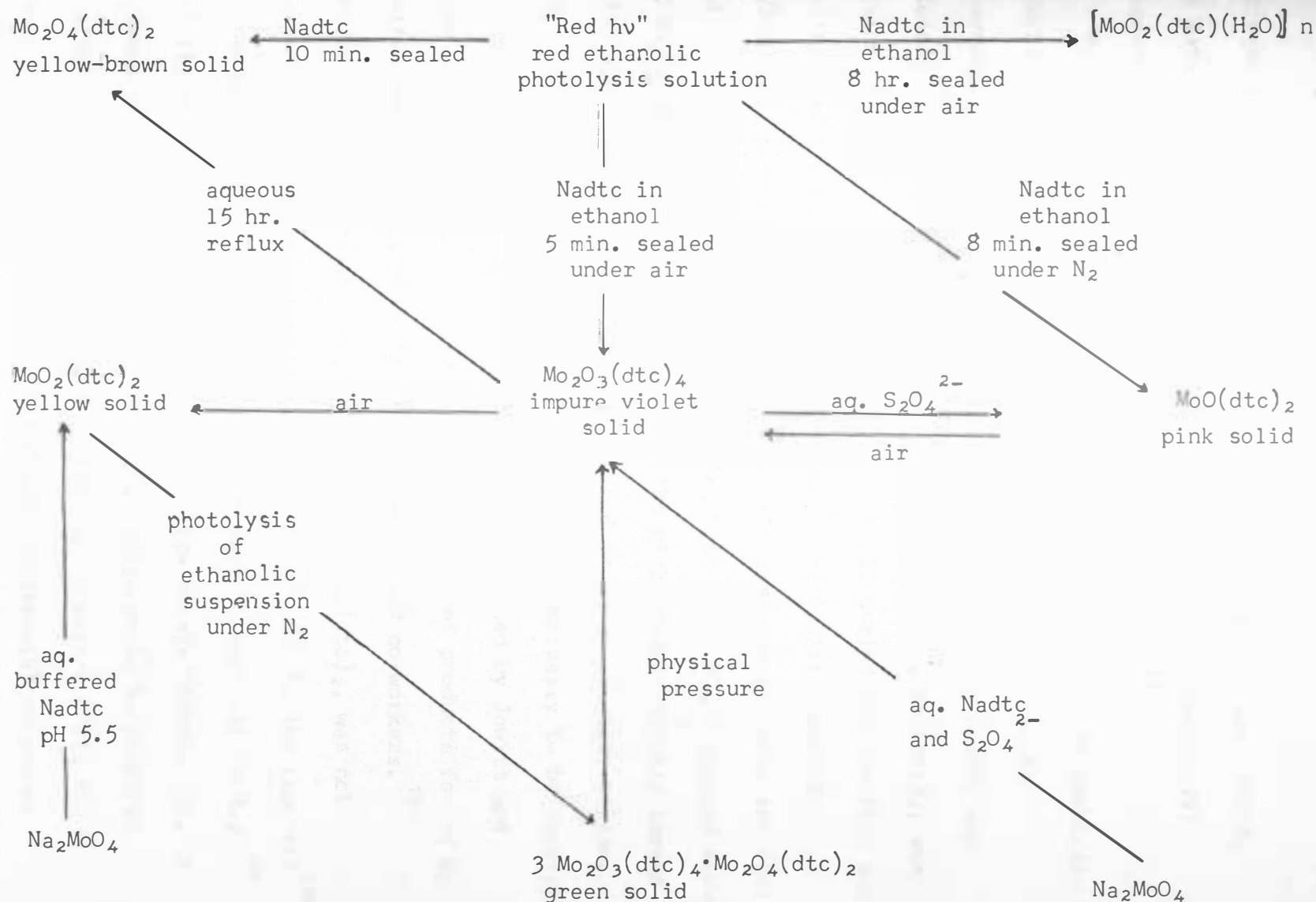
The importance of molybdenum-sulfur bonding in natural systems has already been emphasized. Chelate compounds containing such bonds had been shown to be especially significant to molybdoenzyme systems where

low oxidation state molybdenum compounds could be prepared in addition to those of high oxidation state.<sup>98, 130</sup> The oxomolybdenum diethyldithiocarbamates,  $\text{MoO}_2(\text{dtc})_2$ ,  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ , and  $\text{MoO}(\text{dtc})_2$  where dtc is the diethyldithiocarbamate anion  $\text{C}_5\text{H}_{10}\text{NS}_2$ , had been reported<sup>51, 45</sup> and represent molybdenum oxidation states 6+, 5+, and 4+, respectively. In addition, a second oxomolybdenum(V) compound,  $\text{Mo}_2\text{O}_4(\text{dtc})_2$ , had recently been prepared.<sup>130</sup> Since the low oxidation state compounds were previously prepared by chemical reduction, attempts were also made to prepare them from the "red hv" solutions and from photolysis of a solution of  $\text{MoO}_2(\text{dtc})_2$ .

#### N,N-diethyldithiocarbamates of Photolyzed Dioxobis(acetylacetonato)-molybdenum(VI) Solutions.

The products resulting from the reaction of sodium diethyldithiocarbamate (Nadtc) and the "red hv" solution were extremely dependent upon the degree of rigor followed for oxygen and moisture exclusion in the preparation procedure (see Figure 3). When no special precautions were followed regarding air exposure of the "red hv" and ligand solutions during mixing, a black-violet product of polymeric nature was prepared. When the "red hv" solution was added directly to solid Nadtc and allowed to react in a nitrogen atmosphere, the product was much lighter but still violet in coloration. It was probably related to reported<sup>51-54, 130</sup> "soluble" and "insoluble" forms of the violet oxomolybdenum(V) compound,  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ . Finally, when the reaction flask was preflushed with nitrogen and the photolysis solution was added to solid Nadtc in the flask, all under constant

Figure 3. Scheme of N,N-Diethyldithiocarbamate Reaction Products.



nitrogen flush, the product was a pink prismatic crystalline solid.

The pink product was found to correspond to the oxomolybdenum(IV) compound,  $\text{MoO}(\text{dtc})_2$ , reported by Jowitt and Mitchell.<sup>45</sup>

Both the violet and pink products were also obtained by chemical reduction of sodium molybdate by aqueous dithionite ion in the presence of  $\text{Nadtc}$ , using a modification of the method of Jowitt and Mitchell<sup>51,45</sup> (Figure 3). However, the pink compound,  $\text{MoO}(\text{dtc})_2$ , was obtained only with meticulous exclusion of air during the reaction and isolation of the product. The isolation of the violet compound,  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ , proved to be impossible and infrared spectroscopy verified that the product was a mixture containing both  $\text{MoO}(\text{dtc})_2$  (discussed above) and  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ . When exposed to air, the pink product quickly turned violet and after prolonged standing, turned brown and finally yellow. This yellow product was determined spectrophotometrically to be largely the oxomolybdenum(VI) compound,  $\text{MoO}_2(\text{dtc})_2$ , reported by Jowitt and Mitchell.<sup>51</sup> A similar sequence of air oxidation of products formed by chemical reduction was also observed by Newton and co-workers.<sup>130</sup>

However, another oxomolybdenum(V) compound,  $\text{Mo}_2\text{O}_4(\text{dtc})_2$ , was not observed in this oxidation sequence. This may be due to the reported<sup>130</sup> low temperature stability of the  $\text{Mo}_2\text{O}_3^{4+}$  moiety in contrast to  $\text{Mo}_2\text{O}_4^{2+}$  stability at high temperatures.<sup>62,130</sup> Utilizing this information, it was found that the yellow compound,  $\text{Mo}_2\text{O}_4(\text{dtc})_2$ , could be prepared by refluxing the violet product,  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ , in water. This may be another means of preparation for other oxomolybdenum(V) compounds containing the dioxo bridge.

The infrared spectra of the pink oxomolybdenum(IV) products,

prepared from the "red hv" solution (Appendix Figure 20) and by dithionite ion reduction (Appendix Figure 21), were observed to have a single strong, but sharp, absorption at  $960\text{ cm}^{-1}$  with no significant adjacent lower frequency shoulder, as was typically observed in all previously discussed molybdenum(V) compounds. Due to the absence of the shoulder approximately  $20\text{ cm}^{-1}$  lower in energy than the main terminal  $\text{Mo}=\text{O}$  stretch and the absence of absorptions in the  $700$  to  $850\text{ cm}^{-1}$  region, usually assigned to bridging oxygen, the pink compound could not be considered a bridged oxomolybdenum(V) compound (Table XVII). During the progress of this work the infrared spectrum of the pink compound,  $\text{MoO}(\text{dtc})_2$ , was reported by Jowitt and Mitchell.<sup>45</sup> The band at  $960\text{ cm}^{-1}$  was assigned to the terminal  $\text{Mo}=\text{O}$  stretch. Weak bands at  $900$ ,  $835$ , and  $770\text{ cm}^{-1}$  were assigned to the dithiocarbamate ligand. Thus, the infrared spectra strongly indicated that the pink compound was mononuclear and contained only terminal oxygen.

The elemental analyses of the pink compounds were somewhat low in percent carbon and high in percent molybdenum, especially when prepared from the "red hv" solutions. This could be attributed to the presence of some of the oxomolybdenum(V) compound,  $\text{Mo}_2\text{O}_4(\text{dtc})_2$  (see Table XVIII). X-ray powder patterns of  $\text{MoO}(\text{dtc})_2$  prepared from the "red hv" solution (Appendix Table XXIX) and from dithionite ion reduction (Appendix Table XVIII) were observed to be completely different. In general  $\text{MoO}(\text{dtc})_2$  was extremely unstable in air, even when dry. However, it could be stored indefinitely under nitrogen in sealed glass ampoules without decomposition. Exposure to air for even a few minutes caused the pink solid to turn red and then violet. Extended exposure led to a



Table XVII. Selected Infrared Spectra of Prepared Oxomolybdenum N,N-Diethyldithiocarbamates.

Compound	Color	$\nu(\text{Mo}=\text{O})$	$\nu(\text{Mo}-\text{O}-\text{Mo})$	$\nu(\text{Mo} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{Mo})$	$\nu(\text{Mo}-\text{S})$
$\text{MoO}(\text{dtc})_2$	Pink	960(vs)			370(m)
$\text{Mo}_2\text{O}_3(\text{dtc})_4$	Violet	928(s), 912(m)	775(w), 740(w), 435(m)		367(m)
$\text{MoO}_2(\text{dtc})(\text{H}_2\text{O})_n$	Violet-black	933(s, br), 911(m)	840(s, vbr) 775(w), 435(m) 740(w)		367(m)
$3\text{Mo}_2\text{O}_3(\text{dtc})_4 \cdot \text{Mo}_2\text{O}_4(\text{dtc})_2$	Green	970(w) 935(s) 910(w)	740(w), 425(m)		365(w)
$\text{Mo}_2\text{O}_4(\text{dtc})_2$	Yellow	1040(w), 970(s), 955(m)		728(w), 475(m)	375(m)
$\text{MoO}_2(\text{dtc})_2$	Yellow	912(vs), 881(vs)			385(s)

Legend: vs, very strong; s, strong; m, medium; w, weak; br, broad; vbr, very broad.

Table XVIII. Theoretical Analysis for OxomolybdenumN,N-Diethyldithiocarbamates.

<u>Compound</u>	<u>%C</u>	<u>%H</u>	<u>% Mo</u>	<u>% N</u>
1) $\text{MoO}(\text{dtc})_2$	29.40	4.94	23.49	6.86
2) $\text{Mo}_2\text{O}_3(\text{dtc})_4$	28.84	4.84	23.04	6.73
3) $\text{Mo}_2\text{O}_4(\text{dtc})_2$	21.74	3.65	34.73	5.07
4) $\text{MoO}_2(\text{dtc})(\text{H}_2\text{O})_n$	20.41	4.11	32.61	4.76
5) $\text{MoO}_2(\text{dtc})_2$	28.30	4.75	22.60	6.60
6) $\text{Mo}_2\text{O}_3(\text{dtc})_{3.5}$	28.84	4.84	23.04	6.73
7) $3 \text{ Mo}_2\text{O}_3(\text{dtc})_4 \cdot$ $\text{Mo}_2\text{O}_4(\text{dtc})_2$	27.06	4.54	25.96	6.32

brown and finally a yellow product after several weeks. An infrared spectroscopy study determined the oxidation products obtained from the oxomolybdenum(IV) compound. This study indicated that the first oxidation product was  $\text{Mo}_2\text{O}_3(\text{dtc})_4$  (violet) while the second was indicated to be  $\text{MoO}_2(\text{dtc})_2$  (yellow). As the pink product turned violet, the band at  $960\text{ cm}^{-1}$  diminished in strength and an absorption appeared at  $928\text{ cm}^{-1}$  with a shoulder at  $910\text{ cm}^{-1}$ , indicating the formation of  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ . As oxidation progressed and the violet product turned brown, the  $960\text{ cm}^{-1}$  band disappeared, the  $928\text{ cm}^{-1}$  absorption with shoulder diminished in strength and a doublet at  $912$  and  $881\text{ cm}^{-1}$  became prominent, indicating the formation of  $\text{MoO}_2(\text{dtc})_2$  (see Appendix Figure 19). It has been shown (Table XVIII) that the calculated elemental compositions for all of these compounds in the proposed oxidation sequence;  $\text{MoO}(\text{dtc})_2$ ,  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ , and  $\text{MoO}_2(\text{dtc})_2$ , were very similar since all have a Mo:dtc ratio of 1:2 and similar amounts of oxygen. Hence, the value of elemental analysis as a useful tool for distinction between members of the sequence was minimized. The infrared spectra, as well as the observed coloration of these compounds, however, was quite useful in their identification.

The violet product was not obtained in pure form from the photolysis preparation. It was observed spectrophotometrically in the infrared to be mixed with the pink compound, i.e.,  $960\text{ cm}^{-1}$  absorption. When allowed to stand in the reaction mixture, in an attempt to eliminate  $\text{MoO}(\text{dtc})_2$ , a black compound was obtained. This product was observed to have a strong, but broadened, band at  $933\text{ cm}^{-1}$  with a shoulder at  $911\text{ cm}^{-1}$  (Appendix Figure 22). It was also observed to

have bands at 435 and 367  $\text{cm}^{-1}$ , as did the violet compound (Appendix Figure 24). However, the observation of a strong, but very broad, band in the 800-880  $\text{cm}^{-1}$  region with a peak at 840  $\text{cm}^{-1}$  distinguished it from the violet product. Broad bands in this region were frequently assigned to a Mo-O-Mo-O chain vibration associated with polymeric compounds.<sup>112</sup> The formation of oligomers has been suggested by others to explain deviating analysis and insolubility of  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ .<sup>53,54,139</sup> The presence of a medium, but very broad, band in the 3000-3600  $\text{cm}^{-1}$  region, as well as a weak band in the 1600-1650  $\text{cm}^{-1}$  region, suggested the presence of water. The distinctly different elemental analysis of this compound (Table XVIII) dictates that its molybdenum:ligand ratio is 1:1. Reports<sup>53,54</sup> of decreasing solubility of violet dithiocarbamate compounds appeared to verify the likelihood of formation of a stable polymeric oxomolybdenum(V) compound. It was proposed that a formulation such as  $[\text{MoO}_2(\text{dtc})(\text{H}_2\text{O})]_n$  would fit this compound, but it was likely that  $n$  was large.

Infrared spectra of violet compounds formulated as  $\text{Mo}_2\text{O}_3(\text{dtc})_4$  were reported by Casey, et.al.,<sup>52</sup> and by Jowitt and Mitchell.<sup>51</sup> The violet product prepared in this work (Figure 3) by dithionite ion reduction was observed to give the same absorptions in the infrared spectrum (Appendix Figure 24) as was reported in the literature.<sup>52</sup> Observed was a very strong band at 928  $\text{cm}^{-1}$  with a shoulder at 912  $\text{cm}^{-1}$ , typical of molybdenum(V) terminal Mo=O stretch (Table XVII). Medium bands at 775 and 435  $\text{cm}^{-1}$  indicated the presence of a monooxo bridge.<sup>7</sup> Also observed was a medium band at 367  $\text{cm}^{-1}$  attributed to molybdenum-sulfur bonding. Weak bands at 742 and 570  $\text{cm}^{-1}$  were also observed as

reported previously.<sup>52</sup> The elemental analysis supported the formulation of these violet compounds as  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ , but hazards in placing great reliance on this alone have been discussed above. An X-ray powder pattern was obtained (Appendix Table XVII), but was not similar to the patterns observed for  $\text{MoO}(\text{dtc})_2$ .

A unique photolysis product, orange in coloration, was obtained from the Pyrex filtered photolysis. The infrared spectrum had a terminal  $\text{Mo}=\text{O}$  stretch at  $970\text{ cm}^{-1}$  and a shoulder at  $955\text{ cm}^{-1}$  which was much stronger than observed in any previously discussed lower oxidation state molybdenum compound (Appendix Figure 23). To further support the uniqueness of the compound, it was observed to absorb strongly at  $728\text{ cm}^{-1}$ , the frequency reported<sup>43,62</sup> representative of dioxo bridged dinuclear compounds, and at  $480$  and  $407\text{ cm}^{-1}$ . Representative ligand bands discussed above were present including the molybdenum-sulfur bond at  $375\text{ cm}^{-1}$ . Coupled with the molybdenum analysis, the infrared spectrum suggested the formulation,  $\text{Mo}_2\text{O}_4(\text{dtc})_2$ . Notably, this was the only diethyldithiocarbamate derivative prepared by adding the photolyzed solution directly to the solid ligand (Figure 3). Other derivatives were prepared by mixing the photolyzed solutions with ligand previously dissolved in small amounts of ethanol. It was this distinction which now makes highly questionable any proposal that an orange derivative was unique to solutions photolyzed with a Pyrex filter.

Recently, Newton and co-workers<sup>130</sup> have also reported the preparation of  $\text{Mo}_2\text{O}_4(\text{dtc})_2$  from molybdenum pentachloride and  $\text{NadtC}$ . They reported infrared absorptions for terminal  $\text{Mo}=\text{O}$  and dioxo bridging, as assigned above. Since these authors<sup>130</sup> mentioned that higher

temperatures may favor the formation of dioxo bridged over monooxo bridged compounds, it was decided to attempt the preparation of  $\text{Mo}_2\text{O}_4(\text{dtc})_2$  by refluxing  $\text{Mo}_2\text{O}_3(\text{dtc})_4$  in aqueous media. The yellow compound,  $\text{Mo}_2\text{O}_4(\text{dtc})_2$  was isolated by this method after a fifteen hour reflux. The characteristic infrared absorptions (Appendix Figure 38) were the same as observed for the orange compound above and reported by Newton, et.al.<sup>130</sup> Observed was the 970, 955  $\text{cm}^{-1}$  doublet, as well as the bridging bands at 728 and 475  $\text{cm}^{-1}$ . The identification of a weak band near 1040  $\text{cm}^{-1}$  was somewhat difficult. This infrared data, coupled with the elemental analysis, confirmed the formulation as  $\text{Mo}_2\text{O}_4(\text{dtc})_2$ . The yellow compound discolored quickly to brown-orange upon exposure to air and, when washed with diethyl ether or ethanol, a violet wash solution was collected as the remaining yellow solid was repurified. This appeared to explain the orange coloration for the photolysis product discussed above.

The preparation of diethyldithiocarbamate derivatives from the "red hv" solutions was especially successful. An entire spectrum of oxomolybdenum(IV) and (V) compounds was identified. As was the case with 8-hydroxyquinolate and tropolonate derivatives, compounds containing both the  $\text{Mo}_2\text{O}_3^{4+}$  and  $\text{Mo}_2\text{O}_4^{2+}$  moieties were prepared, although isolation was difficult. The formation of a compound which appeared to be polymeric was unique to this set of derivatives. In addition, the isolation of an oxomolybdenum(IV) compound,  $\text{MoO}(\text{dtc})_2$ , was accomplished for the first time from the "red hv" solution. Although this could indicate the presence of an oxomolybdenum(IV) species in solution, the

reducing characteristic<sup>52</sup> of the dithiocarbamate ion made such a proposal quite dubious, especially without supportive findings of similar oxomolybdenum(IV) compounds with other chelating ligands.

The Product from a Photolyzed *cis*-Dioxobis(N,N-diethyldithiocarbamato)-molybdenum(VI) Suspension.

The starting material was the yellow compound,  $\text{MoO}_2(\text{dtc})_2$ , prepared by Jowitt and Mitchell<sup>51</sup> (Figure 3). The infrared spectrum of the compound was characterized by the doublet absorption at 912 and 881  $\text{cm}^{-1}$ .<sup>45</sup> When the  $\text{MoO}_2(\text{dtc})_2$  was photolyzed as a suspension in dried and deoxygenated ethanol, a finely divided insoluble green product formed. This green solid was very unique for two reasons. First, the product was found to be stable indefinitely in air. This was unexpected since the infrared spectrum was remarkably similar to that of the violet product,  $\text{Mo}_2\text{O}_3(\text{dtc})_4$  (Appendix Figure 24), discussed previously, which was converted in air to  $\text{MoO}_2(\text{dtc})_2$ . The other characteristic of the green product was at least of curious interest. The green solid was found to be extremely sensitive to even minimum pressure. The result of such treatment was the formation of a violet product which in every way had the properties (except analyses) of the reported<sup>52,54,130</sup> violet compound,  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ . This violet solid was, in turn, oxidized in air to  $\text{MoO}_2(\text{dtc})_2$  as followed by infrared spectroscopy. The infrared spectrum of the green compound (Appendix Figure 25) had a very strong terminal  $\text{Mo}=\text{O}$  stretch at 935  $\text{cm}^{-1}$  with a shoulder at 908  $\text{cm}^{-1}$ , a medium band at 770  $\text{cm}^{-1}$ , and weak bands at 970 and 740  $\text{cm}^{-1}$ . This suggested a predominance of a monooxo bridging over dioxo bridging. Since the

970  $\text{cm}^{-1}$  absorption was weak, the fraction of  $\text{Mo}_2\text{O}_4(\text{dtc})_2$  present must be minor, but could still explain the low ligand analysis. The formation of oligomers, as had been reported<sup>54, 130</sup> for the violet  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ , may also explain the low ligand analysis. However, in order to maintain a maximum coordination number of six in a  $\text{--}\overset{\text{O}}{\underset{\text{O}}{\text{Mo}}}\text{--}\overset{\text{O}}{\underset{\text{O}}{\text{Mo}}}\text{--}\text{O}$  chain, one dithiocarbamate would necessarily be lost (or become unidentate). Although representative absorptions for coordinated diethyldithiocarbamate were present, it was not unlikely that oxidation of a portion of the dithiocarbamate ligand concurrently with reduction of the molybdenum could also occur in the heterogeneous system, as was apparently the case in the ethanol- $\text{MoO}_2(\text{acac})_2$  homogeneous system. This would be compatible with product stoichiometries possessing Mo:dtc ratios of less than 1:2. One overriding objection to the oligomer theory was the absence of broad bands in the 700-1000  $\text{cm}^{-1}$  region of the infrared spectrum. These could be considered a prerequisite to  $\text{--Mo--O--Mo--O--}$  chain bridging.<sup>112</sup> The first explanation appeared much more likely with the dithiocarbamate ligand oxidized in the redox process, necessitating the formation of a definite amount of  $\text{Mo}_2\text{O}_4(\text{dtc})_2$  (25%). If this was the case, it was then proposed that for each molybdenum atom reduced from oxidation state 6+ to 5+, one-fourth dithiocarbamate unit was oxidized, i.e.,

$$8 \text{ MoO}_2(\text{dtc})_2 \xrightarrow{\text{hv}} 3 \text{ Mo}_2\text{O}_3(\text{dtc})_4 + \text{Mo}_2\text{O}_4(\text{dtc})_2 + 2 \text{ oxidized dtc}$$

In such a reaction it may be conjectured that  $\text{Mo}_2\text{O}_4(\text{dtc})_2$  was definitely not the favored product but, when dithiocarbamate ion was not present in sufficient supply to yield a Mo:dtc ratio of 1:2, the compound



$\text{Mo}_2\text{O}_4(\text{dtc})_2$  was formed, since only a Mo:dtc ratio of 1:1 was necessary. Comparisons of the X-ray powder pattern (Appendix Table XXX) of the product with those of  $\text{Mo}_2\text{O}_3(\text{dtc})_4$  (Appendix Table XXVII) and  $\text{MoO}(\text{dtc})_2$  (Appendix Tables XVIII and XIX) indicated no significant similarities. The elemental analysis was in excellent agreement with the formulation of  $3 \text{ Mo}_2\text{O}_3(\text{dtc})_4 \cdot \text{Mo}_2\text{O}_4(\text{dtc})_2$  for the product (Table XVIII).

### Cysteinates

The amino acid, cysteine, was especially significant as a molybdenum ligand since the enzyme, nitrogenase, was proposed to include molybdenum-sulfur bonds involving cysteine, the part of the coordinated polypeptide chain proposed to be active in the reduction of dinitrogen.<sup>75</sup> Molybdenum in low oxidation states, i.e., 4+ and 5+ was of prime interest since it was proposed<sup>96, 130</sup> that the metal in nitrogenase was actually responsible for reduction of dinitrogen to ammonia at the active sites. In order to accomplish nitrogen fixation, it has been recently proposed that it could be necessary to have combined simultaneous activity of two molybdenum atoms at the active site,<sup>130</sup> e.g., involving bridging oxygen between these sulfur chelated metal atoms. Consequently, special significance was attached to the preparation of cysteinates from photoreduced solutions, as well as directly from molybdenum(VI) cysteinate salts which contain oxygen bridged nuclei of lower oxidation state molybdenum.

### Cysteinate of Photolyzed Dioxobis(acetylacetonato)molybdenum(VI)

#### Solutions Using Cysteine Hydrochloride.

The addition of cysteine hydrochloride to the "red hv" solutions resulted in the formation of yellow solids. Since chemical tests for chloride were negative and there were no sharp bands in the 300-400  $\text{cm}^{-1}$  region of the infrared spectrum assignable<sup>137, 138</sup> to metal-halogen stretch, the presence of chlorine in the product was discounted. Infrared absorptions in the 700-1050  $\text{cm}^{-1}$  region were broad but distinct (Appendix Figure 26), a characteristic previously reported<sup>62</sup> for  $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{cyst})_2] \cdot 2 \text{H}_2\text{O}$ , where cyst is the dinegative cysteinate anion,  $\text{C}_3\text{H}_5\text{NO}_2\text{S}^{2-}$ . A very strong but broad band at 965  $\text{cm}^{-1}$  was assigned<sup>55</sup> to a terminal  $\text{Mo}=\text{O}$  stretch while a medium broad band at 725  $\text{cm}^{-1}$  was assigned to a dioxo bridge<sup>55, 58</sup> (Table XIX).

The presence of the band at 725  $\text{cm}^{-1}$  confirmed<sup>58</sup> that the compound contained bridging oxygen. The medium broad band observed at 1045  $\text{cm}^{-1}$  had in addition been observed in the infrared spectra from other proposed dioxo bridged compounds prepared in this work.

A medium broad band in the 3300-3600  $\text{cm}^{-1}$  region of the infrared spectrum signified<sup>55</sup> an O-H stretch, indicative of water or ethanol, while a medium broad absorption in the 2900-3200  $\text{cm}^{-1}$  region was assigned<sup>61</sup> to a N-H stretch where nitrogen was coordinated. The uncoordinated N-H stretch had been reported<sup>61</sup> at 3350  $\text{cm}^{-1}$ . An N-H deformation band near 1560  $\text{cm}^{-1}$  could not be identified due to the broad absorption in that region. The absence of an S-H band near 2500  $\text{cm}^{-1}$  suggested that coordination occurs at the ionized sulfhydryl site.<sup>61</sup> Definite assignment regarding the carboxylic acid carbonyl was difficult due to the medium to weak, extremely broad absorption in the 1500-1750  $\text{cm}^{-1}$  region of the spectrum. Some resolution was

Table XIX. Selected Infrared Spectra of Prepared OxomolybdenumCysteates.

<u>Proposed Compound</u>	<u>Color</u>	<u><math>\nu(\text{Mo}=\text{O})</math></u>	<u><math>\nu(\text{Mo}-\text{O}-\text{Mo})</math></u>	<u><math>\nu(\text{Mo} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{Mo})</math></u>
$\text{Mo}_2\text{O}_4(\text{cystH})_2 \cdot \text{C}_2\text{H}_5\text{OH} \cdot 5 \text{H}_2\text{O}$	yellow	1045(m) 965(s,br)		725(m,br)
$\text{Mo}_2\text{O}_4(\text{cystH})_2 \cdot 1.2 \text{C}_2\text{H}_5\text{OH}$	yellow	1035(w) 960(s)		740(m,br)
$\text{Na}_2[\text{Mo}_2\text{O}_4(\text{cyst})_2] \cdot 4 \text{H}_2\text{O} \cdot \frac{1}{2} \text{C}_2\text{H}_5\text{OH}$	brown-yellow	1045(w) 950(s,br) 915(sh)		725(m,br)
$\text{Na}_4[\text{Mo}_2\text{O}_5(\text{cyst})_2(\text{OH})_2] \cdot 4 \text{H}_2\text{O}$	gold	925(s,br) 890(s,br)	730(m,br)	

Legend: s, strong; m, medium; w, weak; sh, shoulder; br, broad.

observed at 1520, 1560, and  $1730\text{ cm}^{-1}$ . The weak band near  $1730\text{ cm}^{-1}$  could be assigned<sup>139</sup> to an asymmetric stretch for uncoordinated unionized carboxylic carbonyl. A symmetric stretch band near  $1400\text{ cm}^{-1}$ , indicative of carboxylate ion,<sup>61</sup> was absent from the spectrum. Similarly, the asymmetric stretch band of the carboxylate ion at  $1600\text{ cm}^{-1}$  was not present in sufficient strength for positive identification.<sup>61</sup> Distinctions between coordinated and uncoordinated carboxylate ion absorptions had been reported<sup>55,61,62</sup> to be very small in oxomolybdenum compounds, i.e.,  $20\text{--}30\text{ cm}^{-1}$ , due to the weak bonds which were formed. Thus the presence of carboxylate ion was discounted for this compound. The reluctance of the carboxylate ion to coordinate indicated that coordination through carboxylic acid would be even less likely. Hence cysteine was proposed to be bidentate with coordination to molybdenum occurring at the ionized sulfhydryl sulfur and the neutral donor amine nitrogen atoms.

By difference the elemental analysis suggested considerable oxygen was present once chlorine and bridging sulfur were discounted. A carbon:nitrogen:molybdenum ratio of 4:1:1 required the presence of ethanol to account for carbon in addition to that found in cysteine. The formulation,  $\text{Mo}_2\text{O}_4(\text{cystH})_2 \cdot \text{C}_2\text{H}_5\text{OH} \cdot 5\text{H}_2\text{O}$ , where cystH is the uninegative bidentate cysteinate anion,  $\text{C}_3\text{H}_6\text{NO}_2\text{S}^-$ , met the requirements of the observed spectra and the elemental analysis. The two unassigned coordination sites, assuming molybdenum coordination number five, were probably trans to the terminal oxygens as reported for the corresponding ethyl cysteinate structure.<sup>63</sup> The assignment of water to these sites would be somewhat arbitrary and possibly dubious since several proposed

dioxo bridged compounds prepared in this work had also shown coordination numbers of five for molybdenum when in the presence of uninegative bidentate chelating anions.

### Cysteinate of Photolyzed Dioxobis(acetylacetonato)molybdenum(VI)

#### Solutions Using Cysteine Free Base.

The reaction of cysteine free base with the photolyzed solutions resulted in the formation of an initial yellow product which was greatly contaminated with the free ligand, cysteine, as evidenced by infrared spectroscopy. On prolonged standing, the mother liquor precipitated a yellow product which, based upon infrared spectroscopy (Appendix Figure 27), did not indicate the presence of the free ligand.<sup>61</sup>

Prominent broad bands were observed in the  $700-1050\text{ cm}^{-1}$  region not unlike the cysteine hydrochloride derivative discussed in the section above. Again the major band was a very strong, but broad absorption, at  $960\text{ cm}^{-1}$  assigned<sup>61</sup> to a terminal  $\text{Mo}=\text{O}$  stretch (Table XIX). A weak absorption at  $1035\text{ cm}^{-1}$  and a medium absorption at  $740\text{ cm}^{-1}$  was again assigned to dioxo bridging.

The primary distinction between these compounds appeared in the  $1620-1670\text{ cm}^{-1}$  region where the cysteine free base product absorbed more strongly than that of cysteine hydrochloride. As discussed for the cysteine hydrochloride derivative, the carboxylic acid group was proposed to be unionized<sup>139</sup> due to the presence of an absorption near  $1730\text{ cm}^{-1}$  and the absence of a symmetric stretch band near  $1400\text{ cm}^{-1}$  indicative of carboxylate ion.<sup>61</sup> Partially resolved absorptions at  $3130$  and  $3210\text{ cm}^{-1}$  were assigned<sup>61</sup> to N-H stretch for coordinated

nitrogen. The presence of N-H deformation bands in the  $1500\text{--}1600\text{ cm}^{-1}$  region was again not well resolved but, as in  $\text{Mo}_2\text{O}_4(\text{cystH})_2 \cdot \text{C}_2\text{H}_5\text{OH} \cdot 5\text{H}_2\text{O}$ , absorptions were observed at about  $1530$  and  $1570\text{ cm}^{-1}$ . The absence of an S-H absorption near  $2500\text{ cm}^{-1}$  was again utilized to suggest coordination at the ionized sulfhydryl site.<sup>61</sup> The presence of an absorption in the  $3200\text{--}3600\text{ cm}^{-1}$  region was not attributed to water. Since the supplier had established the amount of water in the cysteine ligand as less than one-half mole per mole of cysteine and the infrared spectrum of the compound did not detect an absorption in the  $3200\text{--}3600\text{ cm}^{-1}$  region, it was deduced that the OH stretch was attributable to some other source, e.g., ethanol.

When the infrared data was utilized in conjunction with the elemental analysis of the product, the formulation  $\text{Mo}_2\text{O}_4(\text{cystH})_2 \cdot 1.2\text{ C}_2\text{H}_5\text{OH}$ , where cystH is the uninegative bidentate cysteinate anion,  $\text{C}_3\text{H}_6\text{NO}_2\text{S}^-$ , was proposed. The amount of entrapped or bonded ethanol involved per dimer unit was not established as stoichiometric. Indeed the presence of small amounts of ligand impurity not observable in the infrared spectrum could make small contributions to the observed carbon, hydrogen and nitrogen analysis.

#### Cysteinate Salt of Oxomolybdenum(VI).

In order to study the photosensitivity of an oxomolybdenum(VI) cysteinate, an attempt was made to prepare a compound to be used for this purpose. The preparation of the reported<sup>61</sup> compound,  $\text{Na}_2[\text{MoO}_2(\text{cyst})_2] \cdot \text{DMF}$  where DMF is dimethylformamide, was investigated. However, the presence of dimethylformamide was undesirable for reasons

of infrared spectral interference and unknown reactivity to photolysis.

In addition, attempted synthesis of the compound led to unstable products which were difficult to isolate. Upon modification of the procedure, a gold oxomolybdenum(VI) cysteinate was obtained.

The  $700\text{--}1000\text{ cm}^{-1}$  region of the infrared spectrum (Appendix Figure 28) contained strong broad doublet absorptions at  $890$  and  $925\text{ cm}^{-1}$ , verifying the presence of a cis-dioxo species.<sup>115</sup> A very broad medium band in the  $660\text{--}770\text{ cm}^{-1}$  region suggested bridging oxygen (Table XIX). Although there have been no reports of dioxo bridged molybdenum(VI) compounds, monooxo bridged compounds of the highest molybdenum oxidation state had been isolated. A monooxo bridged polymeric chain with the stoichiometry  $\text{NaNH}_4\text{MoO}_3(\text{C}_2\text{O}_4)$  had been reported<sup>113</sup> in addition to a dinuclear monooxo bridged compound,  $\text{K}_2[\text{Mo}_2\text{O}_5(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ .<sup>107</sup> Unfortunately, no infrared data was reported for the latter compound.

An O-H band was observed in the  $3300\text{--}3600\text{ cm}^{-1}$  region and a doublet, assigned to an N-H stretch was observed in the  $3080\text{--}3240\text{ cm}^{-1}$  region suggesting nitrogen coordination,<sup>61</sup> the latter being reported for the compound containing DMF. The presence of an N-H deformation band in the  $1560\text{ cm}^{-1}$  region could not be verified as reported,<sup>61</sup> due to the presence of a very broad band assigned to a carboxylate ion asymmetric carbonyl stretch centered near  $1620\text{ cm}^{-1}$ . In addition, a weak carboxylate ion symmetric carbonyl stretch<sup>61</sup> was observed at  $1400\text{ cm}^{-1}$ . The broad absorption in the  $2900\text{--}3200\text{ cm}^{-1}$  region, attributed<sup>61</sup> to an N-H stretch where nitrogen is coordinated, was observed as in the photolysis derivatives discussed previously. The

absence of an S-H band in the  $2500\text{ cm}^{-1}$  region was again used to suggest ionized sulfhydryl group coordination.<sup>61</sup>

The elemental analysis of the gold solid yielded a Mo:C:H:N of 1:3:9:1 and dictated a Mo:cysteine ratio of 1:1. The compound was found qualitatively to be a conductor in water and quantitatively to contain about two sodium atoms per molybdenum atom. The analysis suggested the presence of considerable oxygen when a Mo:Na ratio of 1:2 was assumed. A reasonable formulation appeared to be  $\text{Na}_4[\text{Mo}_2\text{O}_5(\text{cyst})_2(\text{OH})_2] \cdot 4\text{ H}_2\text{O}$ , where cysteine is the dinegative bidentate ligand,  $\text{C}_3\text{H}_5\text{NO}_2\text{S}^{2-}$ . This satisfied conductivity and infrared spectra observations as well as analysis data. In addition, the darkening of the product in excessive acid was reasonable since protonation of the hydroxyl groups would probably lead to decomposition of the anion.

Cysteinate from a Photolyzed Suspension of Tetrasodium  $\mu$ -Oxobis [*cis*-dioxocysteinatohydroxomolybdate(VI)] tetrahydrate in Ethanol.

The photolysis of the ethanol slurry containing the molybdenum(VI) cysteinate,  $\text{Na}_4[\text{Mo}_2\text{O}_5(\text{C}_3\text{H}_5\text{NO}_2\text{S})_2(\text{OH})_2] \cdot 4\text{ H}_2\text{O}$ , resulted in the formation of a brown-yellow solid whose infrared spectrum substantiated that it was very similar to the molybdenum(V) compound reported by Kay and Mitchell<sup>55</sup> and later by Spivack and Dori.<sup>58</sup> However, the infrared spectrum differed considerably from that of compounds prepared from the "red hv" solutions (Table XIX). A broad band at  $950\text{ cm}^{-1}$  was again assigned<sup>55</sup> to terminal Mo=O stretch (Appendix Figure 29). The presence of a weak shoulder, observed at  $915\text{ cm}^{-1}$  in conjunction with the  $950\text{ cm}^{-1}$  absorption, was typical of molybdenum(V) dinuclear compounds as



discussed earlier. There was observed, in addition, a weak shoulder at  $965\text{ cm}^{-1}$  as well. A triplet was reported by Spivack and Dori<sup>58</sup> in the  $950\text{ cm}^{-1}$  region for the compound  $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{cyst})_2] \cdot 5\text{H}_2\text{O}$ . However, Kay and Mitchell<sup>55</sup> did not mention resolution of the terminal Mo-O band into a triplet. A weak band at  $1045\text{ cm}^{-1}$  was also observed and had been found in this work to be present in the spectra of other dioxo bridged molybdenum(V) compounds. A medium band, observed at  $725\text{ cm}^{-1}$  and assigned to a dioxo bridge stretch, was also in agreement with previous assignments.<sup>55,58</sup> These observations suggested the presence of the  $\text{Mo}_2\text{O}_4^{2+}$  moiety.

The presence of an O-H stretch in the  $3300\text{--}3600\text{ cm}^{-1}$  region suggested that water and/or hydroxyl groups were also present<sup>61</sup> in the photoreduced product of  $\text{Na}_4[\text{Mo}_2\text{O}_5(\text{C}_3\text{H}_5\text{NO}_2\text{S})_2(\text{OH})_2] \cdot 4\text{H}_2\text{O}$ . In addition, a poorly resolved doublet, assigned<sup>55,61</sup> to an N-H stretch, was observed in the  $3080\text{--}3240\text{ cm}^{-1}$  region of the product. This agreed with a similar finding by Kay and Mitchell.<sup>55</sup> Since the frequency was low, the assignment was again that of coordinated  $\text{-NH}_2$ .<sup>55</sup> A very symmetrical strong and broad absorption in the  $1550\text{--}1670\text{ cm}^{-1}$  region was also observed in this same region for the parent oxomolybdenum(VI) compound and corresponded to that reported by Kay and Mitchell.<sup>55</sup> This band was assigned to an asymmetric carboxylate ion carbonyl stretch.<sup>55</sup> A weak symmetric carbonyl stretch was also observed in the  $1400\text{ cm}^{-1}$  region.<sup>61</sup> Since the S-H band was again absent from the  $2500\text{ cm}^{-1}$  region, it was again proposed that coordination occurred at this ionized site.<sup>55,61</sup> Thus, spectral evidence strongly suggested that the photoreduced product was essentially the same as that reported as  $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{cyst})_2] \cdot 5\text{H}_2\text{O}$ .<sup>55,61,58</sup>

The elemental analysis of the product indicated a Mo:N ratio of 1:1.1. This appeared irregular since the elemental analysis of the parent molybdenum(VI) compound had a Mo:N ratio of 1:1. A rationale proposing an erroneously high nitrogen analysis for the photo-reduced compound was contradicted by the N:C ratio of 1:3.5. This latter finding was probably best explained by the presence of some ethanol in the photolysis product replacing the uncoordinated water in the reported compound,  $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{cyst})_2] \cdot 5 \text{H}_2\text{O}$ , whose structure had been determined by Knox and Prout.<sup>56</sup> Due to similarities in the infrared spectrum of the compound, the anion complexation was proposed to be the same, i.e., tridentate cysteinate ion with two bridging oxygens and one terminal oxygen at the six octahedral coordination sites. Discrepancies in the elemental analysis supported the presence of ethanol as a source of additional carbon. Thus, the compound was formulated as  $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{C}_3\text{H}_5\text{NO}_2\text{S})_2] \cdot \frac{1}{2} \text{C}_2\text{H}_5\text{OH} \cdot 4 \text{H}_2\text{O}$ . The coefficient of one-half on ethanol was somewhat indefinite and serves only to fulfill the requirements resulting from the determined elemental analysis. However, the presence of lattice water in  $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{cyst})_2] \cdot 5 \text{H}_2\text{O}$  supported the contention of solvent presence in the compound when prepared in ethanol.

### Pyridine Compounds

The monodentate neutral ligand, pyridine, has been useful in the formation of a wide variety of coordination compounds.<sup>140</sup> Frequently, these compounds were adducts with pyridine bonded at an otherwise unoccupied metal coordination site. Typical were the molybdenum halide

adducts formed by direct combination with halides of molybdenum oxidation states  $2^+$ ,  $3^+$  and  $4^+$ .<sup>141, 145</sup> In addition, mononuclear oxomolybdenum halide adducts have also been prepared, including those of  $\text{MoO}_2\text{Cl}_2$ <sup>146</sup> and  $\text{MoOCl}_3$ .<sup>33</sup> Probably of greatest significance to this work was the apparent ability of pyridine to stimulate formation of dioxo bridged dinuclear compounds. An oxomolybdenum(V) compound, formulated as  $\text{Mo}_2\text{O}_4(\text{oxine})_2(\text{py})_2$ , where py is neutral pyridine,  $\text{C}_5\text{H}_5\text{N}$ , was reported.<sup>44</sup>

Pyridinium salts were prepared with oxo bridged molybdenum compounds as well. Mitchell<sup>43</sup> reported the formation of  $(\text{pyH})_2[\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$  and  $(\text{pyH})_2[\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{C}_5\text{H}_5\text{N})_2]$ , where pyH is the pyridinium ion,  $\text{C}_5\text{H}_6\text{N}^+$ , both of which were proposed to contain the dioxo bridge. Analogous halogen compounds with the same dioxo bridge were reported by Jezowska-Trzebiatowska and Rudolf,<sup>147</sup> i.e.,  $(\text{pyH})_2[\text{Mo}_2\text{O}_4\text{Cl}_4(\text{H}_2\text{O})_2]$  and  $(\text{pyH})_4[\text{Mo}_2\text{O}_4\text{Cl}_2(\text{OH})_4]$ .

A Pyridine-Acetylacetonate Derivative from Photolyzed Dioxobis-(acetylacetonato)molybdenum(VI) Solutions and from Ethanol-Pyridine-Dioxobis(acetylacetonato)molybdenum(VI) Reflux.

The reaction of pyridine with the photolyzed solutions produced a deep red product with large well-formed crystals over a formation period of several days. The reaction vessel was tightly stoppered to prevent air oxidation of the "red hv" solution during the extended reaction period. Regardless of the rigor involved in excluding traces of oxygen and moisture from the ethanolic solution during photolysis, the same product was obtained. Hence, it would appear that the "red hv" solution contained species capable of forming only this insoluble product in the

presence of pyridine and ethanol, regardless of variations in preparation.

The infrared spectra for the pyridine-acetylacetonate compounds prepared from the "red hv" solutions could be considered identical (Appendix Figure 30). The terminal Mo=O stretch was observed at  $945\text{ cm}^{-1}$  and, as in the proposed dioxo bridged compounds of oxine and tropolone, a shoulder was observed at  $925\text{ cm}^{-1}$  (Table XX). The  $945\text{ cm}^{-1}$  absorption was sharp and no other bands were found in the  $900\text{--}970\text{ cm}^{-1}$  region. The complementary band at  $1040\text{ cm}^{-1}$  was observed, as in both tropolone and oxine derivatives, but was partly obscured by a sharp pyridine band in the same region. Three bands were observed in the  $650\text{--}800\text{ cm}^{-1}$  region. The extremely sharp doublet bands at  $680$  and  $690\text{ cm}^{-1}$  and at  $750$  and  $760\text{ cm}^{-1}$  were assigned<sup>140</sup> to pyridine since these and several other pyridine bands are "faithfully reproduced with only minor shifts or splittings in the spectra of the complexes." No other bands in the  $750\text{--}800\text{ cm}^{-1}$  region were observed. Since the Mo-O-Mo band reported<sup>7,54</sup> near  $775\text{ cm}^{-1}$  was absent, a single oxygen bridge was discounted. The band at  $730\text{ cm}^{-1}$  is assigned to a double oxygen bridge.<sup>43,61,62</sup> Other major assigned<sup>140</sup> pyridine bands, not previously mentioned, included those at  $1065$ ,  $1215$ ,  $1445$ ,  $1480\text{ cm}^{-1}$ , and weak triplets in the  $3000\text{--}3100\text{ cm}^{-1}$  and  $620\text{--}640\text{ cm}^{-1}$  regions. Notably absent were pyridinium ion bands assigned<sup>140</sup> at  $3200$ ,  $1535$ ,  $1490$ ,  $1325$ , and  $1240\text{ cm}^{-1}$ . The strong broad carbonyl doublet at  $1520$  and  $1580\text{ cm}^{-1}$  verified the presence of the acetylacetonate anion which occurred in the same positions as in  $\text{Mo}_2\text{O}_3(\text{acac})_4$ . Weak absorptions attributed to alkyl C-H stretch were observed in the  $2800\text{--}3000\text{ cm}^{-1}$  region as well as

Table XX. Selected Infrared Spectra of Prepared Oxomolybdenum Pyridine Compounds.

Compound	Color	$\nu(\text{Mo}=\text{O})$	$\nu(\text{Mo}-\text{O}-\text{Mo})$	$\nu(\text{Mo}-\text{OMo})$	$\nu(\text{C}=\text{O})$
$\text{Mo}_2\text{O}_4(\text{acac})_2(\text{py})_2$	red	1040(w) 945(s) 925(sh)	730(m)		1580(s,br) 1530(s,br)
$\text{MoO}_2(\text{OH})(\text{py})_{0.8}$	red	955(s) 945(s) 935(sh)		750(m,br)	
$(\text{pyH})_4(\text{Mo}_8\text{O}_{26})$	white	935(s,br) 900(s,br)		600-750(m, - vbr)	
$\text{Mo}_2\text{O}_5(\text{acac})_2(\text{py})_2$	pale yellow	935(s) 925(s) 900(s) 890(sh)		720(m,br)	1580(s,br) 1525(s,br)

Legend: s, strong; m, medium; w, weak; sh, shoulder; br, broad; vbr, very broad.

in the 1350-1390  $\text{cm}^{-1}$  region.

The elemental analysis gave extremely good agreement for these products. An empirical stoichiometry of  $\text{MoO}_2(\text{acac})(\text{py})$  was suggested. The infrared spectrum suggested the presence of a dioxo bridge. The dinuclear formulation,  $\text{Mo}_2\text{O}_4(\text{acac})_2(\text{py})_2$ , was proposed for the compound. Pyridine was proposed to be a donor ligand trans to the terminal oxygen, analogous to the 8-hydroxyquinolate analog,  $\text{Mo}_2\text{O}_4(\text{oxine})_2(\text{py})_2$ , reported by Dutta and Chatterjee.<sup>44</sup>

The acetylacetonate anion was apparently only partially lost in the photoredox process, since no insoluble  $\text{Mo}_2\text{O}_3(\text{acac})_4$  was precipitated from the photolyzed solution until additional acetylacetone was added. In the absence of two moles of acetylacetone for each mole of reduced molybdenum, the lone potential oxomolybdenum(V) product,  $\text{Mo}_2\text{O}_4(\text{acac})_2$ , apparently was either too unstable or too soluble to be isolated from ethanol. Since both dioxo bridged 8-hydroxyquinoline and tropolone derivatives were precipitated from ethanol as five coordinate dioxo bridged products in this work, high solubility seems to be an unlikely rationale. The product could be unable to form until pyridine was available for the sixth coordination site of the metal, thus, stabilizing an otherwise unstable dioxo bridged acetylacetonate compound. The low rate of product formation was puzzling but could be due to an extremely high activation energy. This contention was supported by reports<sup>44,62,130</sup> of favored dioxo bridge formation at elevated temperatures, e.g., reflux.

The preparation of this same deep red crystalline compound was also accomplished by refluxing an ethanol-pyridine suspension of  $\text{MoO}_2(\text{acac})_2$

for several hours (Table XXI). The infrared spectrum (Table XX and Appendix Figure 31) and elemental analysis were in excellent agreement with that reported above for the compound prepared from the "red hv" solution. The insoluble product collected initially did not contain acetylacetone, but upon standing several days,  $\text{Mo}_2\text{O}_4(\text{acac})_2(\text{py})_2$  was obtained from the mother liquor. It is apparent that in the presence of pyridine at ethanol reflux temperature,  $\text{MoO}_2(\text{acac})_2$  was reduced. Although there has been a report<sup>148</sup> of pyridine involvement in metal reduction, attributing the reduction and dimerization of molybdenum to the action of pyridine alone could be quite unreasonable. This was considered especially so, since  $\text{MoO}_2(\text{acac})_2$  left to stand in sealed bottles either dry or in the presence of ethanol solvent would completely convert to the brown oxomolybdenum(V) dimer,  $\text{Mo}_2\text{O}_3(\text{acac})_4$ . Although pyridine may enhance the reduction rate, it appeared much more reasonable to attribute reducing properties to acetylacetone, noted for its reducing characteristics.<sup>7,27</sup>

A Pyridine Derivative from Photolyzed Dioxobis(acetylacetonato)-molybdenum(VI) Solutions and from Ethanol-Pyridine-Dioxobis(acetylacetonato)molybdenum(VI) Reflux.

Another red product, distinctly different from  $\text{Mo}_2\text{O}_4(\text{acac})_2(\text{py})_2$  was obtained from the photolyzed  $\text{MoO}_2(\text{acac})_2$  solutions after volume reduction, i.e., rotary evaporation. The red pyridine derivative did not contain acetylacetone. It was also determined to be the same as the first red pyridine product obtained from the sustained reflux of an ethanol-pyridine suspension of  $\text{MoO}_2(\text{acac})_2$  (see Table XXI).

Table XXI. Solvent Effect on Pyridine-Dioxobis(acetylacetonato)-molybdenum(VI) Systems.

<u>Solvent and Conditions</u>	<u>Proposed Product and Color</u>	<u>Proposed Molybdenum Oxidation State</u>
absolute ethanol reflux	$\text{MoO}_2(\text{OH})(\text{py})_{0.8}$ (red) (initial product)	5+
absolute ethanol reflux	$\text{MoO}_4(\text{acac})_2(\text{py})_2$ (red) (second product)	5+
benzene reflux	$(\text{pyH})_4(\text{Mo}_8\text{O}_{26})$ (white)	6+
excess pyridine	$\text{Mo}_2\text{O}_5(\text{acac})_2(\text{py})_2$ (yellowish-white)	6+



No coordinated acetylacetone was observed in the infrared spectrum of either the product from the "red hv" solution (Appendix Figure 32) or the reflux mixture (Appendix Figure 33). Also absent were pyridinium ion bands. However, typical pyridine bands<sup>140</sup> were observed at 700, 1010, 1040, 1065, 1215, 1445, 1480, 1610 and in the 3000-3100  $\text{cm}^{-1}$  region.

The medium absorptions in the 700-800  $\text{cm}^{-1}$  region were attributed to bridging vibrations and since there was considerable broadening involved with the obscuring of two pyridine bands expected in the 750-760 region, there is strong suggestion that the compound was polymeric.<sup>112</sup> The polymeric nature of the product was supported by its very low solubility. In addition, the Mo=O absorption was observed as a partially resolved doublet at 945 and 955  $\text{cm}^{-1}$ . A shoulder was present at about 935  $\text{cm}^{-1}$ , but it was not distinct. These resolved bands suggested a mixture of molybdenum(V) compounds containing both single and double oxygen bridges or a polymer containing both types of bridging. The elemental analysis suggested the formulation as  $\text{MoO}_2(\text{OH})(\text{py})_{0.8}$  which satisfied the suspected oxomolybdenum(V) oxidation state. These formulations were empirical if the compound was polymeric. The analyses were consistently reproducible which makes the likelihood of a mixture of compounds seem quite remote, especially since the compound was prepared by two distinctly different procedures. This stoichiometry corresponded closely to a reported<sup>149</sup> white compound prepared by pyridine reaction with molybdenum trioxide and formulated as  $\text{MoO}_3(\text{py})$ . In addition, the structure of the white oxomolybdenum(VI) compound,  $\text{MoO}_3(\text{trien})$ , where trien is the neutral tridentate diethylene triamine ligand, had been determined<sup>161,200</sup> to be

monomeric with three cis-terminal oxygen atoms. However, the nature of the infrared spectrum and the red color of the compound suggested a reduced form of molybdenum. A red compound whose analysis was reported<sup>150</sup> to correspond to the empirical formula,  $\text{MoO}_4(\text{py})$ , was prepared by allowing a pyridine solution of molybdenum(II) acetate to stand in air as well as by pyridine reaction in ethanol with  $\text{MoOCl}_3$ . Certainly, the formulation,  $\text{MoO}_4(\text{py})$ , was suspect due to the high oxidation state required of molybdenum in a tetraoxide compound. Although the elemental analysis observed was somewhat similar for carbon, hydrogen, and nitrogen; the molybdenum analysis of the compound was more than 3% higher than in the reported<sup>150</sup> red compound. In addition, any similarities between that compound and those prepared in this work were difficult to assess since no infrared spectrum was reported. Extensive attempts to prepare a geometric model to fit the experimental data were unsuccessful.

A Pyridinium Polymolybdate from Benzene-Pyridine Dioxobis(acetyl-acetonato)molybdenum(VI) Reflux.

Solvents of the non-hydroxy type were also investigated. The solvent investigation was pursued to establish the importance of media in reduction and in the formation of oxo bridged products from  $\text{MoO}_2(\text{acac})_2$  (Table XXI). A benzene-pyridine solution containing suspended  $\text{MoO}_2(\text{acac})_2$  resulted in a white product whose infrared spectrum contains rather broad strong bands at 900 and 935  $\text{cm}^{-1}$  (Appendix Figure 34). This was typical of molybdenum(VI) compounds containing the cis-conformation of the terminal oxygen  $\text{MoO}_2^{2+}$  moiety<sup>116</sup>

(Table XX). Also present was a broad irregular absorption in the 600-750  $\text{cm}^{-1}$  region. This was frequently typical of vibrations from polymeric Mo-O-Mo bridging.<sup>112</sup> In many cases<sup>54</sup> single oxygen bridging was detected in the 750-800  $\text{cm}^{-1}$  region (Table VIII) while double oxygen bridging was detected<sup>43</sup> at somewhat lower energies, i.e., 700-750  $\text{cm}^{-1}$  (Table X). An irregular spectrum in the 1020-1060  $\text{cm}^{-1}$  region made it difficult to detect the 1040  $\text{cm}^{-1}$  band observed as typical of the  $\text{Mo}_2\text{O}_4^{2+}$  moiety in other compounds prepared in this work. There was remarkable similarity in the entire 300-700  $\text{cm}^{-1}$  region to that of ammonium paramolybdate,  $(\text{NH}_4)_6(\text{Mo}_7\text{O}_{24}) \cdot 4 \text{H}_2\text{O}$ . Broad bands at 360, 400, 475, 525, 560, 650, and 690  $\text{cm}^{-1}$  appeared in both infrared spectra. Ammonium paramolybdate did not, however, show a doublet at 900 and 935  $\text{cm}^{-1}$ , but rather, a strong broad band at 890  $\text{cm}^{-1}$ . Several bands assignable<sup>140</sup> to coordinated pyridine were notably either weak or absent, e.g., 1445, 1215, 1065, 1040  $\text{cm}^{-1}$ . However, bands observed at 3200, 1535, 1490, 1325, and 1240  $\text{cm}^{-1}$  establish the presence of the pyridinium ion.<sup>43</sup> A weak broad band at 3420  $\text{cm}^{-1}$  suggested the presence of a limited amount of hydroxy species. No carbonyl absorptions were observed in the 1500-1600  $\text{cm}^{-1}$  region, thus establishing the absence of acetylacetone in the compound.

The molybdenum analysis was very high while the carbon analysis was low dictating that there was considerable oxygen in the compound. Utilizing the elemental analysis only, the stoichiometry  $(\text{C}_5\text{H}_6\text{N})_2(\text{Mo}_3\text{O}_{10})$  was suggested. The absence of both pyridine and acetylacetonate absorptions in the infrared as well as the elemental analysis supported this proposal. As indicated from the infrared spectrum of the compound,

pyridine was observed only as a pyridinium cation. The complementary anion was proposed to be a polymolybdate such as  $\text{Mo}_7\text{O}_{24}^{6-}$  or  $\text{Mo}_8\text{O}_{26}^{4-}$ <sup>(111)</sup>. The latter anion in the formulation  $(\text{pyH})_4\text{Mo}_8\text{O}_{26}$  agreed most closely with the elemental analysis. The presence of small amounts of entrapped or combined acetylacetone (or benzene) from the solution, undetectable in the infrared, could explain the low molybdenum and high carbon analysis. On the other hand, small amounts of molybdic oxide,  $\text{MoO}_3$ , present in  $(\text{pyH})_6(\text{Mo}_7\text{O}_{24})$  may explain why the analysis was higher in percent molybdenum and lower in percent carbon in this proposed compound. Another alternative explanation could be the presence of small amounts of water, included in the solid lattice of  $(\text{pyH})_4(\text{Mo}_8\text{O}_{26})$  as was the case with  $(\text{NH}_4)_6(\text{Mo}_7\text{O}_{24}) \cdot 4 \text{H}_2\text{O}$ .<sup>111</sup> This could also explain the source of protons for pyridinium ion formation. However, water could only enter the reaction from the air, assuming that both pyridine and benzene are dry from the supplier, and thus this explanation appeared quite remote. The first two proposals explaining the elemental analysis appeared best since a much better proton source for pyridinium ion formation would be neutral acetylacetone, noted<sup>151</sup> for the labile nature (acidity) of one proton on the central carbon. Further support to pyridinium polymolybdate assignment was the reported<sup>147</sup> preparation of several pyridinium oxychloromolybdates, i.e.,  $(\text{pyH})_4[\text{Mo}_4\text{O}_8\text{Cl}_8(\text{H}_2\text{O})_2]$  and  $(\text{pyH})_5[\text{Mo}_4\text{O}_8\text{Cl}_8(\text{OH})(\text{H}_2\text{O})]$ .

A Pyridine-Acetylacetonate from the Reaction of Dioxobis(acetylacetonato)molybdenum(V) in Pyridine at Room Temperature.

The absence of a solvent other than pyridine itself resulted in

still another product when reacting with  $\text{MoO}_2(\text{acac})_2$  (see Table XXI). In a room temperature reaction, a pale yellowish white product was obtained. This compound had none of the characteristics of the white product formed by a benzene reflux of the same two components. In both cases the lack of color suggested an oxomolybdenum(VI) compound, supported by literature reports of the near absence of color for such compounds and by observations in this work. The molybdenum(VI) compounds of the chelates discussed in this work were all colored yellow while compounds giving the molybdenum(V) test<sup>44</sup> were darker in coloration. The white pyridinium compound discussed above had a doublet at 900 and  $935\text{ cm}^{-1}$  characteristically assigned to symmetric and asymmetric stretch of the cis-dioxo terminal oxygens making up the  $\text{MoO}_2^{2+}$  moiety (Table XX). This pale yellow product did not display the bands assignable to the pyridinium ion but did display a doublet in the  $900\text{--}940\text{ cm}^{-1}$  region (Appendix Figure 35). This doublet appeared to show a splitting of each major absorption, however. The bands appeared to be very sharp and in itself this was somewhat unique. At least partially resolved were bands at  $935$  and  $925\text{ cm}^{-1}$ . A sharp band at  $900\text{ cm}^{-1}$  had a shoulder at  $890\text{ cm}^{-1}$  and a further resolved absorption at  $880\text{ cm}^{-1}$ . Only the  $880\text{ cm}^{-1}$  band in the  $850\text{--}1000\text{ cm}^{-1}$  region could be assigned<sup>140</sup> to coordinated pyridine, where it was observed only as a weak absorption in the spectra of the two red compounds discussed above. A broad absorption in the  $720\text{ cm}^{-1}$  region may be assigned to bridging oxygen. Assigned<sup>140</sup> pyridine complex bands were observed at 1610, 1480, 1445, 1215, 1145, 1065, 1040, 1010, and  $760\text{ cm}^{-1}$ . A doublet in the  $1500\text{--}1600$  region established the presence of acetylacetonate in the compound.

Further evidence for the presence of acetylacetonate were weak bands in the  $2800-3000\text{ cm}^{-1}$  region and a strong doublet in the  $1350-1390$  region. The general broad absorption in the  $680-800$  region suggested the possibility of chain vibrations in a polymeric structure, but the sharpness of the terminal oxygen bands appeared to contradict the idea.

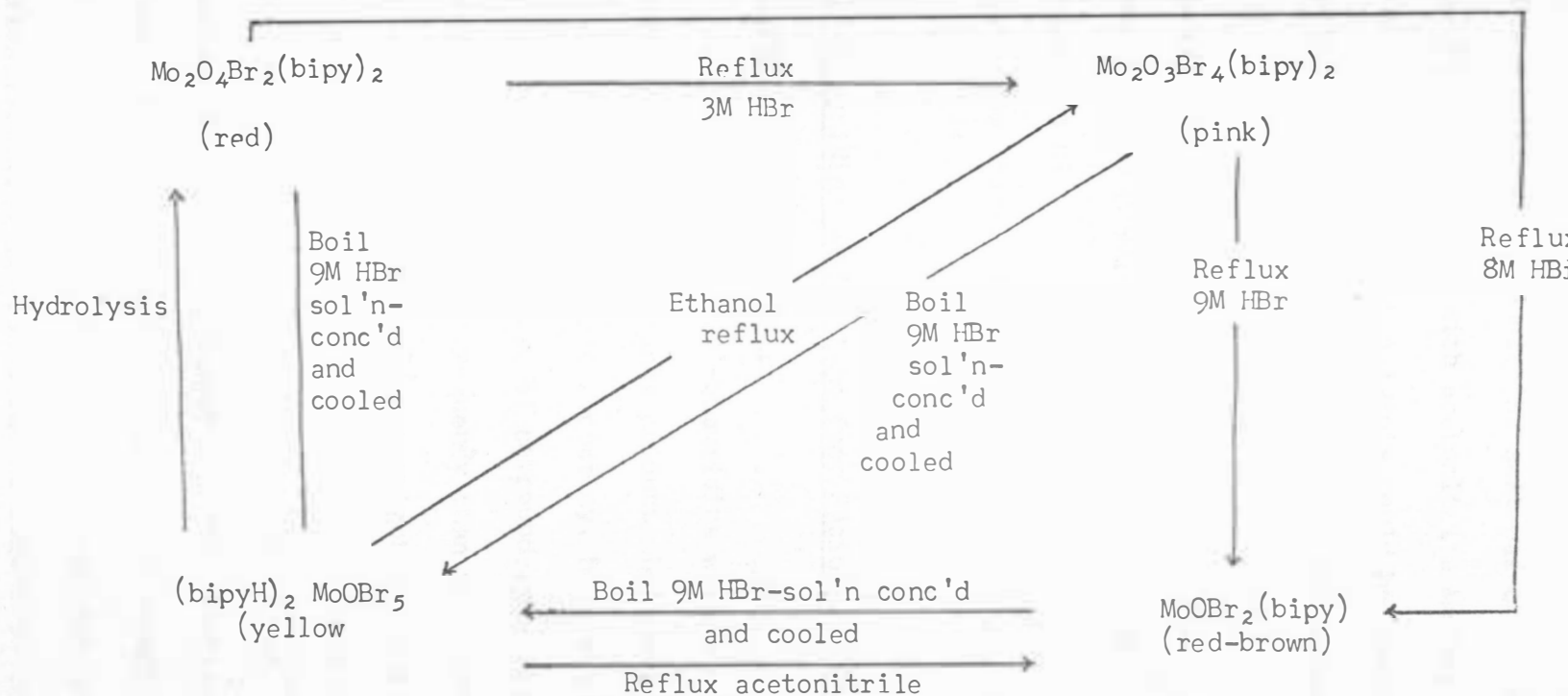
The elemental analysis, as well as infrared data, appeared consistent with the formulation  $\text{Mo}_2\text{O}_5(\text{acac})_2(\text{py})_2$ . The formation of a neutral dinuclear compound containing the  $\text{Mo}_2\text{O}_5^{2+}$  moiety had not previously been reported. However, the anion in the white salt,  $\text{K}_2[\text{Mo}_2\text{O}_5(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ , did contain the  $\text{Mo}_2\text{O}_5^{2+}$  moiety.<sup>107</sup> The structure of the oxalato compound was determined to be centrosymmetric, containing a linear monooxo bridge with two terminal cis- $\text{MoO}_2$  units located cis to the bridging oxygen on opposite sides. This formulation explained the oxo bridging absorption in the  $680-800\text{ cm}^{-1}$  region, as well as the splitting of the doublet in the  $900-940\text{ cm}^{-1}$  region. This appeared as another example of the ability of pyridine to stabilize what were otherwise unisolable oxo bridged compounds. A similar situation was observed for the dioxo bridged oxomolybdenum(V) compound,  $\text{Mo}_2\text{O}_4(\text{acac})_2(\text{py})_2$ . In each case the absence of a donor ligand like pyridine meant that the molybdenum in the compound would be five coordinate only. In these acetylacetonate compounds, the filling of the sixth coordination site appeared to be most important to forming an isolable stable compound.

### 2,2'-Bipyridine Compounds.

The bidentate ligand, 2,2' bipyridine had also been extensively utilized as a molybdenum chelating agent.<sup>152, 153</sup> It had been particularly useful as a donor ligand furnishing neutral bidentate coordination to compounds which were otherwise unable to reach maximum coordination. The behavior of this donor ligand in adduct formation paralleled that of pyridine and indeed one product,  $\text{MoCl}_3(\text{py})(\text{bipy})$  where bipy is the neutral bidentate bipyridine ligand,  $\text{C}_{10}\text{H}_8\text{N}_2$ , which was obtained from the pyridine complex,  $\text{MoCl}_3(\text{py})_3$ , contained both donor ligands.<sup>154</sup> However, this exemplified the importance of its bidentate nature since it had favored stability over the unidentate pyridine, i.e., the chelate effect.<sup>25</sup> Many halogen containing molybdenum compounds of bipyridine were reported<sup>154-160</sup> and several halogen containing oxomolybdenum products as well were obtained.<sup>148, 161, 164</sup> The mononuclear halogen containing dioxomolybdenum(VI) compounds, containing bipyridine and the  $\text{MoO}_2^{2+}$  moiety, were formulated<sup>163, 164</sup> as  $\text{MoO}_2\text{X}_2(\text{bipy})$  where  $\text{X} = \text{Cl}, \text{Br}$ . Molybdenum(V) compounds containing the  $\text{MoO}^{3+}$  moiety were formulated<sup>148, 161, 162, 165</sup> as  $\text{MoOX}_3(\text{bipy})$ .

The formation of dinuclear halogen containing oxomolybdenum(V) bipyridine compounds, containing both the  $\text{Mo}_2\text{O}_3^{4+}$  and the  $\text{Mo}_2\text{O}_4^{2+}$  moiety, had also been reported.<sup>148, 158, 165, 166</sup> Saha and Banerjee<sup>166</sup> proposed that the compounds  $\text{Mo}_2\text{O}_3\text{Br}_4(\text{bipy})_2$  and  $\text{Mo}_2\text{O}_4\text{Br}_2(\text{bipy})_2$  underwent interconversion with those containing the  $\text{MoO}^{3+}$  moiety (see Figure 4). It was shown that less bridging was a result of increasingly greater aqueous solution acidity; in fact, the bipyridinium salt,  $(\text{bipyH})_2 \text{MoOBr}_5$ , was formed with maximum acidity. When refluxed in the

Figure 4. Scheme of Oxobromomolybdenum(V) Interconversion.<sup>16</sup>





hydroxy solvent, ethanol, the salt was converted to the dimer,  $\text{Mo}_2\text{O}_3\text{Br}_4(\text{bipy})_2$ ; but with acetonitrile  $\text{MoOBr}_3(\text{bipy})$  was formed. This suggested that hydroxy solvents could be instrumental in forming the oxo bridged dinuclear species. This was supported by the observation<sup>166</sup> that the bipyridinium salt was hydrolyzed to the dioxo bridged compound  $\text{Mo}_2\text{O}_4\text{Br}_2(\text{bipy})_2$ . A bipyridine compound which also possessed the dioxo bridged  $\text{Mo}_2\text{O}_4^{2+}$  moiety was formulated<sup>167</sup> as  $\text{Mo}_2\text{O}_4(\text{oxine})_2(\text{bipy})$ , containing bipyridine which was proposed to be coordinated to both molybdenum atoms. It was an analog of  $\text{Mo}_2\text{O}_4(\text{oxine})_2(\text{py})_2$  from which it was made.<sup>44</sup>

#### 2,2'-Bipyridine Derivatives from Photolyzed Dioxobis(acetylacetonato)-molybdenum(VI) Solutions.

The reaction of 2,2'-bipyridine with the "red hv" solutions resulted in a yellow-orange product which was initially considered to be a single compound. Closer scrutiny, however, revealed what was concluded to be a mixture of compounds, one with a slightly higher terminal  $\text{Mo}=\text{O}$  stretch frequency than the other (Appendix Figure 26). The absorption at  $970\text{ cm}^{-1}$  was not observed with the same intensity in all preparations. In fact, when it was most prominent, it appeared only as a broadening of the strong band at  $955\text{ cm}^{-1}$  without forming a distinct shoulder at  $970\text{ cm}^{-1}$ . Supporting this distinction was the presence of a weak, but clear, band at  $1035\text{ cm}^{-1}$  to complement the observed  $970\text{ cm}^{-1}$  band, (Table XXII). The tropolone and 8-hydroxyquinoline derivatives also had bands in the  $1020\text{--}1050\text{ cm}^{-1}$  region which complemented the appearance of  $\text{Mo}=\text{O}$  stretch frequencies near  $970\text{ cm}^{-1}$  for the

Table XXII. Selected Infrared Spectra of Prepared Oxomolybdenum  
2,2'-Bipyridine Compounds.

Compound	Color	$\nu(\text{Mo}=\text{O})$	$\nu(\text{Mo}-\text{O}-\text{Mo})$	$\nu(\text{Mo} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \end{smallmatrix} \text{Mo})$	$\nu(\text{C}=\text{O})$
Unassigned	—	1035(w) 970(s)	—	—	1570(s,br) 1520(s,br)
$\text{Mo}_2\text{O}_3(\text{OH})_4 \cdot$ (bipy)	orange	955(s) 935(sh)	700-850(m,br)		

Legend: s, strong; m, medium; w, weak; sh, shoulder; br, broad.

proposed  $\text{Mo}_2\text{O}_4^{2+}$  moieties. Due to broad absorptions in the 700-800  $\text{cm}^{-1}$  region, no definite assignment to bridging oxygen could be made. However, the very presence of these broad absorptions could indicate vibration of the  $-\text{Mo}-\text{O}-\text{Mo}-\text{O}-$  chain. Based on this spectral data, as well as comparable observations for other derivatives prepared from the same "red hv" solutions, it was proposed that this bipyridine derivative component has a dioxo bridging structure similar to the oxomolybdenum(V) tropolonate and 8-hydroxyquinolate compounds discussed earlier.

After prolonged standing of the mother liquor, products with minimal infrared absorptions in the 970 and 1035  $\text{cm}^{-1}$  were collected (Appendix Figure 37). Also greatly diminished were broad absorptions at 1520 and 1570  $\text{cm}^{-1}$ , which were assigned to acetylacetonate carbonyl stretch. The 955  $\text{cm}^{-1}$  absorption with a distinct shoulder at 935  $\text{cm}^{-1}$  was assigned to a terminal  $\text{Mo}=\text{O}$  stretch which appeared very similar in shape and position to that in the  $\text{Mo}_2\text{O}_3^{4+}$  moiety. In addition, this product had broad absorptions in the 700-850  $\text{cm}^{-1}$  region which have frequently been attributed to polymeric bridging.<sup>100, 112, 148</sup>

A broad, medium intensity O-H stretch was observed at about 3400  $\text{cm}^{-1}$ . Small amounts of water could enter the reaction vessel over the extended reaction period as water vapor. In addition, if protons were available in solution, bridging oxygen could be converted to coordinated hydroxy ligands. It has been shown<sup>123</sup> that oxidation of acetylacetone in a redox process yields protons and that acetylacetone itself was noted for its acidity.<sup>151</sup>

Absorptions assigned<sup>148, 154, 168</sup> to coordinated bipyridine were

observed in the 630-660  $\text{cm}^{-1}$  region, at 1020  $\text{cm}^{-1}$ , in the 750-780  $\text{cm}^{-1}$  region, at 1313 and 1600  $\text{cm}^{-1}$ , and in the 3040-3080  $\text{cm}^{-1}$  region. The absence of a bipyridium ion band at 2340  $\text{cm}^{-1}$  in all spectra confirmed that all combined bipyridine was coordinated to molybdenum.<sup>168</sup>

The elemental analysis of the products varied with the reaction time interval utilized before collection. The first product collected had a higher molybdenum and a lower carbon analysis than that of the second product. This, coupled with spectral evidence, contradicted any contention that the initial product contained unreacted bipyridine. However, these analyses observations seem to also exclude the theory that the initial product contains some  $\text{Mo}_2\text{O}_4(\text{acac})_2(\text{bipy})$ , an analog of  $\text{Mo}_2\text{O}_4(\text{acac})_2(\text{py})_2$  which might be expected. Hence, the temptation to assign the component of the initial product contributing absorptions at 970, 1040, 1520, and 1570  $\text{cm}^{-1}$  as  $\text{Mo}_2\text{O}_4(\text{acac})_2(\text{bipy})$  conflicted with the elemental analyses data. The infrared spectra indicated that assignment of the component cannot be  $\text{Mo}_2\text{O}_4(\text{acac})_2$  or  $\text{Mo}_2\text{O}_3(\text{acac})_4$ .

The later product, which did not appear to be a mixture based on spectral evidence, had a Mo:bipy ratio of 2:1. In certain respects this orange product was not unlike the red pyridine product,  $\text{MoO}_2(\text{OH})(\text{py})_{0.8}$ , prepared in this work and discussed in the previous section. The infrared spectrum was quite similar in the 700-1000  $\text{cm}^{-1}$  region. A strong band near 950  $\text{cm}^{-1}$ , a weak absorption at 880  $\text{cm}^{-1}$ , and medium absorptions at 730 and 765  $\text{cm}^{-1}$  were observed for both compounds. In addition, the possible formulation,  $\text{Mo}_2\text{O}_3(\text{OH})_4(\text{bipy})$ , is not greatly different than that of  $\text{MoO}_2(\text{OH})(\text{bipy})_{0.4}$ , the bipyridine analog of  $\text{MoO}_2(\text{OH})(\text{py})_{0.8}$ .

### Benzoin-anti-oximates.

In addition to 8-hydroxyquinoline, the bidentate chelating ligand benzoin-anti-oxime (alpha-benzoin oxime or cupron) has long been used as a standard means of quantitatively precipitating molybdenum in its highest oxidation state in analytical chemistry.<sup>169, 170</sup> The product formed by this method was a flocculent white solid formulated as  $\text{MoO}_2(\text{bao})_2$  where bao is the bidentate benzoin-anti-oximate anion,  $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}^-$ .

### Benzoin-anti-oximate from Photolyzed Dioxobis(acetylacetonato)-molybdenum(VI) Solutions.

Although the only reported oxomolybdenum benzoin-anti-oximate had the oxidation state +6, an attempt was made to prepare lower oxidation state compounds from the "red hv" solutions. Products collected from ethanolic solution were cream to tan in coloration. The infrared spectra of the products (Appendix Figure 13) had a doublet at 905 and  $925\text{ cm}^{-1}$  assigned to the cis- $\text{MoO}_2^{2+}$  moiety. Ligand bands were found at the following frequencies with the proposed assignments: 3075(N-H), 3030 (O-H), 1453 (C-H), 1438 (O-H), 1091, 1048, 1005, 710, and  $690\text{ cm}^{-1}$ . The slowly formed products were determined to be  $\text{MoO}_2(\text{bao})_2$  as established by elemental analyses and infrared spectra. No obvious explanation for this behavior could be found. The ligand has been reported to act as a weak reducing agent in aqueous solution, hence, best quantitative precipitation of molybdenum(VI) was accomplished in the presence of some oxidizing agent during precipitation.<sup>169, 171</sup> Since the photolyzed solutions did not show dark coloration after

addition of the ligand, the possibility of a soluble lower oxidation state complex also appeared unrealistic. Plausible rationale could be that the ligand does not have the proper "bite" dimensions for the lower oxidation state compounds or that there may be some steric factor prohibiting their formation.

### CONCLUSIONS AND SUMMARY

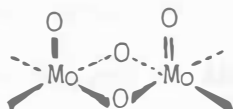
It has been reported that several lower oxidation state oxomolybdenum compounds obtained in this work by photolysis could also be prepared by other means. These reported techniques were varied and require many greatly different, and often expensive, molybdenum starting materials, solvents, conditions, and apparatus. However, it was demonstrated that a photochemical method could be used to synthesize an entire spectrum of compounds, limited only by the ligand resources available and the ingenuity of their collection and separation.

Many previously unreported compounds were obtained as a result of this work. In addition, several products were prepared which were previously obtained by other methods. An oxomolybdenum(IV) compound as well as numerous oxomolybdenum(V) compounds were prepared utilizing photochemical methods. In addition, chemical methods were utilized to prepare several of the same low oxidation state oxomolybdenum compounds for comparative studies. Also, certain oxomolybdenum(VI) compounds were prepared, primarily for utilization as photochemical reactants.

The oxomolybdenum(IV) compound,  $\text{MoO}(\text{dtc})_2$ , was prepared from the red ethanolic photolyzed oxomolybdenum acetylacetonate solutions, hereafter called the "red  $h\nu$ " solutions. This compound was also prepared in the laboratory of Jowitt and Mitchell<sup>45</sup> during the progress of this work. Rapid collection and meticulous exclusion of air was required to isolate the pink compound. Since this was the only oxomolybdenum(IV) compound isolated and no sound evidence for the presence of others was observed, it seemed quite dubious to predict the presence of oxomolybdenum(IV) species in solution. The uncertainty was based upon

the known reducing characteristics of the dithiocarbamate ligand.<sup>52</sup> However, the presence of small amounts of chelated oxomolybdenum(IV) products,  $\text{MoO}(\text{chel})_2$ , where chel is a bidentate uninegative anion, were largely left to infrared detection, noted for its limitations in identifying the presence of minor products in mixtures.<sup>7</sup> The difficulty of detecting small amounts of  $\text{MoO}(\text{chel})_2$  was compounded by the apparent similarity in terminal  $\text{Mo}=\text{O}$  absorption frequency for  $\text{Mo}_2\text{O}_4(\text{chel})_2$ . These absorptions were observed at  $960$  and  $970\text{ cm}^{-1}$  for  $\text{MoO}(\text{dtc})_2$  and  $\text{Mo}_2\text{O}_4(\text{dtc})_2$ , respectively. Fortunately, elemental analysis for the two compounds would differ greatly since the  $\text{Mo}:\text{chel}$  ratio is  $1:2$  for  $\text{MoO}(\text{chel})_2$  but  $1:1$  for  $\text{Mo}_2\text{O}_4(\text{chel})_2$ . This was a helpful indicator except when there was evidence of the presence of  $\text{Mo}_2\text{O}_3(\text{chel})_4$ , another product whose  $\text{Mo}:\text{chel}$  ratio was  $1:2$ . Ordinarily,  $\text{Mo}_2\text{O}_3(\text{chel})_4$  was not formed until late in the reaction interval and was not expected to be a source of difficulty if  $\text{MoO}(\text{chel})_2$  formed early in the reaction as was the case for  $\text{MoO}(\text{dtc})_2$ .

A large number of oxomolybdenum(V) compounds were prepared from the "red hv" solutions. In general, these compounds were collected either as  $\text{Mo}_2\text{O}_4(\text{chel})_2$  or  $\text{Mo}_2\text{O}_3(\text{chel})_4$ . Those containing the  $\text{Mo}_2\text{O}_4^{2+}$  moiety, with geometry depicted<sup>63</sup> as

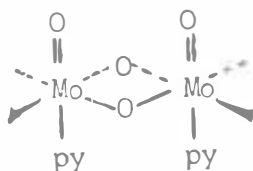


were formed as the predominant product in the early stages of reaction with the "red hv" solutions. Identified were the products,  $\text{Mo}_2\text{O}_4(\text{oxine})_2$ ,



$\text{Mo}_2\text{O}_4(\text{trop})_2$ ,  $\text{Mo}_2\text{O}_4(\text{dtc})_2$ , and solvated  $\text{Mo}_2\text{O}_4(\text{cystH})_2$ . All of these products were previously unreported at the time of preparation. The dithiocarbamate compound was also prepared from the reflux of  $\text{Mo}_2\text{O}_4(\text{dtc})_4$  in water. However, the same compound was recently prepared elsewhere<sup>130</sup> from molybdenum pentachloride.

Based on the possibility that the isolation of dioxo bridged compounds may indeed be assisted by the presence of a potential neutral donor ligand for the unoccupied sixth coordination site, i.e.,



pyridine was added to the "red hv" solution. Without adding additional acetylacetone a product of high purity identified as  $\text{Mo}_2\text{O}_4(\text{acac})_2(\text{py})_2$  was collected, even though it was not possible to collect  $\text{Mo}_2\text{O}_4(\text{acac})_2$  from the photolyzed solution. Although the pentacoordinated compound could be difficult to isolate due to high solubility in ethanol, a more likely explanation appeared to be that it was unstable. This rationale was chosen (1) since the compounds  $\text{Mo}_2\text{O}_4(\text{trop})_2$ ,  $\text{Mo}_2\text{O}_4(\text{oxine})_2$ , and  $\text{Mo}_2\text{O}_4(\text{dtc})_2$  were noticeably unstable particularly in the presence of ligand and solvent and (2) since all dinuclear oxo bridged compounds isolated in this work were observed to be quite insoluble, especially in ethanol. A bipyridine analog of the pyridine compound was expected but isolation of such a product was unsuccessful. Since some acetylacetone was observed in the infrared spectrum of product mixtures collected, it could be that a competing reaction prevented substantial product formation during the lengthy reaction time. A bipyridine

compound not containing acetylacetone but proposed to be oxomolybdenum(V), was obtained from the "red hv" solution with an extended reaction period. Of considerable significance to biological systems was the photochemical preparation of  $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{cyst})_2] \cdot \frac{1}{2} \text{C}_2\text{H}_5\text{OH} \cdot 4 \text{H}_2\text{O}$ , another dioxo bridged oxomolybdenum(V) compound. Such compounds of the amino acid cysteine were closely linked to the reducing site in the molybdoenzyme, nitrogenase; this product was obtained by irradiation of a suspension containing an oxomolybdenum(VI) cysteinate salt. A similar product,  $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{cyst})_2] \cdot 5 \text{H}_2\text{O}$ , was previously reported<sup>58</sup> to contain the tridentate cysteinate anion,  $\text{C}_3\text{H}_5\text{NO}_2\text{S}^{2-}$ , and molybdenum of coordination number six.

Numerous monooxo bridged oxomolybdenum(V) compounds were also prepared from the "red hv" solutions. These compounds, containing the  $\text{Mo}_2\text{O}_3^{4+}$  moiety with geometry depicted<sup>35</sup> as



were generally formed over extended reaction periods and were collected as "final products". Included was the previously unreported compound,  $\text{Mo}_2\text{O}_3(\text{trop})_4$ . In addition, the compounds  $\text{Mo}_2\text{O}_3(\text{acac})_4$ ,<sup>7</sup>  $\text{Mo}_2\text{O}_3(\text{oxine})_4$ ,<sup>42</sup> and  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ <sup>54</sup> were also prepared from the "red hv" solutions.

Pyridine and bipyridine products of unique stoichiometry, but possibly containing the  $\text{Mo}_2\text{O}_3^{4+}$  moiety, were also obtained from these solutions.

The previously unreported compound,  $\text{Mo}_2\text{O}_3(\text{trop})_4$ , was prepared in high purity. This was a testimonial to the usefulness of the photochemical method for preparing new oxomolybdenum(V) compounds.

Although a sealed tube reaction<sup>7</sup> was successful in preparing

$\text{Mo}_2\text{O}_3(\text{acac})_4$ , several previously utilized chemical methods resulted in impure products. The product obtained by photochemical means was obtained in very high purity, also supporting the photochemical method as a useful preparative tool.

There have also been numerous reported <sup>40-45</sup> compounds of  $\text{Mo}_2\text{O}_3(\text{oxine})_4$ . It was established from X-ray powder patterns that one of the compounds prepared from the "red hv" solution had the same crystal structure as reported earlier <sup>126</sup> for an "isomer" of  $\text{Mo}_2\text{O}_3(\text{oxine})_4$ . Another powder pattern was unexplainably simple and others were more complex. The X-ray investigation generally supported the contention <sup>126</sup> of the occurrence of distinct isomers for these compounds.

The isolation of the compound  $\text{Mo}_2\text{O}_3(\text{dtc})_4$  was complicated by the simultaneous formation of  $\text{MoO}(\text{dtc})_2$ . When allowed to stand in air, the product oxidized slowly and finally formed  $\text{MoO}_2(\text{dtc})_2$ . Changes in color were correlated with changes in the infrared spectra of the solids. This series of oxidation products led to a better understanding of the reduction sequence of chemical systems and possibly that of the photochemical system as well.

When the impure violet product,  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ , was left to stand in solution, a compound formulated as  $[\text{MoO}_2(\text{dtc})(\text{H}_2\text{O})]_n$  was obtained. The infrared spectrum of the compound indicated it was polymeric but probably still contained the  $\text{Mo}_2\text{O}_3^{4+}$  moiety.

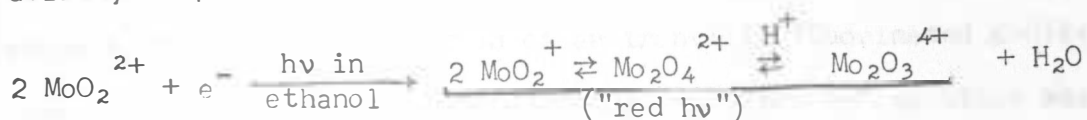
A dimeric or polymeric pyridine derivative, formulated as  $\text{MoO}_2(\text{OH})(\text{py})_{0.8}$ , which contained a possible  $\text{Mo}_2\text{O}_3^{4+}$  moiety was obtained from the "red hv" solution after its volume had been reduced by rotary evaporation. This compound was also prepared in the same stoichiometry

by refluxing a pyridine-ethanol suspension of  $\text{MoO}_2(\text{acac})_2$ . No explanation could be found for the unusual stoichiometry. A bipyridine product was not as well characterized. The formation of these compounds indicated the potential of the photochemical system for preparing compounds of neutral ligands as well.

Without exception the most selective separation of compounds of the general formulation  $\text{Mo}_2\text{O}_4(\text{chel})_2$  required rapid collection immediately after initial addition of chelate ligand to the "red hv" solution. Invariably, longer reaction time meant formation of compounds of the general formulation,  $\text{Mo}_2\text{O}_3(\text{chel})_4$ . Even in the one case of formation of an oxomolybdenum(IV) compound, the product,  $\text{MoO}(\text{dtc})_2$ , upon exposure to air, reverted to a violet product, almost certainly  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ . Only the cysteinate derivatives did not give detectable products containing the  $\text{Mo}_2\text{O}_3^{4+}$  moiety. However, the amino acid cysteine, while complexed, had been reported to stabilize bridging in oxomolybdenum(V) compounds, a characteristic attributed to the presence of sulfur bonds to the metal.

The specific type of species present in the "red hv" solutions was not readily apparent. It was likely that at least one oxomolybdenum(V) species was present in the solution after photolysis was complete. This could be concluded by the large number of products collected containing both the  $\text{Mo}_2\text{O}_3^{4+}$  and  $\text{Mo}_2\text{O}_4^{2+}$  moieties. However, certain chelates were known for their reducing or oxidizing capacity. It would appear that the isolation of  $\text{MoO}(\text{dtc})_2$  from the "red hv" solution could be a result of excess dithiocarbamate ion acting as a reductant to the molybdenum(V) species present. On the contrary it

could not be conclusively said that the "red hv" solution did not contain molybdenum(IV) species. If the solution contained but one (or none) of the bridged species  $\text{Mo}_2\text{O}_4^{2+}$  and  $\text{Mo}_2\text{O}_3^{4+}$ , the other(s) must be readily available through some sort of equilibrium from the other (or another) molybdenum(V) species. The photolysis and availability of product species could be depicted by the sequence:



If both bridging species were readily available in the "red hv" solution the sequence of formation of products containing  $\text{Mo}_2\text{O}_4^{2+}$  and  $\text{Mo}_2\text{O}_3^{4+}$  must be explained by either means. A possibility would be that the initial products, which were observed to be  $\text{Mo}_2\text{O}_4(\text{chel})_2$ , were favored kinetically and that the second (last collected) products, observed to be  $\text{Mo}_2\text{O}_3(\text{chel})_4$ , were favored thermodynamically. Kinetically favored here implied a lower activation energy and, hence, greater reaction rate for the formation of  $\text{Mo}_2\text{O}_4(\text{chel})_2$  while thermodynamically favored suggested a favored free energy (and probably entropy) change to form  $\text{Mo}_2\text{O}_3(\text{chel})_4$ .

The observed near quantitative formation of  $\text{Mo}_2\text{O}_4(\text{acac})_2(\text{py})_2$  from the "red hv" solutions in the presence of pyridine indicated that at least one half of all acetylacetone initially present in the reactant  $\text{MoO}_2(\text{acac})_2$  remained after photo-oxidation-reduction. Since absolutely no  $\text{Mo}_2\text{O}_3(\text{acac})_2$  was precipitated during the extended irradiation periods, it was further proposed that no more than one acetylacetone was present in the "red hv" solution. The great insolubility of  $\text{Mo}_2\text{O}_3(\text{acac})_4$  in

the ethanol solutions was verified by the quantitative precipitation of the compound upon addition of the required acetylacetone to the "red  $h\nu$ " solutions. Thus it was established from the formation of these two derivatives that the reduced molybdenum containing species contained precisely one bonded acetylacetonate ligand per reduced molybdenum atom. Unlike the photochemical reduction of iron(III) and oxidation of ethanol solvent in an ethanol solution of an iron(III) fluorinated  $\beta$ -diketone compound, the acetylacetonate ligand in the "red  $h\nu$ " solution was proposed to be the oxidized species.

Although a high energy source may be necessary to completely reduce the ethanol- $\text{MoO}_2(\text{acac})_2$  solutions, it was observed that sunlight converted these solutions to red-orange through either borosilicate glass or quartz. These solutions were used to prepare a derivative identified as  $\text{Mo}_2\text{O}_3(\text{oxine})_4$ , hence confirming the reduction of molybdenum. Ultraviolet radiation for the formation of the "red  $h\nu$ " solutions was also found to be unnecessary since borosilicate glass filtered nearly all ultraviolet radiation below 280 nanometers. Independence of ultraviolet radiation for the formation of the "red  $h\nu$ " solutions was also observed with the Hanovia high pressure mercury-vapor source.

The photolysis of an ethanol suspension-solution of  $\text{MoO}_2(\text{dtc})_2$  resulted in the formation of a unique green product formulated as the stoichiometric compound,  $3 \text{ Mo}_2\text{O}_3(\text{dtc})_4 \cdot \text{Mo}_2\text{O}_4(\text{dtc})_2$ . The infrared spectrum of the compound was very similar to that of  $\text{Mo}_2\text{O}_3(\text{dtc})_4$  but also indicated the presence of an  $\text{Mo}_2\text{O}_4^{2+}$  moiety. Since the elemental analyses of the green product were very consistent, the stoichiometry was considered to be an outgrowth of ligand oxidation coupled to

metal reduction from the photochemical reaction. This product could well be uniquely prepared only from photochemical systems. A curious characteristic of the stable green solid was its pressure sensitivity. The green solid turned violet with even slight application of pressure. The resulting product oxidized in air with the same color changes as were noted for the impure violet product,  $\text{Mo}_2\text{O}_3(\text{dte})_4$ , prepared from the "red hv" solutions.

The irradiation of an ethanol suspension-solution of  $\text{MoO}_2(\text{oxine})_2$  was unsuccessful in the formation of reduced product. The yellow-green solid collected was determined to be the oxomolybdenum(VI) starting material.

Photolysis of photochemical systems other than those of the ethanol- $\text{MoO}_2(\text{chel})_2$  systems gave widely different results. The irradiation of both of the oxomolybdenum(VI) compounds,  $\text{MoO}_2\text{Cl}_2$  and  $\text{MoOCl}_4$ , in ethanol resulted in yellow-brown solutions which were successfully used to prepare the oxomolybdenum(V) compound  $\text{Mo}_2\text{O}_3(\text{oxine})_4$ .

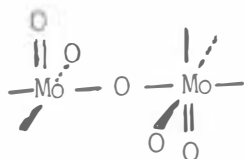
Irradiation of an ethanol suspension of the salt ammonium paramolybdate did not lead to a photoreduced solution as evidenced by the collection of the derivative  $\text{MoO}_2(\text{oxine})_2$ . When an aqueous solution-suspension of ammonium paramolybdate and cysteine was irradiated, a dark solution containing a brown solid resulted. However, no evidence of reduced oxomolybdenum products was observed. Photolysis of an aqueous solution of ammonium paramolybdate and acetylacetone resulted in a red-orange solution. However, a green  $\beta$ -hydroxyquinolate derivative of the photolyzed solution was determined to be  $\text{MoO}_2(\text{oxine})_2$ . Rotary evaporation of the photolyzed solution to dryness was an

unsuccessful method in identifying the brown solid.

These reactions seemed to indicate that ethanol as the solvent was a more successful media for photochemical reduction of molybdenum(VI) in solution or suspension. However, even  $\text{MoO}_2(\text{oxine})_2$  was not appreciably reduced probably due to the oxidizing characteristics of the ligand and/or the great insolubility of the compound in ethanol. On the contrary,  $\text{MoO}_2(\text{dtc})_2$ , which had only limited solubility in ethanol, was reduced as a suspended solid. This suggested that solubility is not a limiting requirement to photoreduction of molybdenum(VI) compounds in ethanol. This was substantiated when the salt,  $\text{Na}_4[\text{Mo}_2\text{O}_5(\text{cyst})_2(\text{OH})_2] \cdot 4 \text{H}_2\text{O}$ , was photoreduced to  $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{cyst})_2] \cdot \frac{1}{2} \text{C}_2\text{H}_5\text{OH} \cdot 4 \text{H}_2\text{O}$  as a suspension in ethanol. Aqueous solutions of a molybdenum(VI) salt did not photoreduce. When the aqueous molybdenum(VI) salt solution contained the soluble ligand acetylacetone, only an oxomolybdenum(VI) derivative was collected, although the solution turned orange-red during the irradiation. It was observed in outdoor illumination experiments as well as experiments in the laboratory that, in the presence of small amounts of water, an ethanol  $\text{MoO}_2(\text{acac})_2$  mixture formed no "red hv" solution but rather solid "molybdenum blue".<sup>25</sup> These findings indicated that the solvent water could not be considered a successful alternate for ethanol in the photochemical systems studied. More extensive solvent investigations on the photoreduction of iron(III) fluorinated acetylacetonates also demonstrated that alcohols, including ethanol and isopropanol were useful solvents but that water, 80% ethanol, chloroform, benzene, and diethyl ether were unsuccessful solvents.



The oxomolybdenum(VI) starting materials for the photochemical reactions were prepared by standard methods when possible. However, a suitable cysteinate compound had not previously been prepared. Synthesis of a product from sodium molybdate was expected to lead to the salt  $\text{Na}_2[\text{MoO}_2(\text{cyst})_2]$ . However, the gold product obtained was formulated as  $\text{Na}_4[\text{Mo}_2\text{O}_5(\text{cyst})_2(\text{OH})_2] \cdot 4 \text{H}_2\text{O}$  containing an  $\text{Mo}_2\text{O}_5^{2+}$  moiety which had been previously reported in  $\text{K}_2[\text{Mo}_2\text{O}_5(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ . This compound was reported to contain the centro-symmetric bridging group indicated by



Other oxomolybdenum(VI) compounds were prepared because of their relationships to other products isolated in this work. The tropolonate compound  $\text{MoO}_2(\text{trop})_2$  was prepared directly from sodium molybdate and the ligand. Isolation from another product of unknown formulation was accomplished by ethanol precipitation from an aqueous solution. This compound indicated some promise as an aqueous photolysis starting material due to its solubility in water.

Two oxomolybdenum(VI) pyridine compounds were prepared. Several solvent systems were investigated with this fascinating ligand. As discussed previously the compounds  $\text{Mo}_2\text{O}_4(\text{acac})_2(\text{py})_2$  and  $\text{MoO}_2(\text{OH})(\text{py})_{0.8}$  were prepared in high purity from the "red  $h\nu$ " solutions and by reflux of  $\text{MoO}_2(\text{acac})_2$  in an ethanol-pyridine mixture. When the reflux solvent ethanol, was replaced with isopropyl alcohol the compounds  $\text{Mo}_2\text{O}_4(\text{acac})_2(\text{py})_2$  and  $\text{MoO}_2(\text{OH})(\text{py})_{0.8}$  were again prepared. When ethanol

was eliminated and pyridine was itself the solvent, the room temperature reaction of  $\text{MoO}_2(\text{acac})_2$  resulted in no reduction of molybdenum in the formation of  $\text{Mo}_2\text{O}_5(\text{acac})_2(\text{py})_2$ . This was the first nonionic compound reported containing the  $\text{Mo}_2\text{O}_5^{2+}$  moiety. The formation of this product coupled with the observed formation of  $\text{Mo}_2\text{O}_4(\text{acac})_2(\text{py})_2$  indicated that pyridine acted to stabilize the oxo bridged compounds, perhaps more specifically those containing the acetylacetonate ligand. This conclusion was drawn on the basis of an inability to isolate either  $\text{Mo}_2\text{O}_5(\text{acac})_2$  or  $\text{Mo}_2\text{O}_4(\text{acac})_2$  by standard techniques.

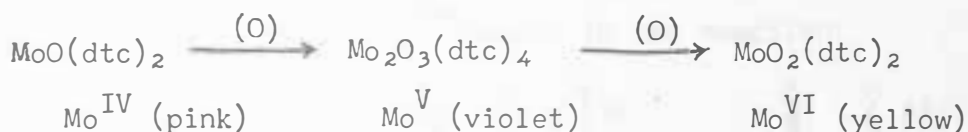
When a benzene-pyridine mixture was refluxed with  $\text{MoO}_2(\text{acac})_2$  the white product formed was determined to be a pyridinium salt. The product was formulated as  $(\text{pyH})_4(\text{Mo}_8\text{O}_{26})$ . These solvent studies on pyridine containing compounds resulting from reflux and room temperature reactions of  $\text{MoO}_2(\text{acac})_2$  indicated that alcohols were the only solvents yielding lower oxidation state oxomolybdenum compounds. It was most probable that the reductant in these reactions was the acetylacetonate ion rather than pyridine since the presence of pyridine with benzene does not lead to a reduced product. Similar rationale indicated that ethanol was not the reductant since ethanol solutions of  $\text{MoO}_2(\text{acac})_2$  were not observed to form reduced species.

Although the oxomolybdenum(IV) and (V) compounds prepared were, in general, either too unstable or too insoluble to obtain molecular weight data or ultraviolet-visible spectra, it was possible to characterize the products utilizing infrared spectra and elemental analysis techniques. This could not have been accomplished were it not for the unobscured and consistently recurring molybdenum-oxygen bands in the

400-1050  $\text{cm}^{-1}$  region of the infrared spectra for the same moieties.

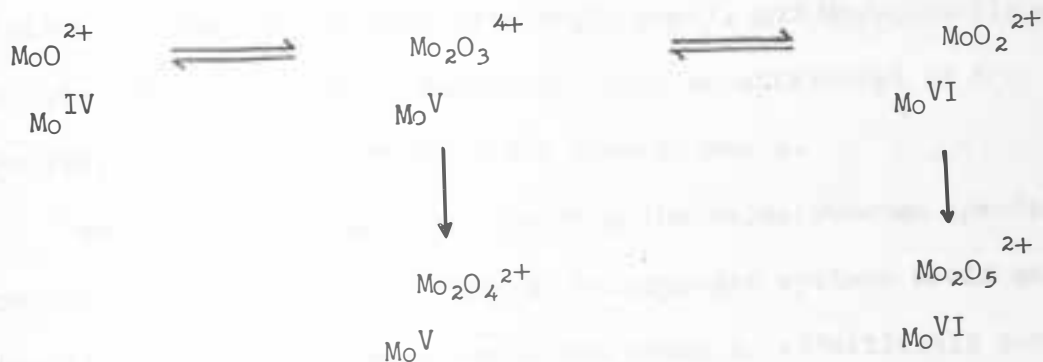
The tool of oxidation state determination by cerimetric titration also proved to be of little value due to the apparent characteristic of slow oxidation of organic ligands coordinated with these compounds.

However, a qualitative test for the presence of molybdenum(V) compounds was utilized successfully. In this test concentrated hydrochloric acid produces a green solution as the molybdenum(V) sample formed the green ion,  $\text{MoOCl}_5^{2-}$ . A limitation of this test was the insolubility of a few compounds. The oxidation of the reduced products prepared in this work would probably be considered parallel to the observations for the diethyldithiocarbamates. The following sequence was observed from an infrared investigation correlated to color changes in the compounds:

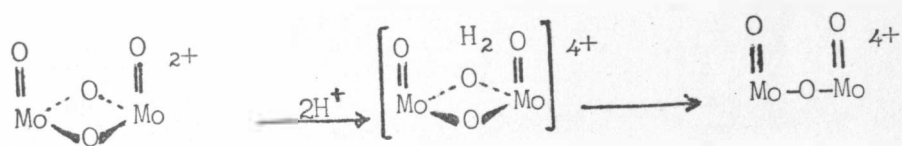


The oxidation sequence did not include the compound  $\text{Mo}_2\text{O}_4(\text{dtc})_2$ . This was reasonable since the compound did not have a Mo:dtc ratio of 1:2 as was the case with other members of the sequence. The discoloration of yellow  $\text{Mo}_2\text{O}_4(\text{dtc})_2$  to brown-orange was probably the result of formation of some  $\text{Mo}_2\text{O}_3(\text{dtc})_4$  evidenced by the violet wash obtained from the brown-orange sample. This was difficult to explain without assuming the presence of excess ligand or a disproportionation reaction.

When all products formed were considered in this work, the oxomolybdenum moieties were found to undergo the following changes:



The significance of this work to biochemical systems stems from reports<sup>130, 173</sup> of possible dinuclear molybdenum at the active sites in the enzyme nitrogenase. It was proposed that both atoms may be necessary to make the site active.<sup>98</sup> While the actual reducing species may be an oxomolybdenum(IV) species, it was proposed<sup>130</sup> that this species could involve the  $\text{Mo}_2\text{O}_4^{2+}$  moiety in the reaction:



followed by a proposed equilibrium disproportionation:



However, Schrauzer and Doemery<sup>98</sup> also proposed that dihapto (side on) binding of dinitrogen could occur at a dinuclear monooxo bridged oxomolybdenum(IV) site which had sulfur ligands labilizing the bridging oxygen. The first reaction above could also be catalyzed by a protonated solvent instead of protons themselves. Since  $\text{Mo}_2\text{O}_4(\text{dtc})_2$  was prepared in aqueous reflux from  $\text{Mo}_2\text{O}_3(\text{dtc})_4$ , it



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APPENDIX

Wavelength	Relative Intensity
2.2	6.2
1.3	6.3
1.2	6.3
1.1	6.1
1.0	7.4
0.9	11.1
0.8	11.1
0.7	11.1

Table XXIII. d Values for the Mixture of Di- $\mu$ -oxo-bis[oxo-8-hydroxy-quinolinatomolybdenum(V)],  $\text{Mo}_2\text{O}_4(\text{C}_9\text{H}_6\text{NO})_2$ , and  $\mu$ -Oxo-dioxotetrakis-(8-hydroxyquinolinato)dimolybdenum(V),  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ .\*

<u>d Values</u>	<u>Relative Intensity</u>	<u>d Values</u>	<u>Relative Intensity</u>
3.40	1.0		
3.40	1.0	1.21	0.2
2.42	0.6	1.13	0.1
2.15	0.1	1.08	0.2
1.70	0.7	0.94	0.1
1.52	0.2	0.91	0.1
1.40	0.2	0.85	0.1
1.30	0.1	0.77	0.1

\*Sealed sample in X-ray capillary tube containing air.

Table XXIV. d Values for  $\mu$ -Oxo-dioxotetrakis(8-hydroxyquinolino)-  
dimolybdenum(V),  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ .\*

<u>d</u> Values	<u>Relative Intensity</u>	<u>d</u> Values	<u>Relative Intensity</u>
11.69	0.6	3.82	0.8
9.65	1.0	3.56	0.2
7.65	0.4	3.44	0.2
7.15	1.0	3.18	0.05
6.34	0.3	2.99	0.1
5.73	0.9	2.83	0.1
5.48	0.2	2.38	0.3
5.02	0.1	2.20	0.1
4.49	0.8	1.99	0.1
4.01	0.8		

\*Sealed sample in X-ray capillary tube containing air.



Table XXV. d Values for the Mixture of Di- $\mu$ -oxo-bis[oxo-8-hydroxy-quinolinatemolybdenum(V)],  $\text{Mo}_2\text{O}_4(\text{C}_9\text{H}_6\text{NO})_2$ , and  $\mu$ -Oxo-dioxotetrakis-(8-hydroxyquinolinato)dimolybdenum(V),  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ .\*

<u>d Values</u>	<u>Relative Intensity</u>	<u>d Values</u>	<u>Relative Intensity</u>
10.51	1.0	3.64	0.3
9.01	1.0	3.42	0.1
7.49	0.8	2.82	0.1
6.65	0.7	2.72	0.1
5.43	0.5	2.34	0.1
4.28	0.2	2.16	0.1
3.88	0.3	1.97	0.05

\* Sealed sample in X-ray capillary tube containing nitrogen.

Table XXVI. d Values for the Mixture of Di- $\mu$ -oxo-bis[oxo-8-hydroxy-quinolinatomolybdenum(V)],  $\text{Mo}_2\text{O}_4(\text{C}_9\text{H}_6\text{NO})_2$ , and  $\mu$ -Oxo-dioxotetrakis-(8-hydroxyquinolinato)dimolybdenum(V),  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ .\*

<u>d</u> Values	Relative Intensity	<u>d</u> Values	Relative Intensity
7.55	0.7	3.45	0.3
7.18	1.0	3.18	0.05
6.31	0.5	2.99	0.1
5.46	0.5	2.71	0.05
4.45	0.5	2.38	0.1
3.83	0.6	2.16	0.05
3.57	0.05	1.86	0.05

\*Sealed sample in X-ray capillary tube containing air.

Table XXVII. d Values for Impure  $\mu$ -Oxo-dioxotetrakis(N,N-diethyl-dithiocarbamato)dimolybdenum(V),  $\text{Mo}_2\text{O}_3(\text{C}_5\text{H}_{10}\text{NS}_2)_4$ , Prepared by Dithionite Ion Reduction.

<u>d Values</u>	<u>Relative Intensity</u>	<u>d Values</u>	<u>Relative Intensity</u>
11.77	0.3	3.05	0.2
10.76	0.3	2.95	0.2
8.18	1.0	2.81	0.1
7.61	0.8	2.69	0.1
7.24	0.3	2.53	0.05
6.64	0.05	2.40	0.1
5.67	0.3	2.37	0.05
5.21	0.5	2.25	0.1
4.95	0.2	2.12	0.05
4.66	0.3	2.09	0.05
4.45	0.3	2.05	0.05
4.03	0.05	1.95	0.1
3.78	0.7	1.89	0.05
3.58	0.05	1.73	0.05
3.28	0.1	1.56	0.05
3.19	0.05	1.53	0.05
		1.52	0.05
		1.46	0.05
		1.43	0.05
		1.35	0.05
		1.33	0.05

Table XXVIII. d Values for Oxobis(N,N-diethyldithiocarbamato)-  
molybdenum(IV),  $\text{MoO}(\text{C}_5\text{H}_{10}\text{NS}_2)_2$ , Prepared by Dithionite Ion Reduction.

<u>d</u> Values	Relative Intensity	<u>d</u> Values	Relative Intensity
10.90	0.4	2.78	0.1
9.10	0.5	2.69	0.05
8.33	0.2	2.60	0.2
7.68	1.0	2.53	0.05
7.24	0.8	2.44	0.1
6.50	0.1	2.27	0.1
6.10	1.0	2.25	0.2
5.56	0.1	2.14	0.2
5.24	0.5	2.10	0.2
4.64	0.1	2.07	0.1
4.37	0.4	2.03	0.1
4.20	1.0	1.97	0.1
3.88	0.05	1.78	0.1
3.72	0.2	1.73	0.1
3.51	0.1	1.62	0.05
3.21	0.2	1.58	0.05
3.14	0.1	1.52	0.05
3.02	0.05	1.46	0.05
2.97	0.05	1.43	0.05
2.88	0.6	1.35	0.05
		1.33	0.05

Table XXIX. d Values for Oxobis(N,N-diethyldithiocarbamato)-  
molybdenum(IV),  $\text{MoO}(\text{C}_5\text{H}_{10}\text{NS}_2)_2$ , Prepared from Photoreduced Ethanol  
Solutions of Dioxobis(acetylacetonato)molybdenum(VI).

<u>d</u> Values	Relative Intensity	<u>d</u> Values	Relative Intensity
8.12	0.4	2.91	0.1
7.30	0.4	2.83	0.05
6.80	0.05	2.71	0.1
6.27	1.0	2.62	0.05
4.87	0.2	2.39	0.05
4.54	0.2	2.19	0.05
4.39	0.05	2.12	0.05
4.16	0.2	2.08	0.1
3.31	0.1		

Table XXX. d Values for  $3 \text{ Mo}_2\text{O}_3(\text{C}_5\text{H}_{10}\text{NS}_2)_4 \cdot \text{Mo}_2\text{O}_4(\text{C}_5\text{H}_{10}\text{NS}_2)_2$ 

Prepared by Photoreduction of an Ethanol Suspension of Dioxobis-

(N,N-diethyldithiocarbamato)molybdenum(VI).

<u>d Values</u>	<u>Relative Intensity</u>	<u>d Values</u>	<u>Relative Intensity</u>
13.17	0.1	3.17	0.05
11.46	0.1	3.08	0.1
10.38	0.1	3.03	0.05
9.01	1.0	2.93	0.05
8.03	1.0	2.87	0.1
7.49	1.0	2.70	0.3
6.36	0.2	2.64	0.05
6.18	0.2	2.55	0.05
5.67	0.1	2.48	0.05
5.18	0.8	2.35	0.05
4.84	0.2	2.31	0.1
4.66	0.1	2.21	0.05
4.50	0.2	2.15	0.1
4.32	0.2	2.08	0.1
4.11	0.2	2.02	0.1
3.98	0.2	1.98	0.05
3.88	0.2	1.93	0.1
3.76	0.2	1.83	0.05
3.53	0.4	1.63	0.05
3.26	0.1		

Figure 7. Six-Oxomolybdenum(8-hydroxyethylthiocarbamate)molybdenum(VI),  
 $3 \text{ Mo}_2\text{O}_3(\text{C}_5\text{H}_{10}\text{NS}_2)_4 \cdot \text{Mo}_2\text{O}_4(\text{C}_5\text{H}_{10}\text{NS}_2)_2$

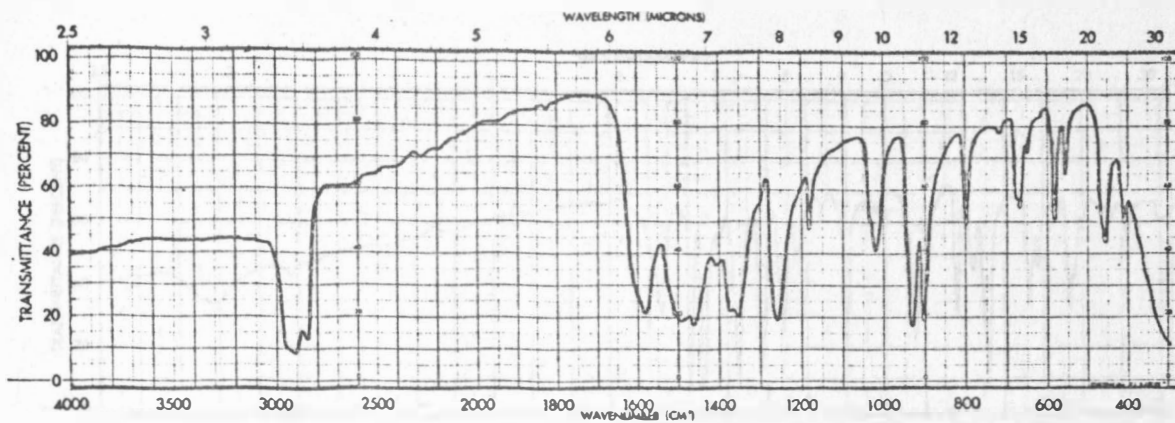


Figure 5. cis-Dioxobis(acetylacetonato)molybdenum(VI),  $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$

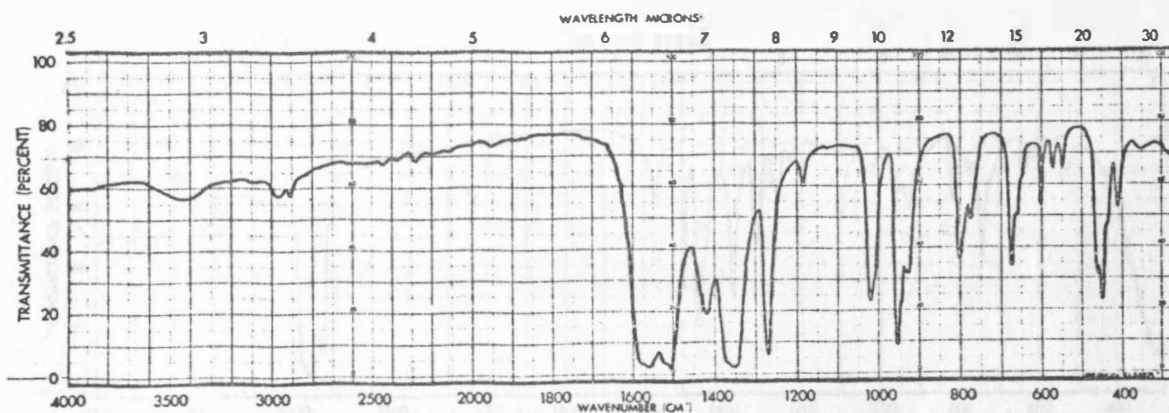


Figure 6.  $\mu$ -Oxo-dioxotetrakis(acetylacetonato)dimolybdenum(V),  $\text{Mo}_2\text{O}_3(\text{C}_5\text{H}_7\text{O}_2)_4$ .

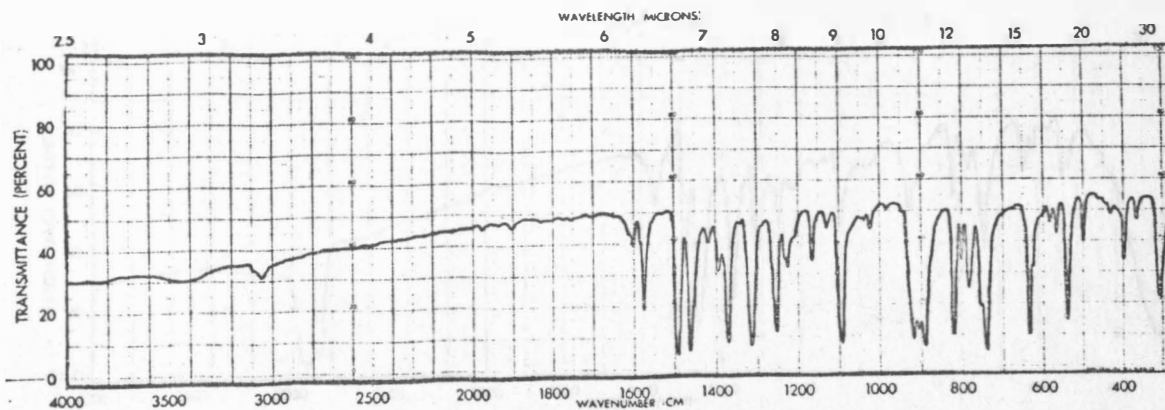


Figure 7. cis-Dioxobis(8-hydroxyquinolinato)molybdenum(VI),  $\text{MoO}_2(\text{C}_9\text{H}_6\text{NO})_2$ .

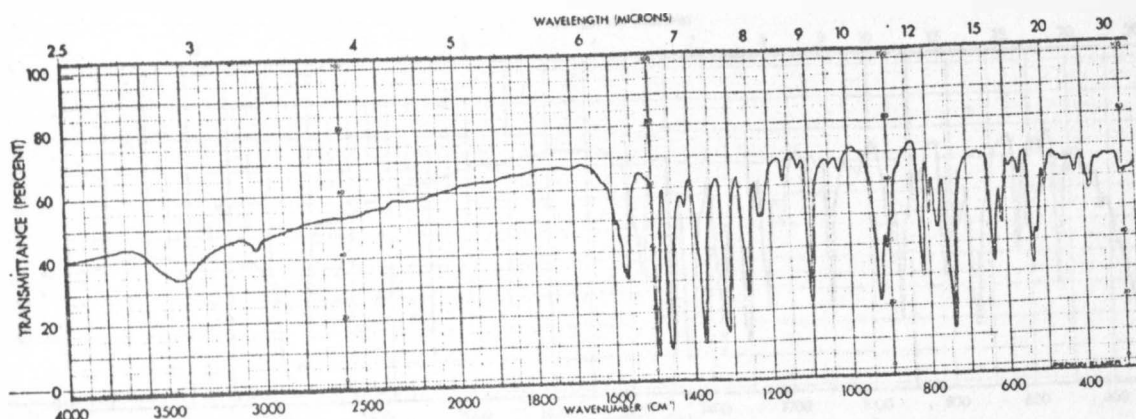


Figure 8.  $\mu$ -Oxo-dioxotetrakis(8-hydroxyquinolinato)dimolybdenum(V),  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ .

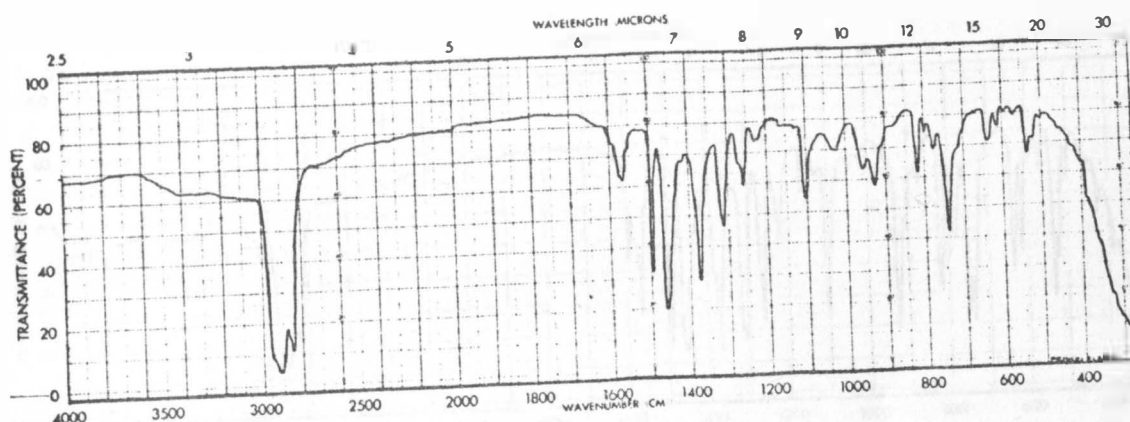


Figure 9. A Mixture of Di- $\mu$ -oxobis[oxo-8-hydroxyquinolinatomolybdenum(V)]  $\text{Mo}_2\text{O}_4(\text{C}_9\text{H}_6\text{NO})_2$  and  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ .

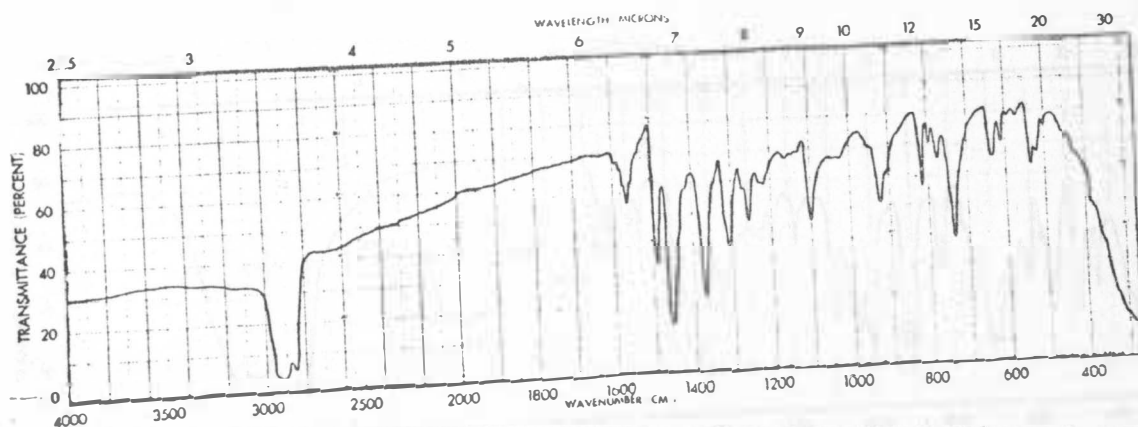


Figure 10. A Mixture of  $\text{Mo}_2\text{O}_4(\text{C}_9\text{H}_6\text{NO})_2$  and  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ .



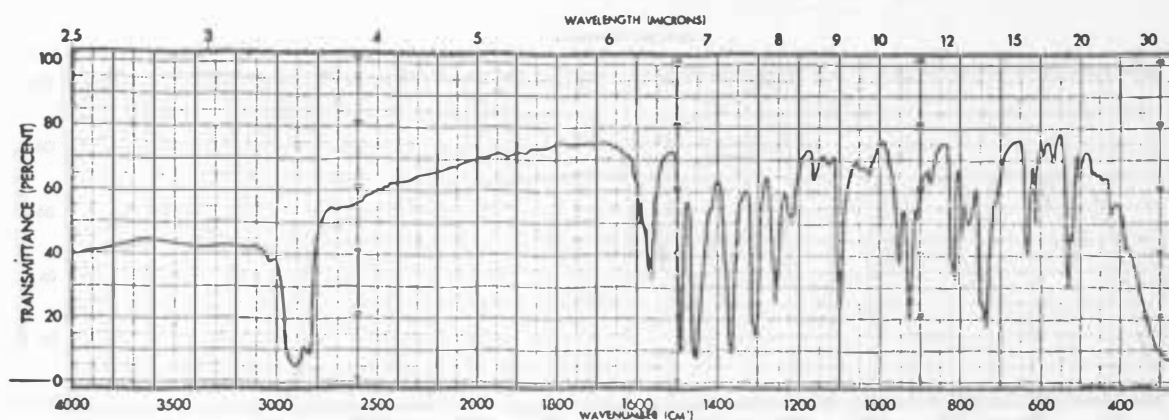


Figure 11. A Mixture of  $\text{Mo}_2\text{O}_4(\text{C}_9\text{H}_6\text{NO})_2$  and  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ .

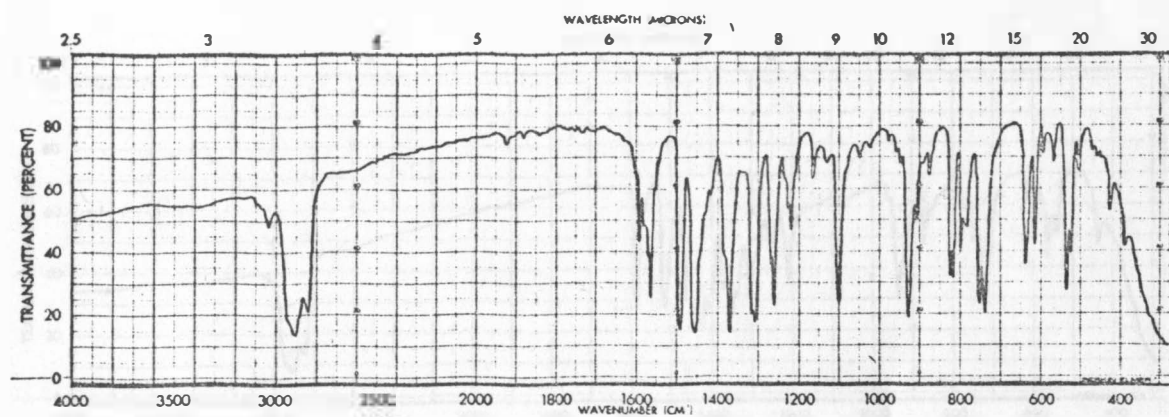


Figure 12.  $\mu$ -Oxo-dioxotetrakis(8-hydroxyquinolinato)dimolybdenum(V),  $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$ .

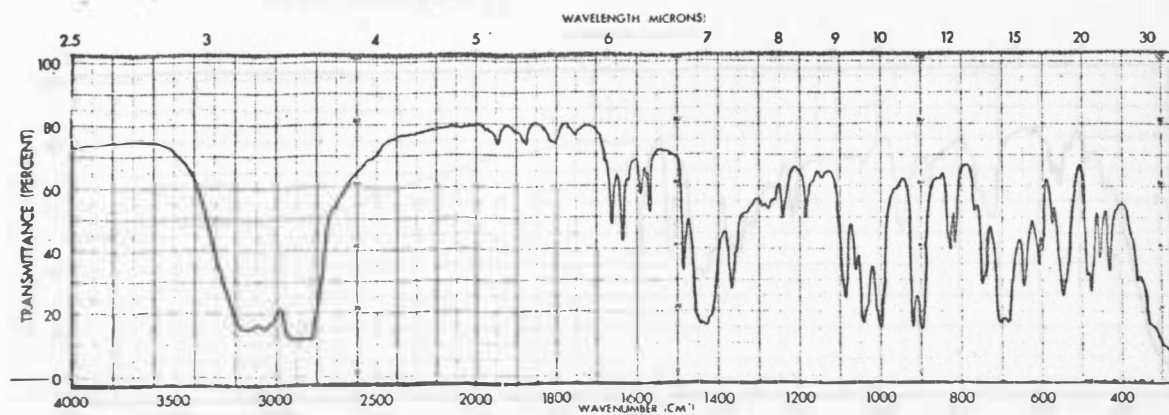


Figure 13. cis-Dioxobis(benzoin-anti-oximato)molybdenum(VI),  $\text{MoO}_2(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N})_2$ .

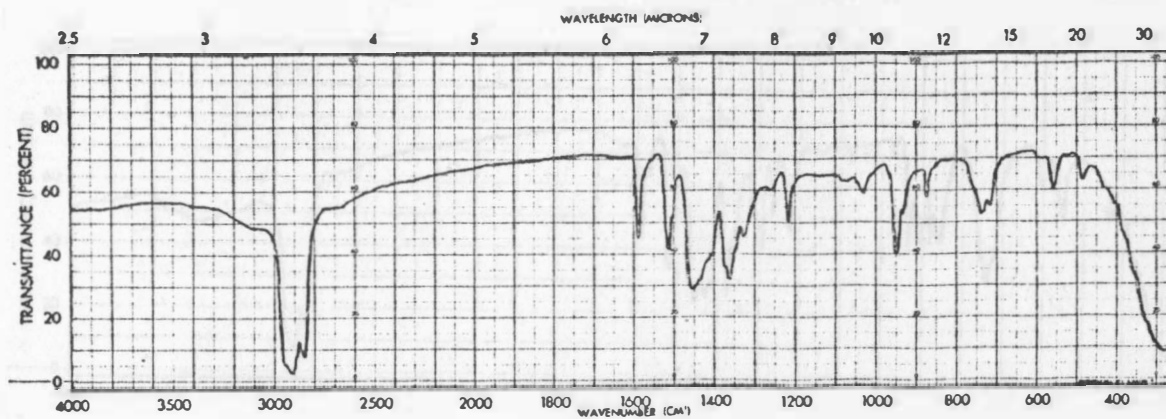


Figure 14. Di- $\mu$ -oxobis[oxotropolonatomolybdenum(V)],  $\text{Mo}_2\text{O}_4(\text{C}_7\text{H}_5\text{O}_2)_2$ .

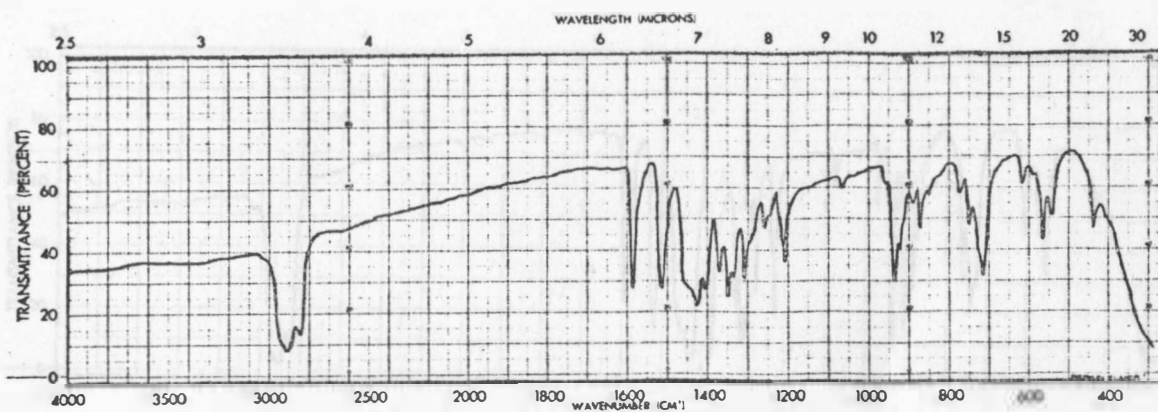


Figure 15.  $\mu$ -Oxo-dioxotetrakis(tropolonato)dimolybdenum(V),  $\text{Mo}_2\text{O}_3(\text{C}_7\text{H}_5\text{O}_2)_4$ .

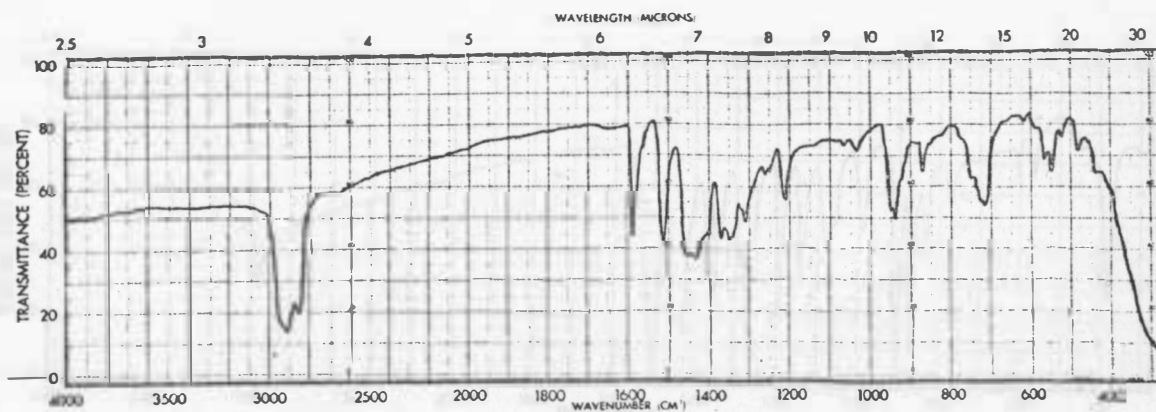


Figure 16. A Mixture of  $\text{Mo}_2\text{O}_4(\text{C}_7\text{H}_5\text{O}_2)_2$  and  $\text{Mo}_2\text{O}_3(\text{C}_7\text{H}_5\text{O}_2)_4$ .

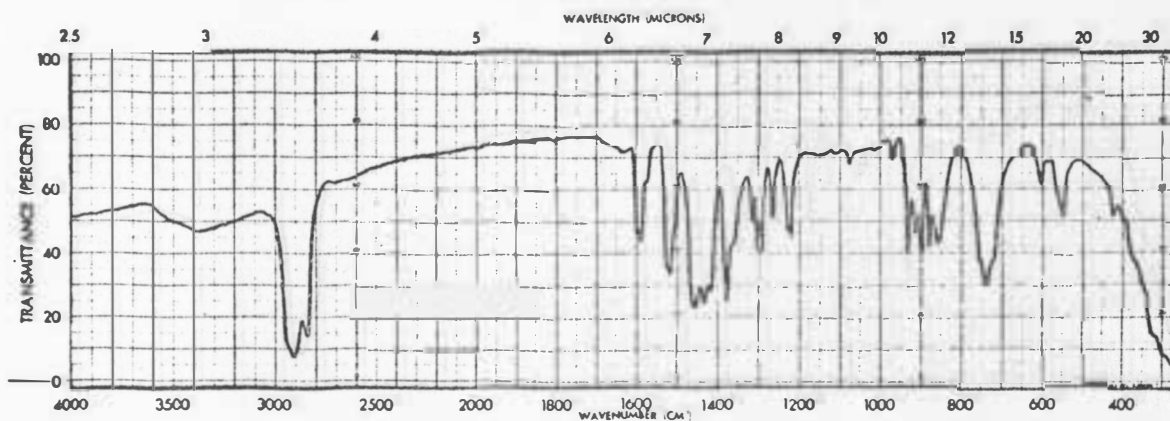


Figure 17. A Mixture Containing cis-Dioxobis(troponato)molybdenum(VI),  $\text{MoO}_2(\text{C}_7\text{H}_5\text{O}_2)_2$ .

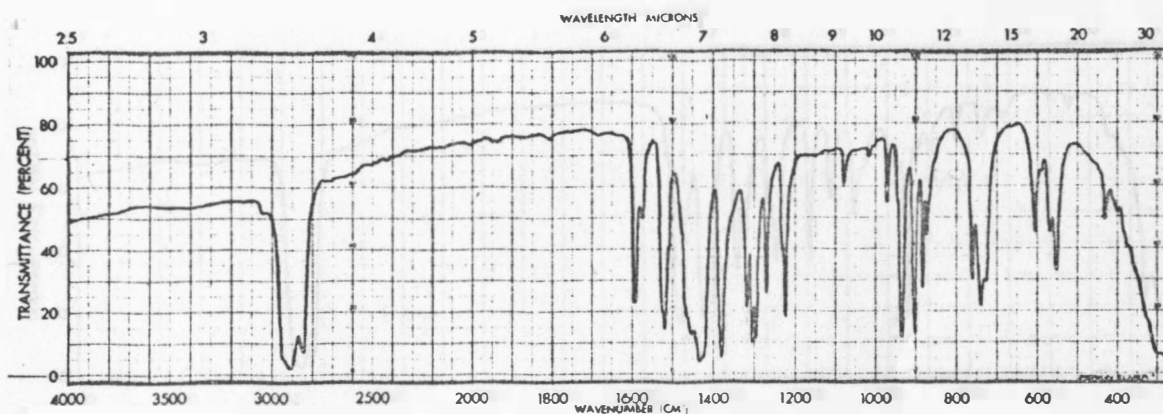


Figure 18. cis-Dioxobis(tropolonato)molybdenum(VI),  $\text{MoO}_2(\text{C}_7\text{H}_5\text{O}_2)_2$ .

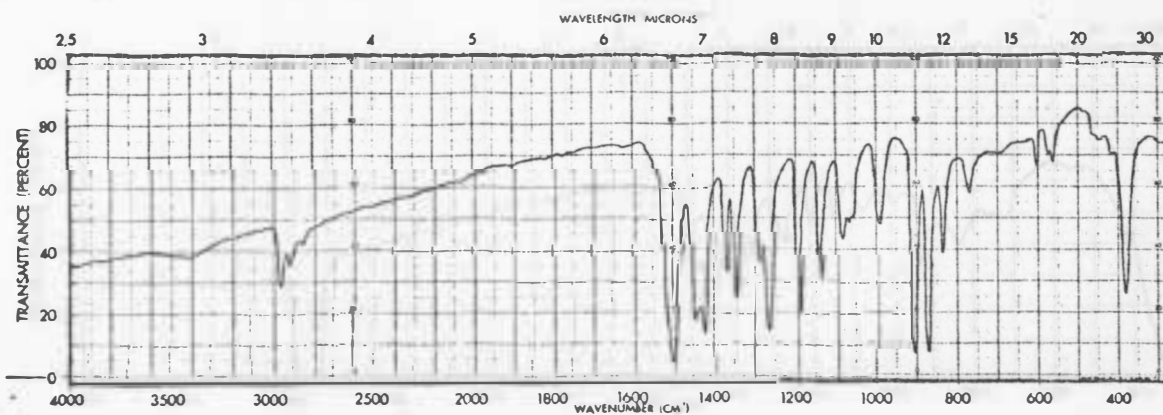


Figure 19. cis-Dioxobis(N,N-diethyldithiocarbamato)molybdenum(VI),  $\text{MoO}_2(\text{C}_5\text{H}_{10}\text{NS}_2)_2$ .

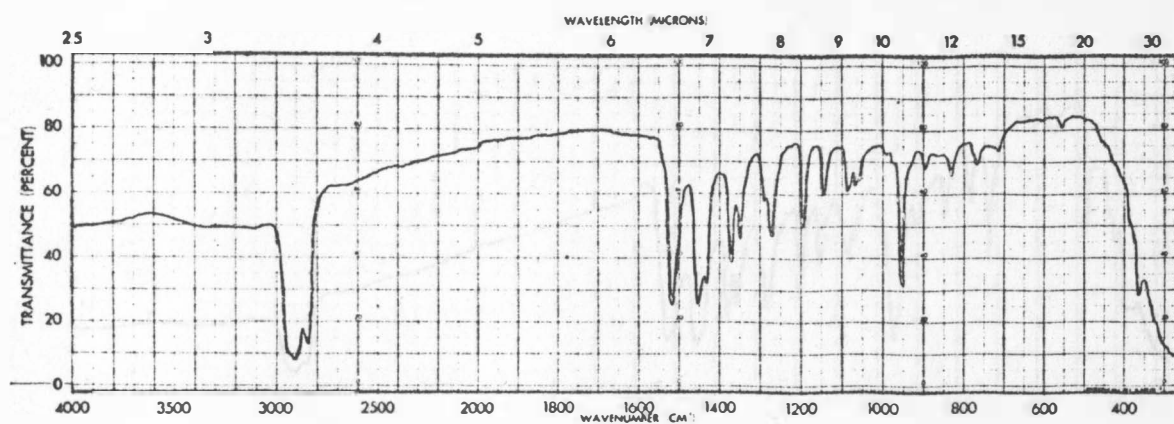


Figure 20. Impure Oxobis(N,N-diethyldithiocarbamato)molybdenum(IV),  $\text{MoO}(\text{C}_5\text{H}_{10}\text{NS}_2)_2$ .

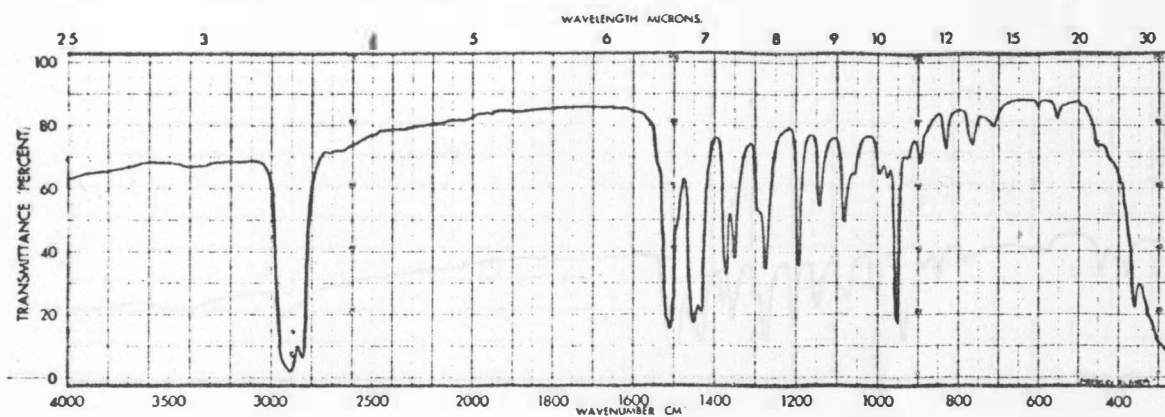


Figure 21. Oxobis(N,N-diethyldithiocarbamato)molybdenum(IV),  $\text{MoO}(\text{C}_5\text{H}_{10}\text{NS}_2)_2$ .

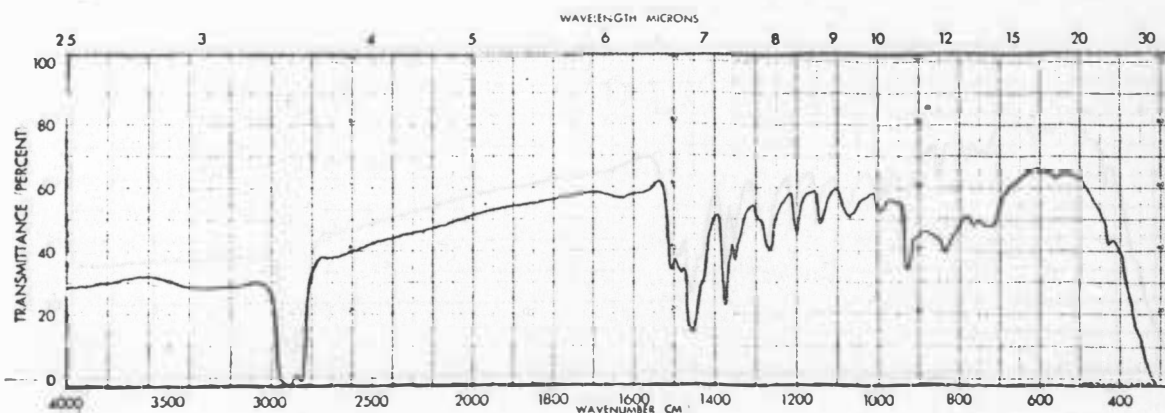


Figure 22. The Polymer,  $[\text{MoO}_2(\text{C}_5\text{H}_{10}\text{NS}_2)(\text{H}_2\text{O})]_n$ .

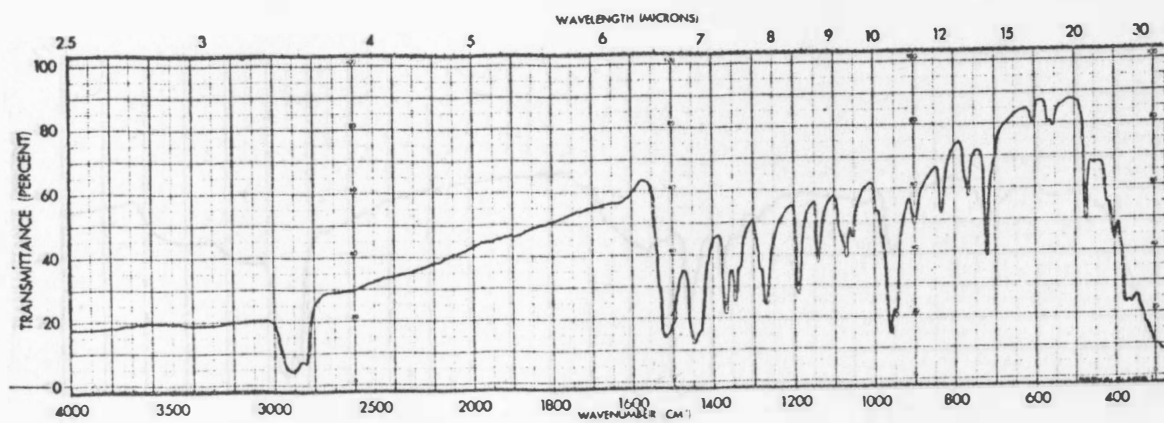


Figure 23. Di- $\mu$ -oxobis[Oxo-N,N-diethylthiocarbamatomolybdenum(V)].  
 $\text{Mo}_2\text{O}_4(\text{C}_5\text{H}_{10}\text{NS}_2)_2$

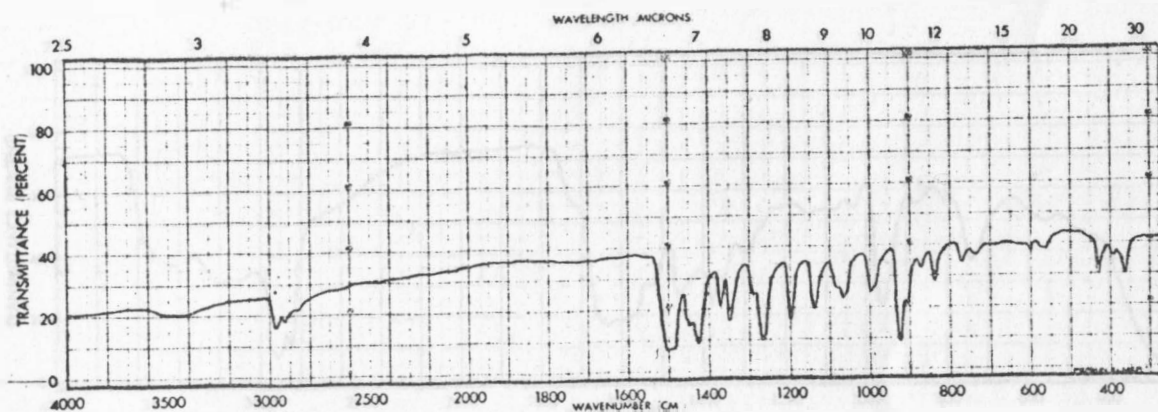


Figure 24. Impure  $\mu$ -Oxo-dioxotetrakis(N,N-diethylthiocarbamato)dimolybdenum(V),  $\text{Mo}_2\text{O}_3(\text{C}_5\text{H}_{10}\text{NS}_2)_4$ .

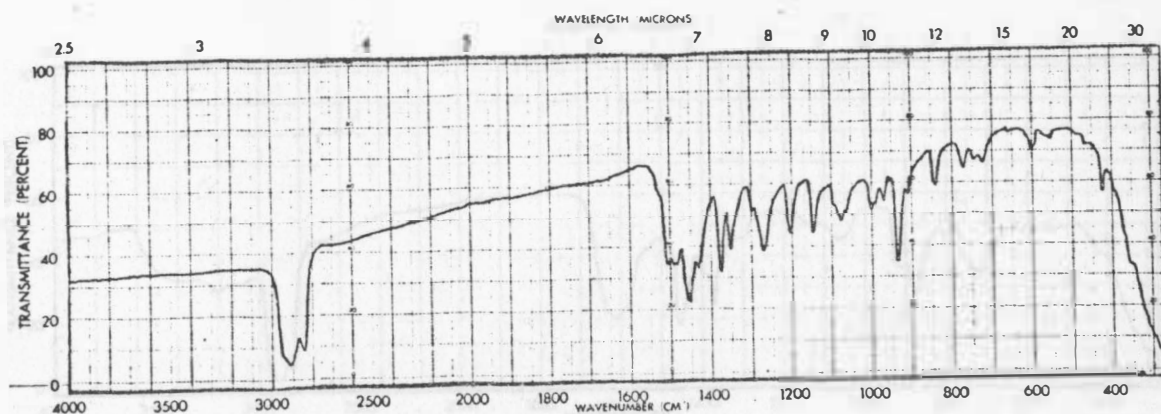


Figure 25. The Product,  $3 \text{ Mo}_2\text{O}_3(\text{C}_5\text{H}_{10}\text{NS}_2)_4 \cdot \text{Mo}_2\text{O}_4(\text{C}_5\text{H}_{10}\text{NS}_2)_2$ .



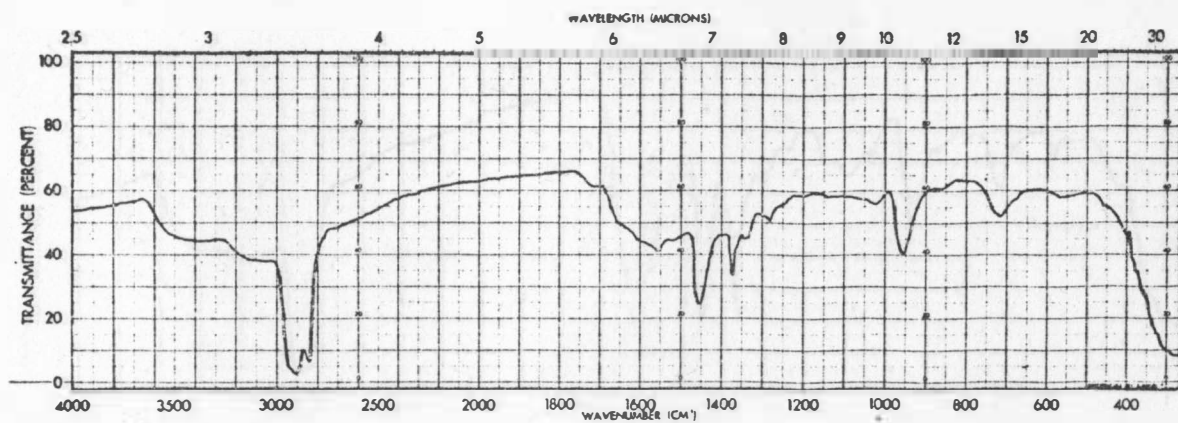


Figure 26. Di- $\mu$ -oxobis[oxocysteinatomolybdenum(V)]-1-ethanol-5-water,  
 $[\text{Mo}_2\text{O}_4(\text{C}_3\text{H}_6\text{NO}_2\text{S})_2] \cdot \text{C}_2\text{H}_5\text{OH} \cdot 5 \text{H}_2\text{O}$ .

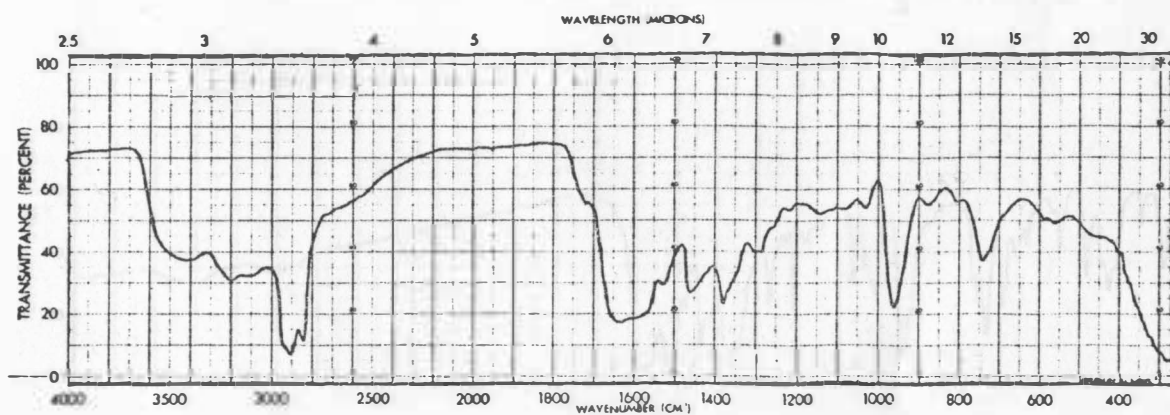


Figure 27. Di- $\mu$ -oxobis[oxocysteinatomolybdenum(V)]-1.2-ethanol,  
 $[\text{Mo}_2\text{O}_4(\text{C}_3\text{H}_6\text{NO}_2\text{S})_2] \cdot 1.2 \text{C}_2\text{H}_5\text{OH}$ .

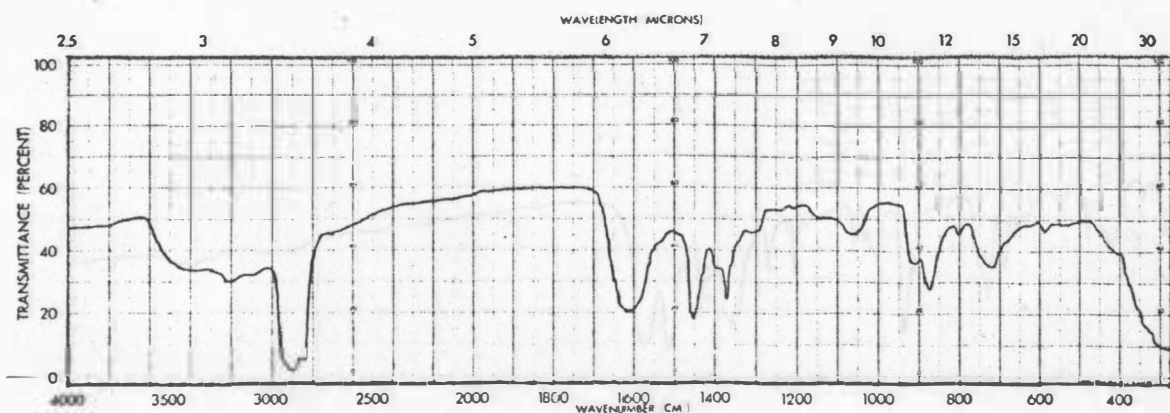


Figure 28. Tetrasodium  $\mu$ -Oxobis[cis-dioxocysteinato-hydroxo-molybdate(VI)] tetrahydrate,  
 $\text{Na}_4[\text{Mo}_2\text{O}_5(\text{C}_3\text{H}_5\text{NO}_2\text{S})_2(\text{OH})_2] \cdot 4 \text{H}_2\text{O}$

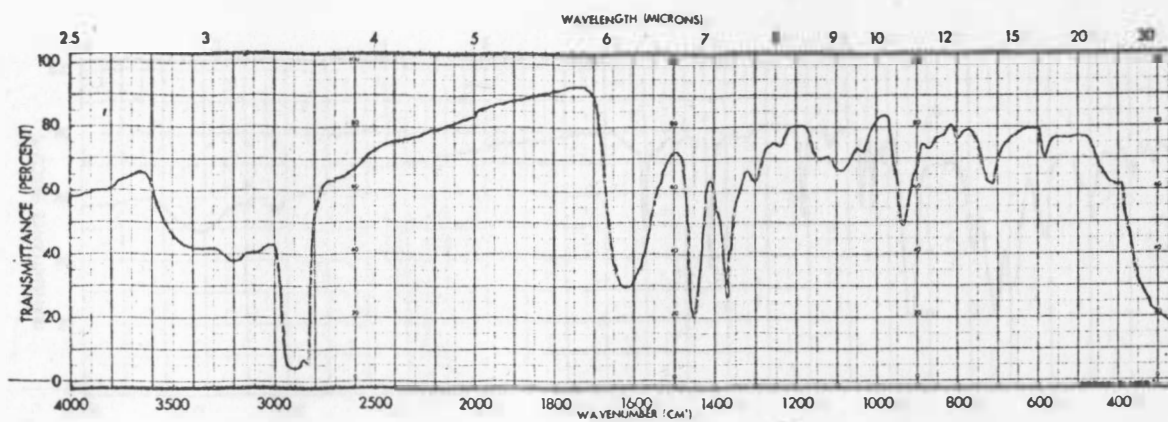


Figure 29. Disodium Di- $\mu$ -oxobis[oxocysteinate molybdate(V)]  $\cdot \frac{1}{2}$  ethanol  $\cdot \frac{4}{2}$  water,  $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{C}_3\text{H}_5\text{NO}_2\text{S})_2] \cdot \frac{1}{2}\text{C}_2\text{H}_5\text{OH} \cdot \frac{4}{2}\text{H}_2\text{O}$ .

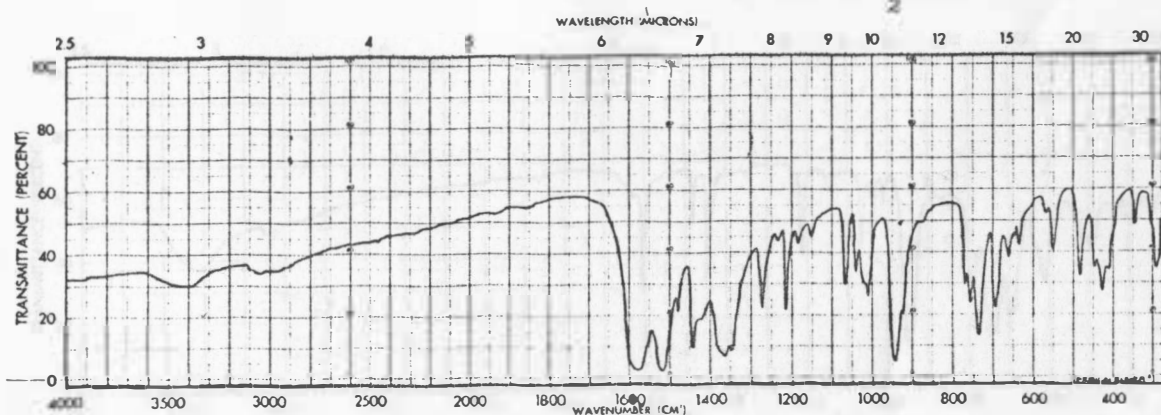


Figure 30. Di- $\mu$ -oxobis[oxoacetylacetonatopyridine molybdenum(V)],  $\text{Mo}_2\text{O}_4(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_5\text{H}_5\text{N})_2$ .

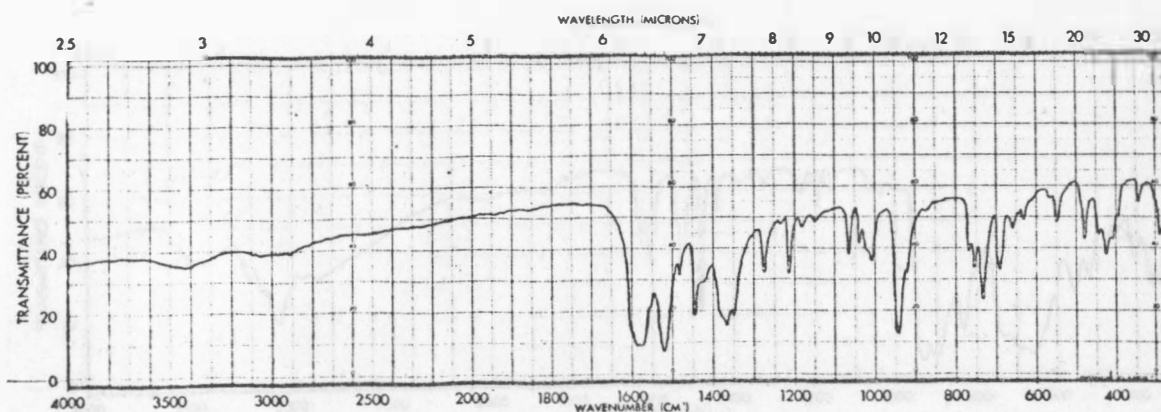


Figure 31. Di- $\mu$ -oxobis[oxoacetylacetonatopyridine molybdenum(V)],  $\text{Mo}_2\text{O}_4(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_5\text{H}_5\text{N})_2$ .

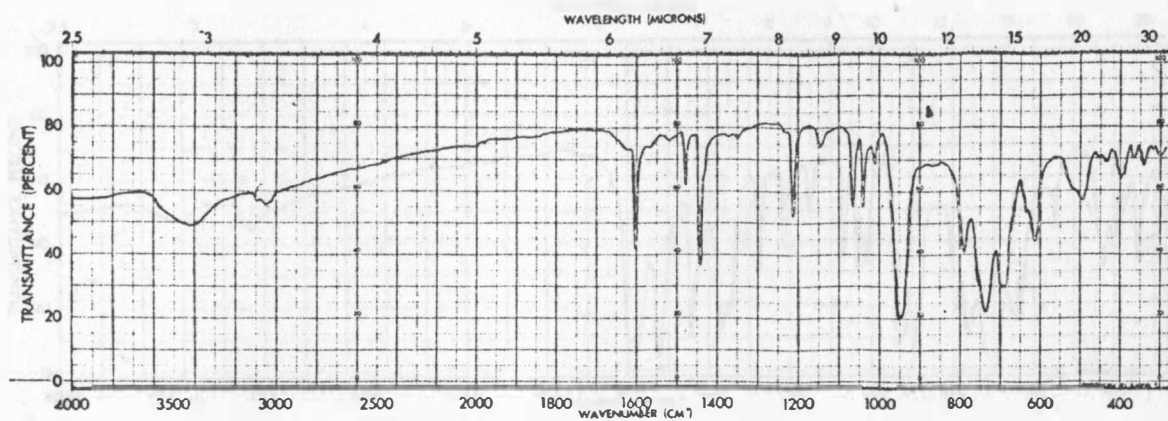


Figure 32. The Compound,  $\text{MoO}_2(\text{OH})(\text{C}_5\text{H}_5\text{N})_{0.8}$ .

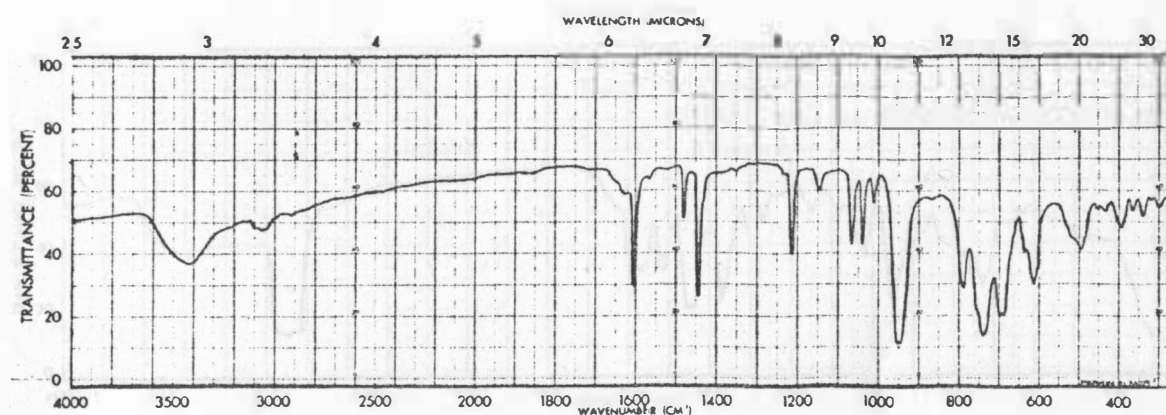


Figure 33. The Compound,  $\text{MoO}_2(\text{OH})(\text{C}_5\text{H}_5\text{N})_{0.8}$

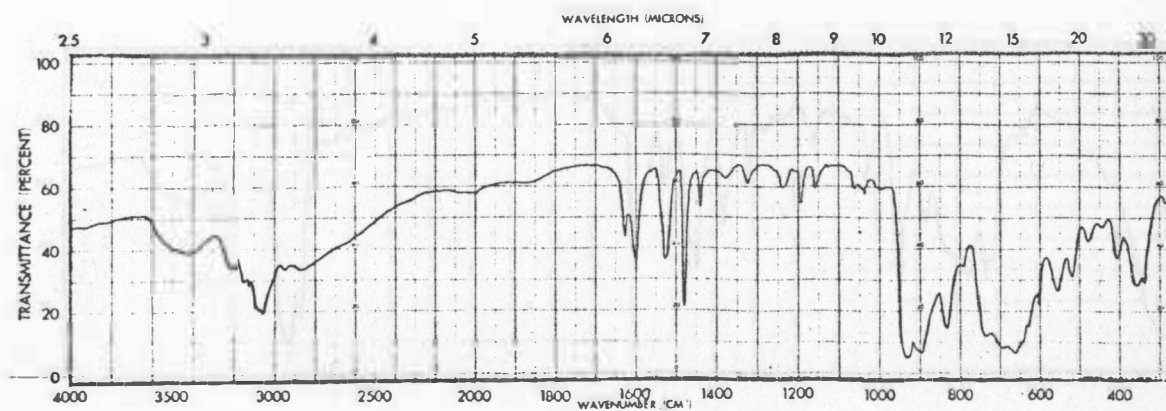


Figure 34. The Pyridinium Polymolybdate,  $(\text{C}_5\text{H}_6\text{N})_4(\text{Mo}_8\text{O}_{26})$



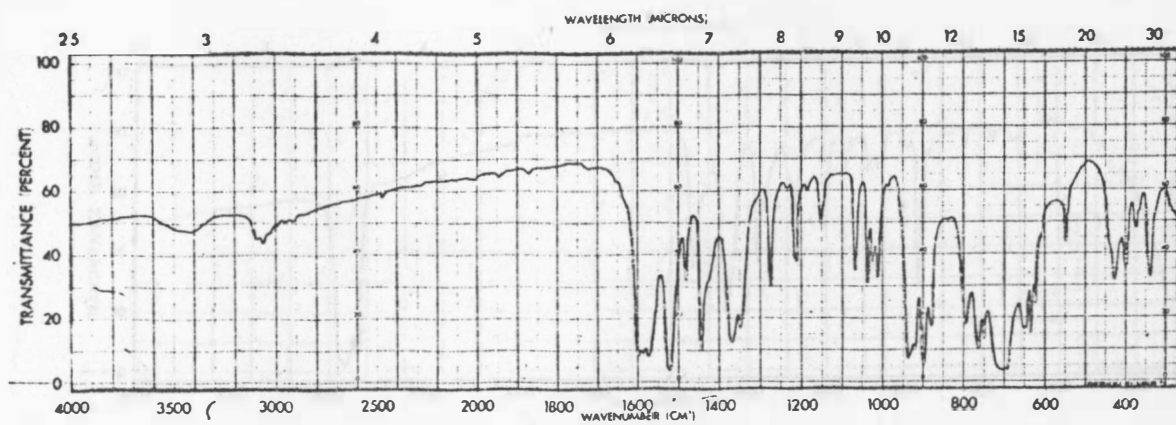


Figure 35.  $\mu$ -Oxo-bis(cis-dioxo-acetylacetonatopyridinemo)lybdenum(VI),  
 $\text{Mo}_2\text{O}_5(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_5\text{H}_5\text{N})_2$

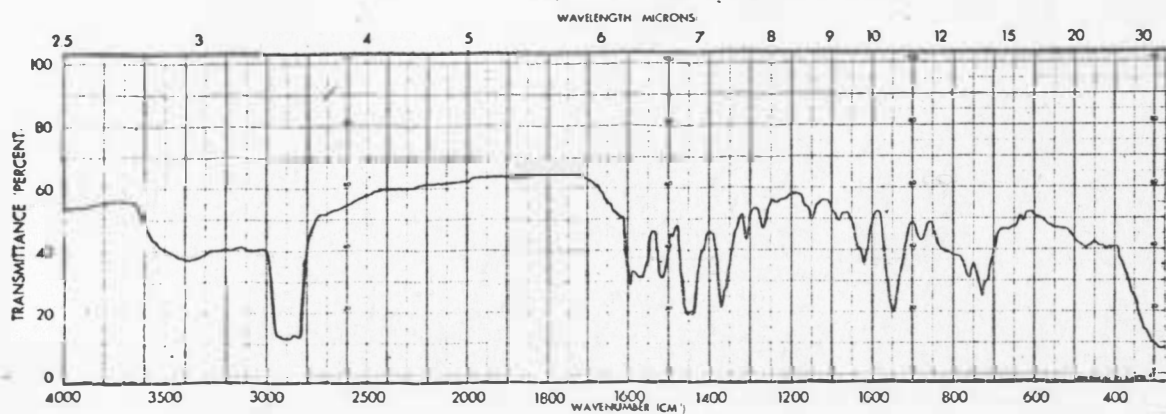


Figure 36. A Mixture Containing  $\text{Mo}_2\text{O}_3(\text{OH})_4(\text{bipy})$

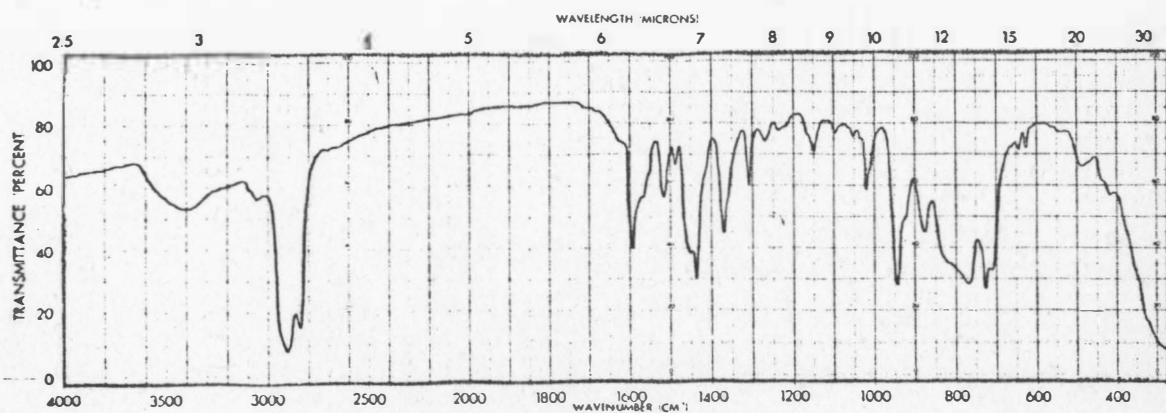


Figure 37. The Compound,  $\text{Mo}_2\text{O}_3(\text{OH})_4(\text{bipy})$

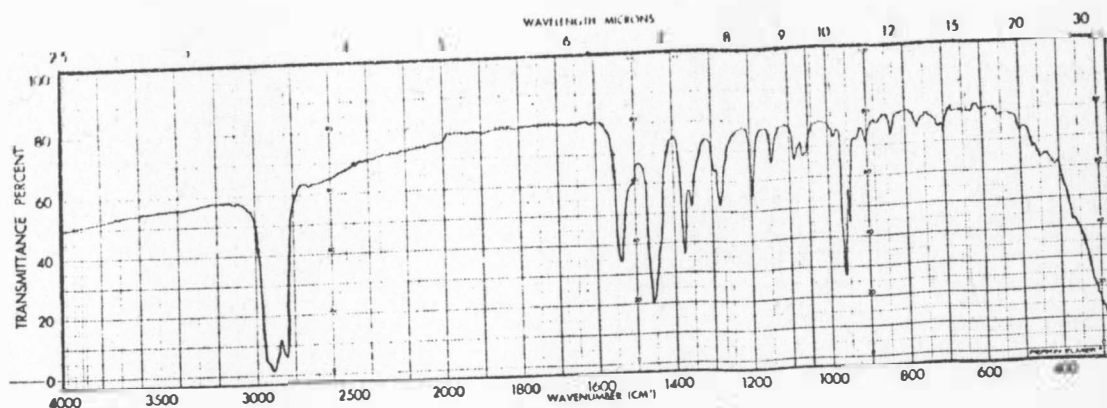


Figure 38. Di- $\mu$ -oxobis[oxo-N,N-diethyldithiocarbamato-molybdenum(V)],  $\text{Mo}_2\text{O}_4(\text{C}_5\text{H}_{10}\text{NS}_2)_2$ .