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MOLYBDENUM PHTHALOCYANINE COMPOUNDS

BY

ROBERT JOHN LOSINSKI

A thesis submitted
in partial fulfillment of the requirements for the
degree Master of Science, Major in
Chemistry, South Dakota
State University.

1971

MOLYBDENUM PHTHALOCYANINE COMPOUNDS

This thesis is approved as a creditable and independent investigation by a candidate for the degree Master of Science and is acceptable as 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.

Thesis Advisor Date

Head, Chemistry Department Date

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INTRODUCTION

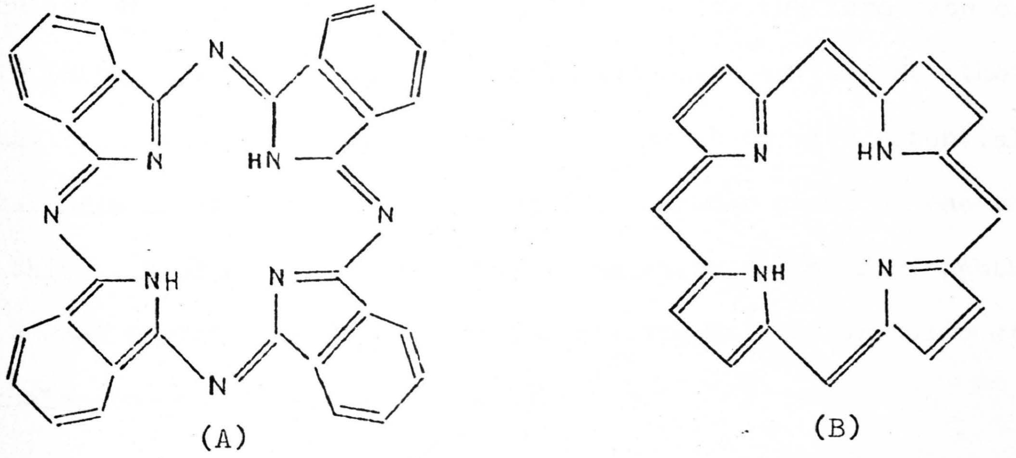
As part of an investigation into the chemistry of molybdenum underway at South Dakota State University it became necessary to investigate the possible existence of the linear dioxomolybdenum (VI) (MoO_2^{2+}) moiety. In order to attain this goal, a planar quadradentate chelate of very limited flexibility was necessary. A chelate which satisfied this criterion was phthalocyanine. A literature search revealed no evidence of a molybdenum complex containing the linear dioxomolybdenum (VI) group. While molybdenum phthalocyanine complexes had been reported, chemical and physical evidence to substantiate the formulation was limited and in several instances was contradictory. Therefore it was decided to investigate the molybdenum phthalocyanine system in an attempt to resolve the conflicting reports.

Since molybdenum can exist in oxidation states from zero to plus six, this research project affords the opportunity to develop procedures for the preparation of a variety of phthalocyanine derivatives. The information attained from these studies also will provide a first step toward the ultimate goal of the isolation of molybdenum porphyrin compounds. This is possible since phthalocyanine is related to porphyrin, the fundamental nucleus of chlorophyll and hemoglobin, and in many instances metal phthalocyanine complexes have served as the basis for biological model system investigations.

HISTORICAL

A metal phthalocyanine was first discovered at Grangemouth, Scotland, in 1928. Inside an iron vessel used by a Scottish dyer for the preparation of a dye precursor, phthalimide, a dark blue compound containing iron was isolated. Later, the compound was identified as iron (II) phthalocyanine.[1] This discovery was followed by extensive investigation into the chemistry of phthalocyanine and its derivatives,[2,3] which are obtained by incorporating metal or metalloid ions into the phthalocyanine ring by replacement of the two central hydrogen atoms. This interest was due to the unique structure of the compound, its high thermal and chemical stability, and its relationship to porphyrin.

Linstead and his colleagues have shown that phthalocyanine (abbreviated Pc) possesses a ring system of four isoindole units linked by aza nitrogen atoms (Figure I-A).[3] A similar ring structure is possessed by the porphyrin derivatives (Figure I-B), which form the building units for many biologically important pigments, such as hemin and chlorophyll a.[4]



(A) (B)

Figure I. Structures of Phthalocyanine (A) and Porphyrin (B).

Metal complexes of phthalocyanine may be prepared by various methods,[2] the most general procedures are: (1) the reaction of o-phthalonitrile with a metal or metal salt (metal = M); (2) the reaction of phthalic anhydride, phthalic acid, or phthalamide with urea, a metal or metal salt, and, in some cases, a catalyst; (3) the reaction of o-cyanobenzamide with a metal or metal salt; and (4) the reaction of phthalocyanine or labile metal phthalocyanine with a metal ion thus forming a more stable complex. These reactions have been summarized in Figure II. While not as commonly used as the above methods, phthalocyanines have also been made from mixtures of phthalimide and urea with a metal or metal salt, and from monoiminophthalimide or diiminophthalimide (also called 1,3-diiminoisoindoline) with a metal or metal salt, reactions E and F respectively in Figure II.

A knowledge of the mode of formation of phthalocyanine may be useful, since such information may lead to a fuller understanding of the reaction pathway by which porphyrins are synthesized in nature. Ring formation may occur by the condensation of four isoindole units symmetrically into one ring, as shown in Scheme I for the formation of copper (II) phthalocyanine.[5] This mechanism was based on the fact that metal phthalocyanines were prepared by methods starting with potential reaction intermediates (Figure II, A, E, and F). Further proof of the validity of this mechanism is the fact that phthalimide and monoiminophthalimide have been isolated from the reaction mixture in the formation of phthalocyanines (Scheme I, B and C).

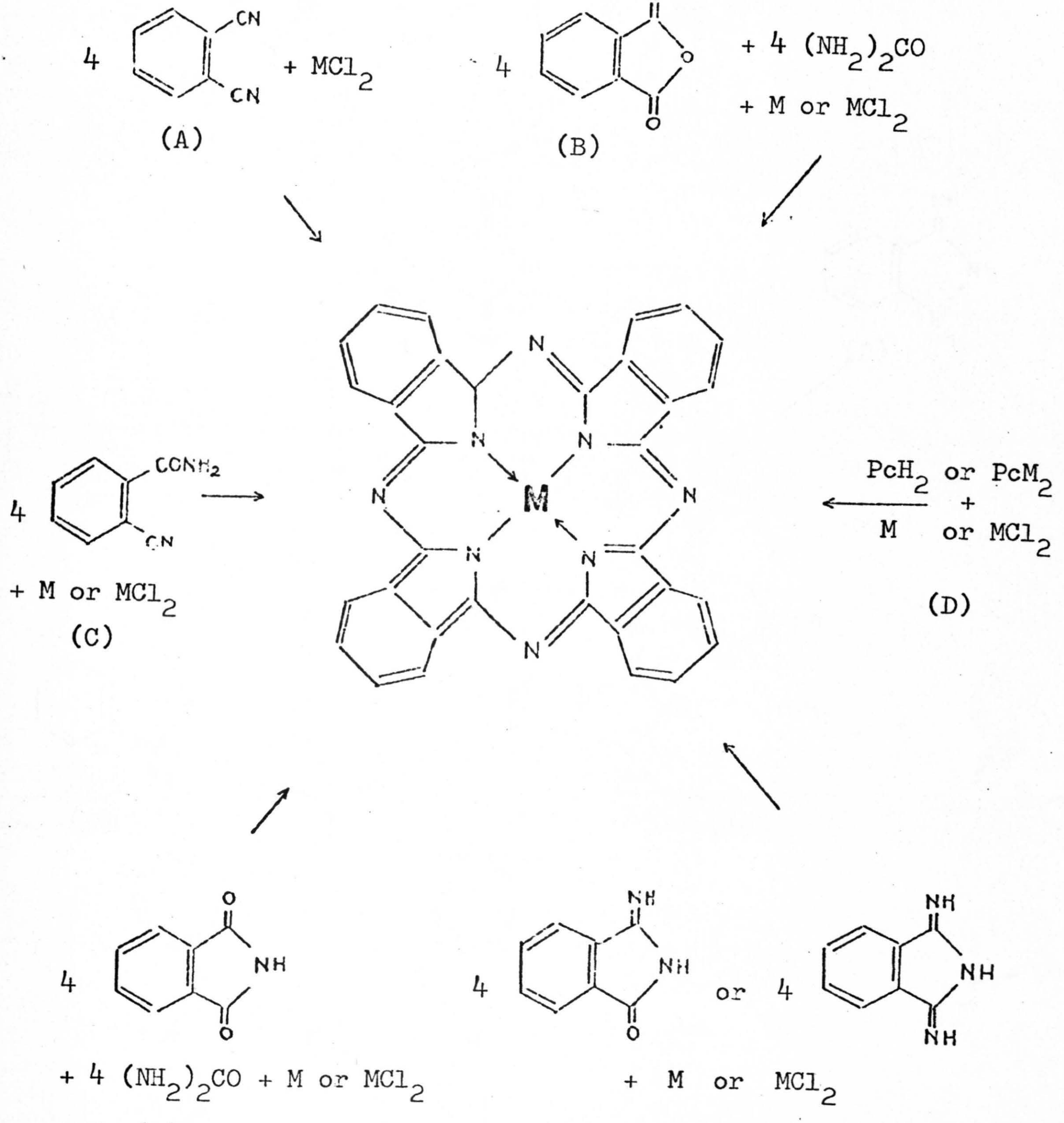
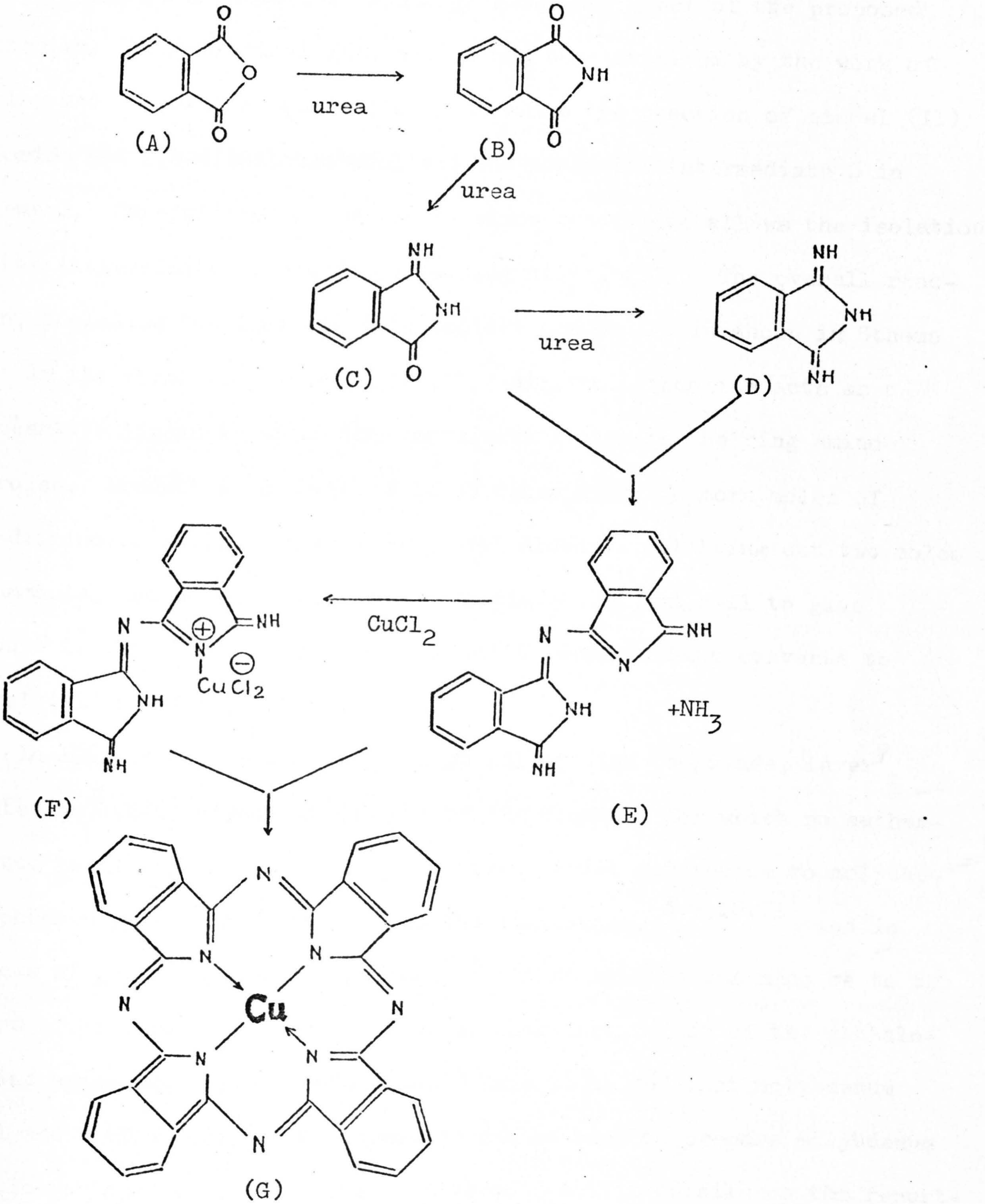


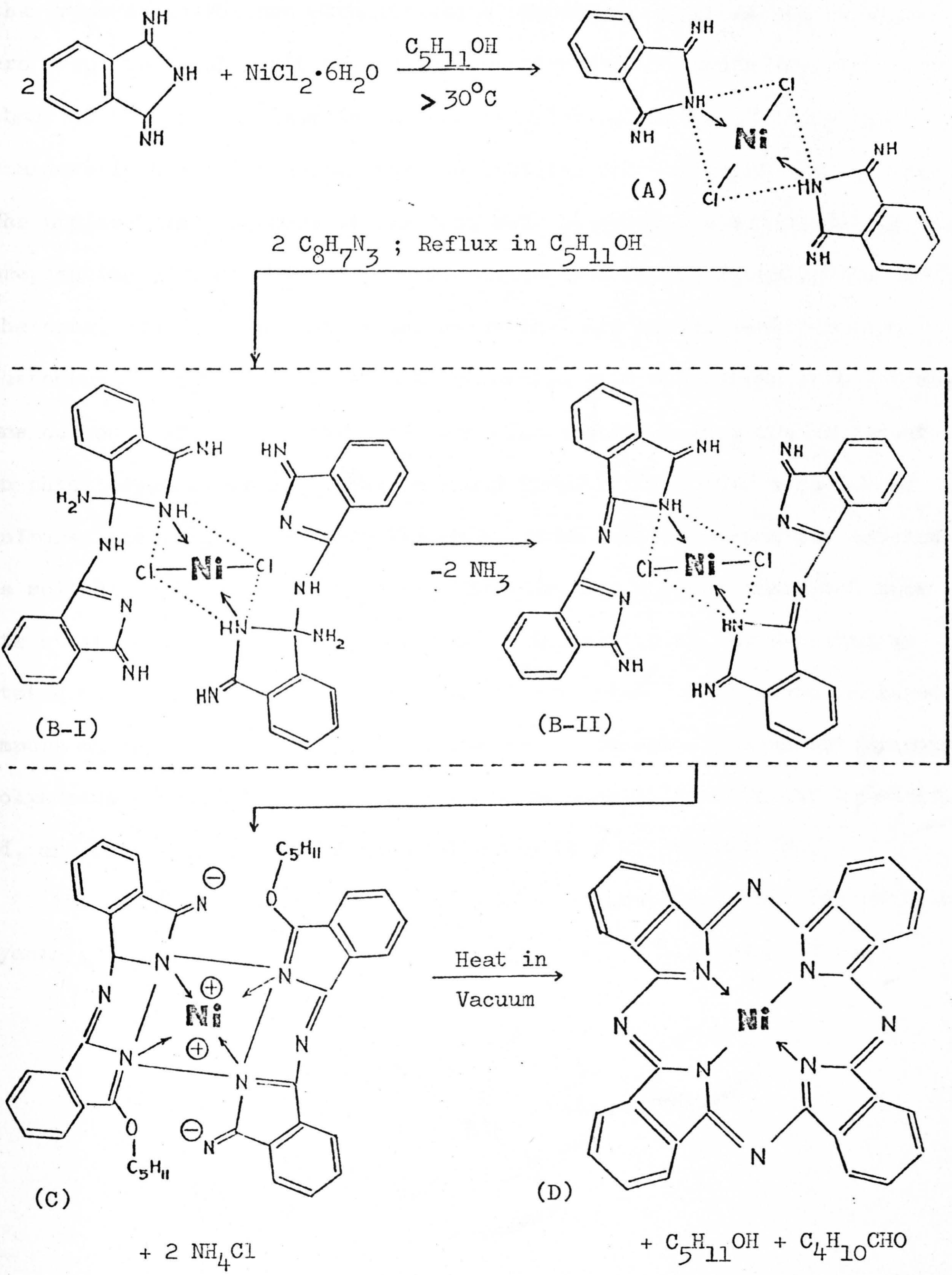
Figure II. Six Methods of Preparing Metal Phthalocyanine Complexes. M is any metal that will coordinate with the ring.



Scheme I. Formation of Copper (II) Phthalocyanine.

While the mechanism may be correct, the isolation of the intermediate complex (Scheme I-F) would give further proof of the proposed mechanism. This critical information has been supplied by the work of Hurley and co-workers[6] who followed stepwise the reaction of nickel (II) chloride and 1,3-diiminoisoindoline, the potential intermediate D in Scheme I. Careful control of the reaction conditions allows the isolation of the intermediate compounds containing nickel (II). The overall reaction, including the isolated intermediate compounds, is shown in Scheme II. In the formation of product A, 1,3-diiminoisoindoline acts as a monodentate ligand in which the coordinating atom is the ring amino nitrogen. Product A is proposed to condense with two more moles of 1,3-diiminoisoindoline in refluxing amyl alcohol, splitting out two moles of ammonia, and passing through intermediates B-I and B-II to give product C. The latter compound, product C, upon heating converts to nickel (II) phthalocyanine.

In 1965 in a review article on phthalocyanine compounds, Lever[7] pointed out that molybdenum was one of the elements for which no authenticated phthalocyanine compound was known. Brief references to molybdenum phthalocyanine have appeared in the literature,[8,9,10,11] and in reviews of phthalocyanine compounds,[2,3] but no mention was made as to the method of preparation, purification, or characterization of the phthalocyanine compound. Patent references[12] have indicated that molybdenum metal and various molybdenum compounds can be used to prepare molybdenum phthalocyanines, but these patents give no specific details on the reported compounds. To further illustrate the lack of definitive evidence for



Scheme II. Formation of Nickel (II) Phthalocyanine.

the proposed molybdenum phthalocyanine compounds, Linstead and co-workers[8] reported that positive indications of a phthalocyanine complex were observed when cyanobenzamide was reacted with molybdenum. There was no characterization of the physical and chemical properties of the compound. The preparation procedure of Linstead and co-workers[8] was utilized in the preparation of a molybdenum phthalocyanine used in the investigation of the catalysis of chemiluminescent oxidation[9] and in the rectification phenomena of phthalocyanines.[11] A tetrasulfonated molybdenum phthalocyanine compound of unknown character was also mentioned in a French patent on phthalocyanine dyes.[10] Shurvell and Pinzuti[13] reported a number of infrared spectrograms of metallic phthalocyanines, including one labeled as molybdenum (II) phthalocyanine. However, the authors indicated that its spectrum was poorly resolved "due to impurities in the compound as stated by the manufacturor". It has been reported[12] that Sharp isolated impure oxygen bridged compounds analysing for dioxomolybdenum and hydroxomolybdenum phthalocyanines. However, these compounds could not be purified, and there was no indication of their method of preparation.

The first fully characterized complex was oxomolybdenum (IV) phthalocyanine,[12] ($MoOC_{32}H_{16}N_8$) as shown in Figure III. This compound was

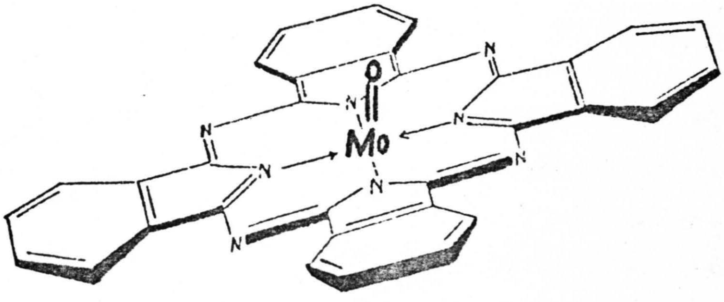


Figure III. Oxomolybdenum (IV) Phthalocyanine.

prepared by the reaction of molybdenum dioxydichloride with phthalonitrile and urea in N,N-dimethylformamide (DMF) under a nitrogen atmosphere. The same product was obtained by the reaction of molybdenum dioxydichloride with phthalonitrile in DMF under an argon atmosphere, and by the reaction of molybdenum tetrachloride with phthalonitrile and urea in DMF under an argon atmosphere. It was mentioned that a variety of molybdenum phthalocyanine compounds were noted as impurities, which the authors[12] attributed to the many possible oxidation states of molybdenum. Another characterized compound of molybdenum phthalocyanine was reported by Buslaev and co-workers.[14] These authors reported the preparation and characterization of molybdenum (II) phthalocyanine by the reaction of molybdenum pentachloride with o-phthalonitrile in quinoline under an atmosphere of argon. However, the infrared spectrogram was different from that reported by Shurvell and Pinzuti for the same compound.

While our investigation was underway, three tetraphenylporphine molybdenum complexes were reported[15] (Figures IV and V). This structure

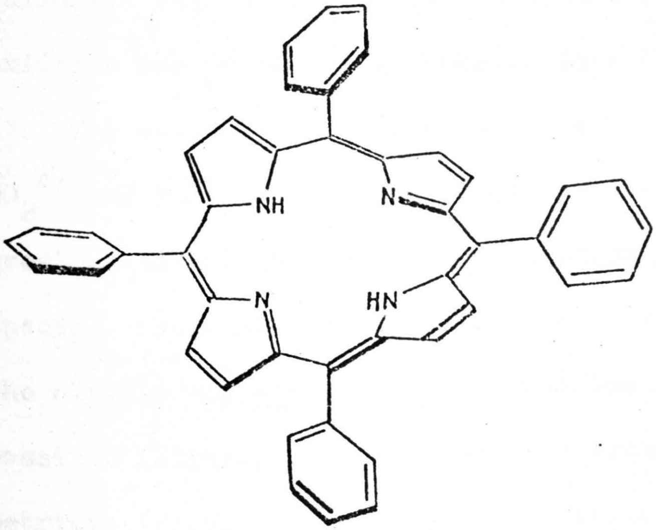


Figure IV. Tetraphenylporphine.

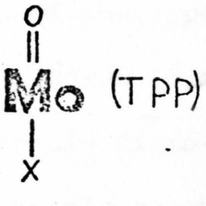


Figure V. Derivatives of Tetraphenylporphine (TPP). X is Hydroxy-, Chloro-, or Perhydroxy- Ligands.

closely resembles that of the porphyrins (Figure I-B). The first compound, oxohydroxomolybdenum (V) tetraphenylporphine, was prepared by refluxing a mixture of tetraphenylporphine with molybdenum hexacarbonyl in decalin under a nitrogen atmosphere. The second compound, oxochloromolybdenum (V) tetraphenylporphine hydrochloride, was prepared by stirring a chloroform solution of oxohydroxomolybdenum (V) tetraphenylporphine with concentrated hydrochloric acid. The third compound, oxoperhydroxomolybdenum (V) tetraphenylporphine, was prepared by dissolving oxochloromolybdenum (V) tetraphenylporphine hydrochloride in benzene and chromatographing the benzene solution on a column packed with activated alumina.

Recently, Arzoumanidis and O'Connell[16] reported the preparation of a substituted dioxomolybdenum (VI) phthalocyanine compound which was used in an investigation on the electrocatalytic oxidation of D-glucose. The compound was formulated as (MoO_2Pc4S^{4-}) with 4S referring to four sulfonate anions (SO_3^-), but no preparation procedure or experimental exidence was presented to substantiate this formulation.

The evidence for the presence of a metal-oxygen bond of the types MO_2^{n+} and MO^{n+} (n is the oxidation state of the moiety) is based to a great extent on the infrared absorption of the moiety. For the dioxo-species, the number of infrared active stretching modes depends on whether the oxygens are _cis_ or _trans_. The bent or _cis_ configuration has two possible infrared active modes: the symmetrical (Figure VI-A) and asymmetrical (Figure VI-B) stretching vibrations, which are infrared active since both change the dipole moment of the moiety. The observed

Symmetrical
(A)

Asymmetrical
(B)

Figure VI. *Cis* Metal-Oxygen Infrared Active Modes. M is any metal which forms a dioxo- species.

frequencies for the *cis* dioxo- complexes of various compounds containing Mo, W, and V were found in the range from 876 to 967 cm^{-1} for the symmetrical absorption and from 813 to 922 cm^{-1} for the asymmetrical absorption.[17] The linear or *trans* configuration also has two possible stretching modes: the symmetrical vibration (Figure VII-A), which is infrared inactive because there is no change in the dipole moment of the moiety, and the asymmetrical stretching vibration (Figure VII-B), which is infrared active since there is a change in the dipole moment of the moiety. The observed asymmetrical stretching frequencies for *trans* dioxo- complexes of various compounds containing rhenium were found in

Symmetrical
(A)

Asymmetrical
(B)

Figure VII. *Trans* Metal-Oxygen Stretching Modes. The symmetrical mode is infrared inactive and the asymmetrical mode is infrared active. M is any metal which forms a dioxo- species.

the range from 768 to 824 cm^{-1} [17,18,19] and those containing osmium in the range from 790 to 883 cm^{-1}.[19,20] The terminal metal-oxygen species, MO^{n+}, would possess infrared stretching frequencies for the multiple bonds that are infrared active because there is a change in dipole moment of the moiety. The observed frequencies were found in the range from 850 to 1020 cm^{-1}.[19,21]

Predictions about the stereochemistry of the MO_2^{n+} moiety can be based upon the electronic configuration of the central metal atom. It has been reported[17,22] that d^o configurations have cis rather than trans arrangements of oxygen atoms for the elements in groups VB, VIB, VIIB, and VIII. Thus, the higher oxidation states of these elements would possess the cis configuration, and the lower oxidation states would possess the trans configuration. These views are substantiated by the X-ray crystal structure of compounds containing the $(OsO_2)^{2+}$, $(ReO_2)^+$, and $(VO_2)^{1-}$ [17,22] groups. The cis and trans predictions are based on the following consideration. It is assumed that the s and p orbitals of the metal do not affect the symmetry of the metal-ligand complex (on cartesian axis, used to define metal-ligand positions), therefore the $p_\pi - d_\pi$ orbital overlap (p orbitals of oxygen π- bonding with d orbitals of the metal) is the only overlap to be considered. In a cis configuration for a d^o compound, the strong π- donating oxygen ligands would have exclusive use of one t_{2g} orbital each, and share a third orbital since there are no non-bonding metal electrons. For example, the oxygen ligand along the z axis would π- bond to the d_{xz} orbital of the metal, and the oxygen ligand along the y axis would π- bond to the d_{yz} orbital of the metal. This formation results in a *cis* configuration since there are no metal electrons occupying the non-bonding metal d orbital, d_{xy}, thus allowing this orbital to be shared between the two *cis* oxygen ligands. This interaction of metal and ligand orbitals is not allowed in the *trans* configuration. This *cis* dioxo- complex would then possess multiple bond character for d^o complexes, such as Mo^{VI}, W^{VI}, and V^V, which would result in higher frequencies for the symmetrical and asymmetrical infrared absorptions.[17] In the *trans* dioxo- complex, such as the OsO_2^{2+} moiety in $K_2[OsO_2(OH)_4]$, the two oxygen ligands would share two metal d orbitals, the d_{xy} and d_{yz}. The third orbital, d_{xz}, which is shared by the two oxygen ligands in the *cis* configuration, would be occupied by the electron pair of the d^2 complex. Thus, the dioxo- complex would possess the *trans* configuration, which would offer the greatest amount of stability.

The infrared frequencies in Table I clearly indicate that the data obtained from the infrared spectra is in agreement with the theoretical predictions. According to the authors,[17] these bonds have more multiple character, hence give higher frequencies than those expected for double bond character.

Although multiple bonds from terminal oxygen to molybdenum absorb in the range from 850 to 1000 cm^{-1},[17] the actual value depends on the oxidation state of molybdenum and on the other ligands present.[21] A lowering of molybdenum-oxygen stretching frequencies may be correlated with an increasing number of π- bonding ligands; for example, in the molybdenum (VI) species, such as MoO^{4+}, MoO_2^{2+}, and MoO_3, the asymmetric stretching frequencies occur at 997, 914, and 839 cm^{-1} respectively.[21]

Table I. Infrared Frequencies of Cis and Trans Dioxo- Compounds of Mo, W, V, Re, and Os.

	Compound	Ref.	ν^{s} (MO_2)	ν^{as} (MO_2)
CIS	$K_2[MoO_2F_4]\cdot H_2O$	17	960 vs	917 vs
	$(NH_4)_3[MoO_2F_5]$	17	953 vs	887 vs
	$Na_2|MoO_2Cl_4|$	17	960 m	992 s
	$K_2[WO_2F_4]\cdot H_2O$	17	959 vs	901 vs
	$Cs_2[WO_2Cl_4]$	17	937 s	891 vs
	$K_3[VO_2F_4]$	17	920 vs	883 vs
	$(NH_4)_3[VO_2(C_2O_4)_2]$	17	907 s	879 vs
TRANS	$K_3[ReO_2(CN)_4]$	17	-----	768 vs
	$[RePy_4O_2]Cl\cdot 2H_2O$ *	18	-----	812 vs
	$[Re(en)_2O_2]Cl\cdot 2H_2O$ *	18	-----	814 vs
	$K_2[OsO_2(OH)_2(NO_2)_2]$	20	-----	840 vs
	$[OsO_2(NH_3)_4]Cl_2$	20	-----	808 vs
	$K_2[OsO_2(OH)_4]$	20	-----	790 vs

* Py is pyridine and en is ethylenediamine.

As the amount of π - bonding increases from MoO^{4+} to MoO_3, the stretching frequency decreases. The oxidation state of the metal has little effect on the molybdenum-oxygen asymmetric stretching frequency, such as $MoOCl_3^{1-}$, $MoOCl_4^{1-}$, and $MoOCl_4$, which absorb at 1020, 1000, and 997 cm^{-1} respectively.[21] However, the frequency decreases with increased negative charge on the complex because the metal is a poorer π- bond acceptor.

In addition to the information obtained from the metal-oxygen stretching modes, more information about the nature of the complex can be obtained from the infrared modes attributed to the phthalocyanine molecule. Due to the complex structure of phthalocyanines, theoretical infrared absorptions assigned to the metal-ligand vibrations are difficult, but a comparison between metal-free phthalocyanine and its metal derivatives is possible. Metal-free phthalocyanine shows two strong absorptions at 715 and 999 cm^{-1}, due to N-H out-of-plane deformation and in-plane deformation respectively.[23] These absorptions are absent in metal phthalocyanine complexes due to the loss of the two hydrogens attached to the isoindoline ring nitrogens. A characteristic infrared absorption peak of metal derivatives of phthalocyanines is dependent on the metal ion used and appears in the range from 888 to 919 cm^{-1}.[23] This frequency is assigned to the bonding between the metal ion and the four surrounding isoindole nitrogens in the ring. Substitution of a divalent metal ion, versus a tri- or tetra- valent ion, does not significantly change the infrared-active frequencies of the phthalocyanine ring system.

EXPERIMENTAL

Infrared Spectra

The spectra of all complexes were obtained as potassium bromide wafers in the region from 250 to 4000 cm^{-1}, or nujol mulls in the region from 400 to 4000 cm^{-1}. The instrument used was a model 521 Perkin-Elmer Grating Spectrophotometer.

Ultraviolet-Visible Spectra

All ultraviolet-visible spectra were done on a Beckman DK-2A spectrophotometer.

Molybdenum Dioxide

Molybdenum dioxide was used as received from Climax Molybdenum Company.

Molybdenum Pentachloride

Molybdenum pentachloride was used as received from Climax Molybdenum Company.

Molybdenum Hexacarbonyl

Molybdenum hexacarbonyl was used as received from Climax Molybdenum Company.

Molybdenum Tetrachloride Dipyridine

Molybdenum tetrachloride dipyridine was used as received from Climax Molybdenum Company.

Molybdenum Dioxydichloride

Molybdenum dioxydichloride was prepared by the action of chlorine on anhydrous molybdenum dioxide at 375°C.[24]

Quinoline

Quinoline was obtained from Eastman Organic Chemicals and purified by distillation at 156°C and 15 mm pressure. It was further distilled under nitrogen directly into the reaction vessel as needed.

Urea

Urea was used as received from Fisher Scientific Company.

o-Phthalonitrile

o-phthalonitrile was obtained from Eastman Organic Chemicals and recrystalized from benzene; melting point 140-140.5°C. Literature melting point is 141°C.[25]

1,2,4 - Trichlorobenzene

1,2,4-trichlorobenzene was used as received from Eastman Organic Chemicals.

Nitrogen Gas

Nitrogen gas was obtained from Linde and the oxygen impurity removed by two different methods: (1) by bubbling through alkaline pyrogallol;[26] (2) by passing through BASF catalyst.[27]

Pyridine

Pyridine was obtained from Fisher Scientific Company, previously dried over potassium hydroxide for 12 hours and then distilled, with the fraction boiling at 113°C and atmospheric pressure being used.

BASF Catalyst (R3-11)

BASF catalyst was obtained from BASF Corporation and generated by passing hydrogen over it at 175°C.[27]

N,N-Dimethylformamide

N,N-dimethylformamide was obtained from Fisher Scientific Company. It was freshly distilled with the fraction boiling at 150-151°C and atmospheric pressure being used.

Ceric Sulfate

Ceric sulfate was used as received from Fisher Scientific Company.

Analysis

Some carbon-hydrogen-nitrogen analysis were obtained from Galbraith Laboratories, Inc., while the remaining carbon-hydrogen and molybdenum analysis were obtained from analysts at South Dakota State University.

MOLYBDENUM DETERMINATION

A 0.2 to 0.3 g sample of the compound to be analysed was dissolved in 15-20 ml concentrated sulfuric acid and oxidized by the continued addition of 20 ml portions of concentrated nitric acid. The solution was heated gently during the addition of the nitric acid. Nitric acid is added until the solution remained clear. The excess nitric acid was then removed by evaporation of the solution to near dryness on a hot plate. To insure removal of nitric acid, 5-10 ml sulfuric acid was added to the near dry residue a minimum of six times with the solution being evaporated to near dryness after each addition. The appearance of a blue color during the evaporation process when nearing dryness indicates the presence of molybdenum (V) which was then oxidized by the addition of a few more drops of concentrated nitric acid (USE CAUTION). The solution was then boiled down in the presence of concentrated sulfuric acid as before. After the oxidation process was complete the residue was dissolved in 100 ml of 3% aqueous sulfuric acid.

In a receiving flask attached to the Jones Reducing Column[28] was placed an excess amount (30 ml was used) of 10% iron (III) alum and 4 ml syrupy phosphoric acid. The solution of molybdenum (VI) was reduced to molybdenum (III) by passing the acidified solution through a column of amalgamated zinc (Jones Reducing Column). Since molybdenum (III) is sensitive to oxygen, the reduced molybdenum (III) solution was added directly to the iron (III) solution in the receiving flask via a glass tube, attached to the reducing column, and extending beneath the surface of the iron (III) solution. To facilitate passage of the solution through the reducing column into the iron (III) solution a slight vacuum was applied to the system. In the iron (III) solution, molybdenum (III) was oxidized to molybdenum (VI) as an equivalent amount of iron (III) was reduced to iron (II). Titration of the reduced iron immediately with standard ceric sulfate solution in the presence of ferroin indicator (o-phenanthroline ferrous sulfate complex) gave the amount of molybdenum reduced by the amalgamated zinc. The reactions are shown in Scheme III, and the percent molybdenum was calculated as indicated.

$$\mathrm{Mo}^{\mathrm{VI}} \xrightarrow{\mathrm{Zn(Hg)}} \mathrm{Mo}^{\mathrm{III}} \xrightarrow{(\text{Excess Fe}^{\mathrm{III}}\text{Alum})} \mathrm{Mo}^{\mathrm{VI}} + 3\ \mathrm{Fe}^{\mathrm{II}}$$

$$3\ \mathrm{Fe}^{\mathrm{II}} \xrightarrow{(\text{Titrated with Ce}^{\mathrm{IV}}\text{ Standard})} 3\ \mathrm{Fe}^{\mathrm{III}} + 3\ \mathrm{Ce}^{\mathrm{III}}$$

$$\text{Equivalence Ce}^{\mathrm{IV}}\text{ Titrant Used} \div 3 = \text{Equivalence Mo}^{\mathrm{III}}$$

$$\text{Equivalence Mo}^{\mathrm{III}} \times 95.96\text{ g Mo Per Equivalent} = \#\text{ g Mo Present}$$

Scheme III. Reactions and Calculation for Molybdenum Determination.

Determination of the Molybdenum Oxidation State

The procedure used for rhenium oxidation state determination[29] can also be used for molybdenum. A 20-30 mg sample of the molybdenum compound was dissolved in 5-8 ml concentrated sulfuric acid. Then a known excess (30 ml was used) of standard ceric sulfate solution was added at a very slow rate to avoid precipitation of the molybdenum complex. After the addition of the ceric sulfate, the solution was warmed on a hot water bath to insure oxidation of the complex. After cooling, a known excess (30 ml was used) of standard iron (II) sulfate solution was added to convert remaining cerium (IV) to cerium (III). The amount of unreacted iron (II) sulfate was then determined by titration with standard ceric sulfate in the presence of ferroin indicator. The oxidation of molybdenum in the compound was then calculated, first by finding the equivalence of molybdenum in the compound, and then dividing this by the grams of molybdenum previously found. This value, which was the change in oxidation state was subtracted from the highest oxidation state possible for molybdenum, molybdenum (VI), giving the original oxidation value for molybdenum in the compound, as indicated in Scheme IV.

NOTE: Pure iron wire dissolved in concentrated hydrochloric acid will suffice in place of iron (II) sulfate standard and is prepared as needed. Care should be taken that the solution does not remain dark after addition of ceric sulfate standard and warmed on the hot water bath. The addition of ceric sulfate solution should be done dropwise at a rate of 3-5 drops per 30 seconds with constant swirling for the first 5 ml, and then 3-5 ml per 5 minutes.

$$\begin{tikzcd}[column sep=large]
\mathrm{Mo}^{?} + \mathrm{Ce}^{IV} \\ \text{(Excess Ce}^{IV}\text{ Standard)} \arrow[rr] & & \mathrm{Mo}^{VI} + \mathrm{Ce}^{III} + \mathrm{Ce}^{IV} \arrow[dll, "\text{(Excess Fe}^{II}\text{ Standard)}"'] \\
\mathrm{Ce}^{III} + \mathrm{Fe}^{III} + \mathrm{Fe}^{II} \arrow[rr, "\text{(Titrated with Ce}^{IV}\text{)}", "\text{(Standard)}"'] & & \mathrm{Fe}^{III} + \mathrm{Ce}^{III}
\end{tikzcd}$$

$$\frac{\text{Equivalent of Ce}^{IV}_{\text{(Initial)}} - \text{Equivalent Fe}^{II}_{\text{(Titrant)}}}{\text{g Molybdenum in the Compound}} \quad \text{EQUALS} \rightarrow$$

CHANGE IN OXIDATION STATE OF THE MOYLBDENUM

(THUS)

$$\begin{array}{c}\text{Highest Oxidation}\\ \text{State of Molybdenum (Mo}^{VI}\text{)}\end{array} - \begin{array}{c}\text{Change in Oxidation}\\ \text{State - Found}\end{array} = \begin{array}{l}\text{Original}\\ \text{Oxidation}\\ \text{State of}\\ \text{Molybdenum}\end{array}$$

Scheme IV. Reactions and Calculation for Oxidation State of Molybdenum.

I. 1,3 - Diiminoisoindoline ($C_8H_7N_3$).

The reaction was carried out using the procedure reported by Kenney and co-workers.[30] Ammonia gas was slowly bubbled into a stirring mixture of 160 g (1.25 moles) of o-phthalonitrile and 3 g (0.055 moles) of sodium methoxide dissolved in 800 ml of methanol over a 40 minute period. The mixture was then rapidly brought to reflux temperature and maintained at this temperature for 3.5 hours with continued stirring and changes from light tan, to green, to dark brown occurred, with the formation of greenish-blue crystals. The product was isolated by filtration, washed with methanol and ether, and dried. The yield was 18.7 g (10 %) of greenish-blue crystals. Further cooling of the filtrate to 0°C yielded 28.7 g (16 %) of yellowish crystals. After some evaporation of the mother liquor, and the addition of ether, another crop of 45.5 g (26 %) was obtained, giving a total of 74.2 g (52 %). Recrystalization of the product from methanol-ether (charcoal) gave bone white crystals. Melting point; 135-145° turning green, decomposition at 194-195°C. Literature is 196° C decomposing.[31]

Analysis: Calculated for $C_8H_7N_3$: %C, 66.19; %H, 4.86; %N, 28.95

Found : %C, 66.70; %H, 4.80; %N, 28.42

The infrared spectra are reported in Tables V and VI of the appendix.

GENERAL REACTION PROCEDURE

In procedures II-B, E through H, III and IV, nitrogen was deoxygenated with BASF catalyst.[27] In procedures II-A, C and D, nitrogen was deoxygenated using alkaline pyrogallol.[26] The set-up illustrated in Figure VIII was used for the reactions which follow unless otherwise stated. The entire system was first purged with and then kept under a dry, deoxygenated nitrogen atmosphere. The nitrogen was bubbled through the solvent in flask A, passed through flask B and then bubbled through flow meter C. The solvent used in the flow meter was the same as the solvent used for the reaction. The solvent for the reaction was distilled as required from flask A into flask B. Flask B, containing the reaction mixtures, was equipped with a condensor for refluxing. After each reaction the system was allowed to cool to room temperature before being opened.

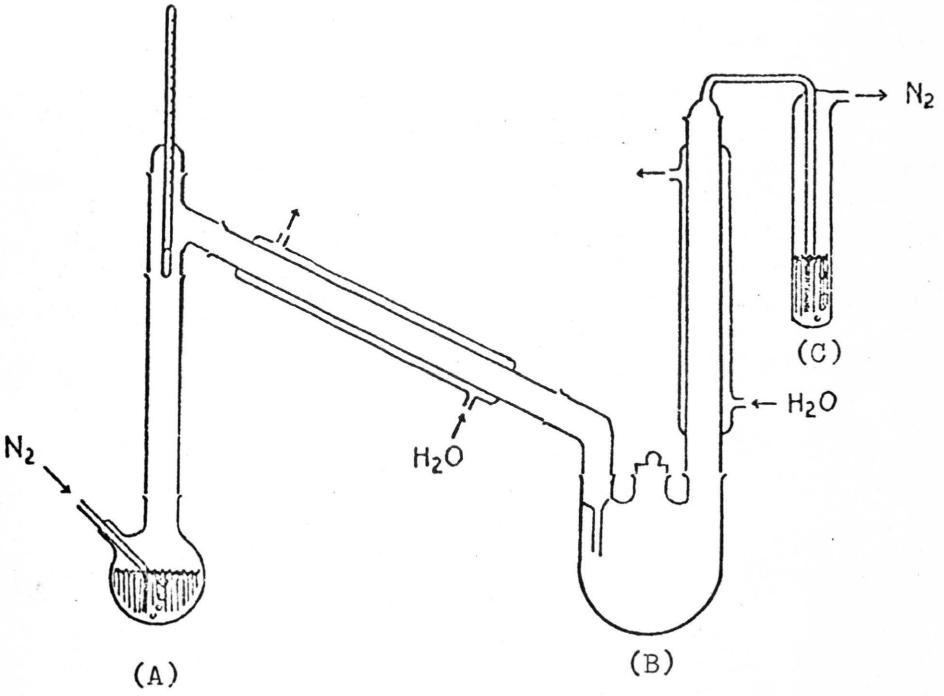


Figure VIII. General Reaction Set-Up.

II. Oxomolybdenum (IV) Phthalocyanine ($MoOC_{32}H_{16}N_8$).

A. Preparation from o-Phthalonitrile, Urea, and Molybdenum Dioxydichloride.

Oxomolybdenum (IV) phthalocyanine was prepared using the procedure reported by Hill and Norgett.[12] A mixture of 10 g (78 mmole) o-phthalonitrile and 24 g (400 mmole) urea was added to a solution of 3.8 g (18.2 mmole) molybdenum dioxydichloride in 200 ml of DMF distilled under a nitrogen atmosphere. The solution was refluxed under nitrogen for one hour, during which a series of color changes from clear, to yellow, to blue occured. The mixture was cooled to room temperature before it was opened to the atmosphere. The dark blue crystalline product was isolated by filtration, washed with 50 ml water and then 50 ml of methanol, and twice precipitated with water from concentrated sulfuric acid. The collected product was then sublimed in a nitrogen purged pyrex tube at 400°C and 2 mm pressure. The yield was 0.54 g (4.8 %) of blue crystals. The analytical data are summarized in Table II and solubility characteristics are reported in Table III. The infrared spectra are reported in Tables VII and VIII, and the ultraviolet-visible spectrum is reported in Table XIV, of the appendix.

B. Preparation from o-Phthalonitrile and Molybdenum Pentachloride.

This reaction was carried out using the procedure reported by Buslaev and co-workers,[14] except that nitrogen was used in place of argon. In a nitrogen atmosphere a mixture of 33.3 g (260 mmole) o-phthalonitrile and 16 g (58.3 mmole) molybdenum pentachloride was placed in a 250 ml flask. To this was added 200 ml quinoline, previously distilled under a nitrogen atmosphere. The mixture was maintained at 220°C for four hours with continuous stirring, and then cooled to room temperature before it was opened to the atmosphere. The only change in color was from colorless to dark blue. The dark blue crystalline product was isolated by filtration, washed five times with 50 ml portions of acetone and air dried. The yield was 29.6 g (92 %) of blue crystals. The analytical data are summarized in Table II and the solubility characteristics are reported in Table III. The infrared and ultraviolet-visible spectra are identical to that reported for oxomolybdenum (IV) phthalocyanine (Preparation II-A).

C. Preparation from o-Phthalonitrile, Urea, and Molybdenum Tetrachloride Dipyridine.

A mixture of 6 g (100 mmole) of urea, 5 g (39 mmole) o-phthalonitrile, and 3 g (7.6 mmole) molybdenum tetrachloride dipyridine was placed in flask B. About 100 ml DMF was distilled into flask B from flask A, the mixture refluxed for twenty hours, and then cooled to room temperature before opening to the atmosphere. The only change in color was from colorless to dark blue. The dark blue crystalline product was isolated by filtration, washed twice with 40 ml portions of DMF, and then dried in an abderhalden at 80°C and 5 mm pressure for 10 hours. The yield was 0.26 g (4.3 %) of blue crystals. The analytical data are summarized in Table II and the solubility characteristics are reported in Table III. The infrared and ultraviolet-visible spectra are identical to that reported for oxomolybdenum (IV) phthalocyanine (Preparation II-A).

D. Preparation from 1,3 - Diiminoisoindoline and Molybdenum Tetrachloride Dipyridine.

A mixture of 9 g (60 mmole) 1,3-diiminoisoindoline and 3 g (7.4 mmole) molybdenum tetrachloride dipyridine was placed in flask B. About 150 ml DMF was distilled into flask B from flask A, the mixture refluxed for 3 hours, and then cooled to room temperature before opened to the atmosphere. The only change in color was from colorless to dark blue. The dark blue product was isolated by filtration, washed with 100 ml acetone and then air dried. The yield was 2.25 g (48 %) of blue crystals. The reaction was found to proceed in the same manner when quinoline was used as the solvent. The analytical data are summarized in Table II and the solubility characteristics are reported in Table III. The infrared and ultraviolet-visible spectra are identical to that reported for oxomolybdenum (IV) phthalocyanine (Preparation II-A).

E. Preparation from 1,3 - Diiminoisoindoline and Molybdenum Trichloride Tripyridine.

A mixture of 1.1 g (2.6 mmole) molybdenum trichloride tripyridine* and 1.7 g (11.6 mmole) 1,3-diiminoisoindoline was placed into flask B. About 100 ml quinoline was distilled into flask B from flask A, the mixture was maintained at a constant temperature of 200°C for 3 hours with constant stirring, and then cooled to room temperature before opening to the atmosphere. The only change in color was from colorless to dark blue. The dark blue crystalline product was isolated by filtration, washed with 100 ml acetone and air dried. The yield was 1.54 g (99 %) of blue crystals. The analytical data are summarized in Table II and the solubility characteristics are reported in Table III. The infrared and ultraviolet-visible spectra are identical to that reported for oxomolybdenum (IV) phthalocyanine (Preparation II-A).

*The gift of this material from Mr. Richard Dendinger is appreciated.

F. Preparation from 1,3 - Diiminoisoindoline and Molybdenum Tetrachloride Dipyridine.

A mixture of 4.5 g (31 mmole) of 1,3-diiminoisoindoline and 1.5 g (3.78 mmole) molybdenum tetrachloride dipyridine was placed into flask B. About 75 ml of quinoline was distilled into flask B from flask A, the mixture was refluxed for 2.5 hours, and then cooled to room temperature before opening to the atmosphere. A series of color changes occurred from clear, to yellow, to green, to dark blue, and a dark blue crystalline product was isolated by filtration under a nitrogen atmosphere. The product was washed twice with 50 ml portions of dry diethyl ether (dried over sodium) and air dried. The yield was 2.05 g (94 %) of blue crystals. The analytical data are summarized in Table II and the solubility characteristics are reported in Table III. The infrared and ultraviolet-visible spectra are identical to that reported for oxomolybdenum (IV) phthalocyanine (Preparation II-A).

G. Preparation from 1,3 - Diiminoisoindoline and Molybdenum Dioxydichloride.

A mixture of 12 g (83 mmole) of 1,3-diiminoisoindoline and 3.7 g (17.2 mmole) molybdenum dioxydichloride was placed into flask B. About 75 ml quinoline was distilled into flask B from flask A, and the mixture refluxed for one hour, then cooled to room temperature before opening to the atmosphere. The only change in color was from colorless to dark blue. The dark blue crystalline product was isolated by filtration, washed twice with 50 ml portions of water and methanol, and then dried in an abderhalden at 100°C and 5 mm pressure for 12 hours. The yield was 9.03 g (84 %) of blue crystals. The analytical data are summarized in Table II and the solubility characteristics are reported in Table III. The infrared and ultraviolet-visible spectra are identical to that reported for oxomolybdenum (IV) phthalocyanine (Preparation II-A).

H. Preparation from 1,3 - Diiminoisoindoline and Molybdenum Pentachloride.

A mixture of 27 g (185 mmole) of 1,3-diiminoisoindoline and 11.2 g (41 mmole) molybdenum pentachloride was placed into flask B. About 75 ml of quinoline was distilled into flask B from flask A, the mixture refluxed for five hours, and then cooled to room temperature before opening to the atmosphere. The only change in color was from colorless to dark blue. The dark blue crystalline product was isolated by filtration, washed with 200 ml acetone and air dried. The yield was 25 g (98 %) of blue crystals. The analytical data are summarized in Table II and the solubility characteristics are reported in Table III. The infrared and ultraviolet-visible spectra are identical to that reported for oxomolybdenum (IV) phthalocyanine (Preparation II-A).

Table II. Analytical Data for Oxomolybdenum (IV) Phthalocyanine.

Sample	Oxidation Value	Molybdenum Per Cent	Carbon Per Cent	Hydrogen Per Cent
A	4.36	15.15	61.80	2.63
	4.18	15.23		
B	4.43	15.38	61.53	3.08
	4.36	15.31	61.72	2.78
	4.16	15.30		
C	4.22		61.45	3.08
D	3.79	15.10	61.81	3.03
	4.15	15.25	61.37	3.54
D*			61.75	2.94
			61.32	2.72
E	4.25		61.30	2.96
			61.44	3.42
F	3.85	15.15		
	3.62	15.31		
G		15.29		
		15.21		
		15.23		
H		15.43		
		15.36		
		15.38		

*Quinoline was used as the solvent.

The calculated value for $MoOC_{32}H_{16}N_8$: %Mo, 15.37; %C, 61.56; %H, 2.56

The theoretical oxidation state is four.

Table III. Solubilities of Oxomolybdenum (IV) Phthalocyanine.

Solvent	Hot	Cold
Chloronapthalene	SS	VSS
Quinoline	SS	VSS
Chloroform	NS	NS
Dichloromethane	NS	NS
Acetone	NS	NS
Ethanol	NS	NS
Pyridine	NS	NS
Benzene	NS	NS
Diethyl Ether	NS	NS
Chlorobenzene	SS	VSS
Dimethylsulfoxide	SS	VSS
Nitrobenzene	NS	NS
Phenol/Methanol (1:1)	NS	NS
Diglyme	NS	NS
Tetrahydrofuran	NS	NS
N,N-Dimethylformamide	SS	VSS
1,2,4-Trichlorobenzene	SS	VSS
Sulfuric Acid (Concentrated)	VS	VS

VS-Very Soluble
SS-Slightly Soluble
VSS-Very Slightly Soluble
NS-Not Soluble

III. Molybdenum (II) Phthalocyanine ($MoC_{32}H_{16}N_8$).

The entire reaction was carried out in a nitrogen atmosphere. A mixture of 3.3 g (22.7 mmole) of 1,3-diiminoisoindoline and 1.5 g (5.7 mmole) molybdenum hexacarbonyl was placed in a three neck flask, which had been previously flame dried. About 75 ml of distilled quinoline was added to the flask by means of a separatory funnel. The mixture was refluxed for 1.5 hours with constant stirring. During this time a series of color changes from colorless, to orange, to deep red occurred. The mixture was cooled to room temperature before being opened to the atmosphere. A deep red crystalline product was isolated by filtration, washed twice with 60 ml portions of dry diethyl ether (dried over sodium) and dried in an abderhalden at 100°C and 2 mm pressure for 12 hours. The yield was 2.6 g (75 %) of deep red crystals. When the reaction was carried out at approximately 160°C for one hour no product was obtained upon filtration and no further attempt was made to isolate a product.

Analysis: Calculated for $MoC_{32}H_{16}N_8$:

%Mo, 15.77; %C, 63.18; %H, 2.63; %N, 18.41

Found: %Mo, 15.55; %C, 64.18; %H, 2.90; %N, 18.72

The oxidation state of the compound was found to be in the range from 1.78 to 2.30, the theoretical is 2.0. The infrared spectra is shown in Tables IX and X and the ultraviolet-visible spectrum is shown in Table XV, of the appendix.

When a small amount of molybdenum (II) phthalocyanine was dissolved in concentrated sulfuric acid a blue-green solution was produced. The addition of water precipitated a fluffy blue solid which settled on standing. A dark blue-violet crystalline product was isolated by filtration, washed with water and dried in an abderhalden at 100°C and 2 mm pressure. The infrared spectrum of the collected product (Table XI) was identical to the spectrum of molybdenum (II) phthalocyanine, except for a medium-weak absorption at 1720 cm^{-1}.

IV. Oxocarbonylmolybdenum (IV) Phthalocyanine $[MoO(CO)C_{32}H_{16}N_8]$.

The entire reaction was carried out in a nitrogen atmosphere. A mixture of 2 g (7.6 mmole) of molybdenum hexacarbonyl, 4.9 g (38 mmole) o-phthalonitrile, and 2.28 g (38 mmole) urea was placed in a three neck flask, which was previously flame dried. About 75 ml of distilled quinoline was added to the flask by means of a separatory funnel. The mixture was maintained at a temperature of 160-170°C for 1 to 1.5 hours, with constant stirring. During this time a series of color changes occurred, from colorless, to orange, to deep red, to dark brown. The mixture was then cooled to room temperature before it was opened to the atmosphere. The dark brown crystalline product was isolated by filtration, washed twice with 60 ml portions of dry diethyl ether (dried over sodium) and dried in an abderhalden at 100°C and 2 mm pressure for 12 hours. The yield was 0.44 g (10 %) of dark brown crystals. When the reaction was carried out from 110-130°C, for the same length of time, no product was obtained upon filtration and no further attempt was made to isolate a product. When the temperature was increased to 180-200°C, for the same length of time, oxomolybdenum (IV) phthalocyanine was collected.

Analysis: Calculated for $MoO(CO)C_{32}H_{16}N_8$:

%Mo, 14.71; %C, 60.76; %H, 2.45; %N, 17.17

Found: %Mo, 14.68; %C, 60.25; %H, 2.81; %N, 18.76

The oxidation value of the compound was found to be in the range from 3.95 to 4.35, the theoretical is 4.0. The infrared spectra are reported in Tables XII and XIII, and the ultraviolet-visible spectrum is reported in Table XVI, of the appendix.

When a small amount of oxocarbonylmolybdenum (IV) phthalocyanine was dissolved in concentrated sulfuric acid a blue solution was produced. The addition of water precipitated a fluffy blue solid which settled on standing. A dark blue crystalline product was isolated by filtration, washed with water and dried in an abderhalden at 100°C and 2 mm pressure. The infrared spectrum of the collected product was identical to the spectrum of oxomolybdenum (IV) phthalocyanine.

V. Attempted Oxomolybdenum (IV) Phthalocyanine Reactions.

A. Attempted Preparation of a Pyridine Derivative of $MoOC_{32}H_{16}N_8$

Into a 250 ml flask was placed 0.1 g(.160 mmole) of oxomolybdenum (IV) phthalocyanine and 75 ml dry pyridine. The mixture was refluxed four hours and then cooled to room temperature. A dark blue crystalline product was isolated by filtration and dried in air. The infrared spectrum of the product indicated that only starting material was present.

B. Attempted Preparation of Dioxomolybdenum (IV) Phthalocyanine

Into 60 ml of chloronapthalene was placed 0.1 g(.160 mmole) of oxomolybdenum (IV) phthalocyanine. Dry air was bubbled through the mixture for four hours at room temperature. A dark blue crystalline product was isolated by filtration, washed with acetone, and air dried. The infrared spectrum was identical to that of the starting material. Air was passed through the mixture for 18 hours, but there was no change in the infrared spectrum of the isolated product. The temperature was then increased, first to 50°C with a reaction time of 3.5 hours and then for 6 hours with continued bubbling of air through the solution. There was no change in the infrared spectrum of the isolated product. With a reaction time of 6 hours and a temperature above 80°C in the presence of a stream of air, decomposition occurred. The resultant product gave a tarry appearance, and an infrared spectrum of the product showed very broad and weak absorptions, indicating a break down of starting material.

C. Attempted Preparation of a Sulfonated Derivative of $MoOC_{32}H_{16}N_8$

Into a 250 ml flask was placed 143.7 g (75 ml) of chlorosulfonic acid and 3.3 g (5.3 mmole) oxomolybdenum (IV) phthalocyanine was added slowly with stirring. The blue solution was maintained at a temperature of 145°C for 3 hours and then cooled to room temperature. The solution was then added dropwise to one liter of water at 0°C, with a bluish-green product precipitating. After standing 12 hours, the mixture was decanted and the product isolated by filtration and washed with water. The infrared spectrum indicated that a reaction had taken place, as evidenced by a strong broad absorption in the range from 1150 to 1250 cm^{-1}, which is indicative of a sulfate group, and a strong absorption in the range from 875 to 900 cm^{-1}, indicative of a molybdenum-oxygen absorption. Qualitative analysis gave evidence of the presence of molybdenum and sulfate groups present in the collected product. The reaction was also carried out using 2 g (3.2 mmole) of oxomolybdenum (IV) phthalocyanine and 20 ml of chlorosulfonic acid. The solution was warmed to 45° C and immediately added dropwise to 500 ml of water at 0°C.

The results of the collected product were identical to that previously found.

D. Attempted Replacement Reaction of the Lithium Portion of Dilithium Phthalocyanine with Molybdenum

Into a 250 ml flask was placed 1 g (2.4 mmole) of molybdenum tetrachloride dipyridine and 1.85 g (3.53 mmole) of dilithium phthalocyanine. To this was added 175 ml of freshly distilled DMF. The solution was refluxed 12 hours and then cooled to room temperature. A blue crystalline product was isolated by filtration, washed with 100 ml portions of hot water and ethanol and air dried. The blue product was dissolved in concentrated sulfuric acid and precipitated with the addition of water. The blue crystals were allowed to settle and the majority of solution decanted off. A dark blue product was isolated by filtration, washed with 100 ml portions of water and ethanol and air dried. The yield was 0.48 g (30 %) of blue crystals. An infrared spectrum of the product was identical to that of a spectrum of phthalocyanine crystals obtained from J. T. Baker Chemical Company.

DISCUSSION

Our investigation of molybdenum phthalocyanine compounds was centered on the chemistry of oxomolybdenum (IV) phthalocyanine. The studies were concentrated on methods to increase the yield, on an investigation concerning the origin of the oxygen, and on attempts to prepare derivatives soluble in organic solvents. The preparation of a linear MoO_2^{2+} moiety was attempted, but not achieved. Two new compounds, molybdenum (II) phthalocyanine and oxocarbonylmolybdenum (IV) phthalocyanine were prepared and characterized.

I. Oxomolybdenum (IV) Phthalocyanine.

A. Attempts to Improve the Yield.

Three different methods of preparation of oxomolybdenum (IV) phthalocyanine in a nitrogen atmosphere have been reported[12]: (1) the reaction of molybdenum dioxydichloride with phthalonitrile and urea in dimethylformamide; (2) the reaction of molybdenum dioxydichloride with phthalonitrile in dimethlyformamide; and (3) the reaction of molybdenum tetrachloride with phthalonitrile and urea in dimethylformamide.

In order to acquire techniques in the preparation and isolation procedures of oxomolybdenum (IV) phthalocyanine, the reaction of molybdenum dioxydichloride with phthalonitrile and urea was repeated.

This offered an opportunity to obtain the physical data on oxomolybdenum (IV) phthalocyanine which would be useful in further studies. The physical characteristics of the product obtained were identical to those reported,[12] but a slight increase in yield was obtained (4.8 % from preparation II-A versus 0.8 % reported).

Since the quantity of product was unsatisfactory for detailed chemical studies, it was necessary to investigate various factors which could alter the yield. The factors considered to be primarily responsible for the low yield were the nature of the molybdenum reagent and/or the organic compounds used as the starting materials for the formation of the phthalocyanine compound. The variety of conditions used in this phase of the investigation are summarized in Table IV.

The *cis* configuration of the oxygens in molybdenum dioxydichloride[32] was considered to be partly responsible for the low yield. From X-ray determination,[2,3] phthalocyanine rings are known to be rigidly planar. The coplanar molybdenum phthalocyanine would require a *trans* dioxo-species. The metal phthalocyanine compound may be formed in one of two ways: first, the insertion of the metal ion into the phthalocyanine ring; or second, the formation of the phthalocyanine ring around the metal ion. The replacement of the labile lithium ion from dilithium phthalocyanine with the molybdenum (IV) ion was unsuccessful. This suggests that the metal ion is not inserted into the ring but rather that the organic complex is formed around the metal. This view is supported by the stepwise formation of nickel (II) phthalocyanine, in which a bidentate complex of nickel (II) chloride and 1,3-diiminoiso-

Table IV. Summarization of Reactions in Preparation II.

Preparation	% Yield	Molybdenum Reagent	Organic Reagent	Oxygen Absorber	Solvent
II-A	4.8	MoO_2Cl_2	$C_6H_4(CN)_2$ with urea	Pyrogallol	DMF
II-B	92	$MoCl_5$	$C_6H_4(CN)_2$	BASF	Quinoline
II-C	4.3	$MoCl_4 \cdot 2Py^*$	$C_6H_4(CN)_2$ with urea	Pyrogallol	DMF
II-D	48	$MoCl_4 \cdot 2Py$	$C_8H_7N_3^{**}$	Pyrogallol	DMF
II-D	48	$MoCl_4 \cdot 2Py$	$C_8H_7N_3$	Pyrogallol	Quinoline
II-E	99	$MoCl_3 \cdot 3Py$	$C_8H_7N_3$	BASF	Quinoline
II-F	94	$MoCl_4 \cdot 2Py$	$C_8H_7N_3$	BASF	Quinoline
II-G	84	MoO_2Cl_2	$C_8H_7N_3$	BASF	Quinoline
II-H	98	$MoCl_5$	$C_8H_7N_3$	BASF	Quinoline

* Py is Pyridine

** $C_8H_7N_3$ is 1,3-diiminoisoindoline

indoline is produced prior to the formation of nickel (II) phthalocyanine.[6] Since the product contains only one oxygen, reduction must occur, but the exact mode of reduction of the MoO_2^{2+} moiety is not known. Therefore, the related factors of the reduction of the MoO_2^{2+} moiety and the cis configuration of the oxygens may be responsible for the low yield.

To overcome these problems, a compound containing the molybdenum (IV) ion and having the proper configuration, molybdenum tetrachloride dipyridine, was chosen for the next phase of the investigation. In order to remove the possibility that additional variables could influence the course of the reaction, all other conditions were unaltered (Preparation II-C). These modifications did not increase the yield of oxomolybdenum (IV) phthalocyanine, which suggested that the molybdenum complex was not a main factor in obtaining a low yield.

The next factor considered responsible for the low yield was the structure of the organic precursor. Using molybdenum tetrachloride dipyridine, 1,3-diiminoisoindoline was substituted for phthalonitrile and urea and the remaining conditions were unaltered (Preparation II-D). This change increased the yield from 4.3% to 48%, indicating that the organic precursor was indeed important. It is possible that the urea, used as a source of nitrogen, was responsible for the low yield. It has been noted that the reaction of phthalimide and magnesium, in the presence of ammonia, required more careful control than normal.[8] In addition the yield was reduced by fifty percent. Therefore, the utilization of 1,3-diiminoisoindoline eliminated the preliminary reaction of phthalonitrile and urea which might have contributed to the low yield of the phthalocyanine moiety.

Other reactions were carried out using 1,3-diiminoisoindoline with various molybdenum compounds (Preparation II-E through H), and yields close to the theoretical value were obtained. It should be noted that the reaction of molybdenum dioxydichloride with 1,3-diiminoisoindoline (II-G) resulted in a slightly decreased yield (84 %), which suggests that the ease of reduction of the MoO_2^{2+} moiety is a factor in obtaining a lower yield. Therefore, a dioxo- complex of molybdenum phthalocyanine cannot be prepared in this manner.

In the above reactions which increase the yield of oxomolybdenum (IV) phthalocyanine, it was noted that the use of molybdenum (IV) and the steric hindrence of the cis dioxo- moiety of the molybdenum reagent might influence the yield of oxomolybdenum (IV) phthalocyanine. The solvent did not affect the yield. The greatest factor in obtaining a satisfactory yield must have been the use of 1,3-diiminoisoindoline. Any increase in yield in the numerous reactions using 1,3-diiminoisoindoline is thought to be the result of improved technique.

B. Possible Sources of Oxygen.

In each attempted preparation of molybdenum (II) phthalocyanine the product obtained was oxomolybdenum (IV) phthalocyanine, which was not anticipated since the systems were thought to be oxygen free. As an oxygen free molybdenum phthalocyanine was desired, the question was raised: what is the origin of the oxygen? The possibilities would be: (1) the solvent itself or an impurity present in the solvent; (2) atmospheric contamination; (3) oxygen impurity in the nitrogen, which escaped reduction by the reducing agent; (4) oxygen from the organic or inorganic precursor(s); and (5) oxygen from the vessel wall.

To eliminate the possibility that the solvent was a source of oxygen, the following precautions were taken. First, quinoline, a non-oxygen containing solvent (C_9H_7N) was used in place of dimethylformamide (C_3H_7NO). Second, the solvent was distilled twice prior to each reaction: the first distillation was carried out under reduced pressure, and the second under a nitrogen atmosphere. In the latter the solvent was distilled directly into the reaction flask (Figure VIII). However, oxomolybdenum (IV) phthalocyanine was obtained from each reaction, which suggests that the source of oxygen was not the solvent.

It is possible that the product could have absorbed oxygen from the atmosphere during the work-up procedure. Therefore, work-ups of preparation II-E through G, including the preparation of the nujol mulls, were carried out in a nitrogen atmosphere; nevertheless, the same product was obtained. This indicates that the oxygen was not absorbed from the atmosphere during the work-up procedure.

In order to eliminate the possibility that the nitrogen gas which was used to maintain an inert atmosphere was the source of oxygen, these precautions were taken. Initially bubbling nitrogen through alkaline pyrogallol[26] was considered to be effective. The continued presence of oxygen in the product resulted in the replacement of alkaline pyrogallol by another reducing agent, BASF catalyst. The BASF catalyst has a greater capacity for oxygen removal than alkaline pyrogallol and is considered more efficient at high flow rates.[27] However, oxygen was still present in the product which suggests that the source of oxygen was not its presence as an impurity in the nitrogen.

It may be possible that the source of oxygen is the organic reactant. Urea is known to decompose at high temperatures thus giving products of unknown composition, as well as to act as a source of nitrogen in the formation of monoimino- and diiminoisoindoline (Scheme I).[5] In the decomposition reaction urea could also act as a source of oxygen, thus giving the product oxomolybdenum (IV) phthalocyanine. The other organic precursor, 1,3-diiminoisoindoline, cannot be neglected even though it does not contain oxygen. An oxygen containing impurity is suggested from the fact that imines (or diiminoisoindoline, Scheme I) can hydrolyze to form the carbonyl.[33] Also, 1,3-diiminoisoindoline can be oxidized to form phthalic acid. The possibility of impurities is suggested because of the irregular elemental analyses (2-3 % low) which was obtained for the recrystalized product. However, the melting point of the product was in agreement with the literature,[31] and the infrared spectrum received from Kenney[34] was identical to the infrared spectrum of the product from preparation I. The low and irregular elemental analyses can be explained by incomplete combustion of the sample as well as the presence of impurities, such as those mentioned above.

Another possible source of oxygen is the presence of oxygen in the molybdenum reagent, either as water of hydration or as a molybdenum-oxygen moiety. Molybdenum pentachloride is extremely hydroscopic, and, although the container was opened in a nitrogen atmosphere, there may have been water present in the compound prior to its use. The reaction of molybdenum pentachloride with water results in molybdenum oxytrichloride and two moles of hydrochloric acid which may explain the presence of oxygen in the molybdenum phthalocyanine compound. Molybdenum tetrachloride dipyridine and molybdenum trichloride tripyridine are not known to be hydroscopic, and the infrared spectrum of each complex showed no evidence of molybdenum-oxygen absorption. This would indicate that these complexes are not the source of oxygen.

If it is assumed that all previous possible sources of impurity are not contributors of oxygen, then the only remaining possibility is the vessel wall. This is considered unlikely but it cannot be completely disregarded. However this possibility was not pursued further.

It should be noted that in the preparation[15] of oxohydroxomolybdenum (V) tetraphenylporphine, prepared by the reaction of tetraphenylporphine and molybdenum hexacarbonyl in decalin under a nitrogen atmosphere, the product also contained oxygen. The authors state that the source of oxygen was unknown. The present work has not established the source of the oxygen impurity.

C. Problems of Solubility and Analyses.

Two important properties of oxomolybdenum (IV) phthalocyanine which led to problems in the study of its chemistry were solubility and elemental analyses. The irregular elemental analyses led to problems in determining the purity of the compound. The low solubility of oxomolybdenum (IV) phthalocyanine, 9 mg per liter in 1,2,4-trichlorobenzene, will be seen in a later section to preclude chemical investigations in solvents other than sulfuric acid.

The problem encountered with solubility may be attributed to the highly delocalized electrons and strong crystal lattice forces from dipole-dipole interaction between the molecules. Metallated phthalocyanine complexes have an off-set stacking in their crystal structure as shown by X-ray studies.[35] Phthalocyanine compounds with a metal-oxygen moiety generally have a M-O-M linkage which is usually linear and often quite stable chemically. For example, oxosilicon (IV) phthalocyanine is not affected by hydrofluoric acid at 100° C, by aqueous 2M sodium hydroxide at reflux temperature, or by sulfuric acid at room temperature.[36] X-ray powder patterns of the metal-oxygen phthalocyanines of silicon, germanium, and tin have indicated that the rings are parallel and that the chain is linear; however, after heating the germanium compound the metal-oxygen absorption frequency shifted from 864 to 899 cm^{-1}, thus indicating the formation of a stronger metal-oxygen bond, and the X-ray pattern "became more crystalline" which suggested that an ordering of the complex has taken place.[36] This tendency of the phthalocyanines to re-orient themselves suggests that the molecules have preferred orientations with respect to each other thus increasing dipole interaction which may contribute to their insolubility.

It should be noted that the molybdenum tetraphenylporphine compound has much greater solubility than oxomolybdenum (IV) phthalocyanine. This difference in solubility may be related to resonance and the lattice forces in the compounds. It was recently established by X-ray powder data that the porphyrin molecule (Figure I-B) is not completely rigid, as is the phthalocyanine molecule (Figure I-A), and that its geometry is greatly influenced by intermolecular interaction in crystalline form.[37] The porphine molecule is almost planar and becomes skewed with the addition of ligands to the outside ring; phenyl groups give the greatest amount of distortion to the plane of the porphine and result in the "very ruffled tetraphenylporphine" complex[37] (Figure IV). The phenyl groups in tetraphenylporphine are almost perpendicular to the "mean plane" of the porphine ring, which prevent π-interaction between the aromatic phenyl rings and the π-system of the porphine ring.[37] These out-of-plane phenyl groups decrease intermolecular crystal interaction and therefore reduce the attractive forces between molecules, and increase the solubility in organic solvents. The meso carbon atoms in the porphyrin compound greatly reduce the dipole character of the porphyrin compared to phthalocyanine, which may also contribute to the differences in solubility.

Therefore, several factors seem to influence the solubility of phthalocyanine compounds, of which the main two are listed. First, the close packed structure of the crystals may contribute to the insolubility of the compound. Second, the presence of the aza nitrogen atoms may increase the dipole within the molecule thus forming stronger crystal lattice forces.

When a concentrated solution of oxomolybdenum (IV) phthalocyanine in 1,2,4-trichlorobenzene was allowed to stand open to the atmosphere for an extended period of time (10 to 20 days), the solution turned from dark green to light green to colorless, indicating that oxidation of the phthalocyanine complex occurred. This was also reported by Hill and Norgett.[12] The disappearance of the color is enhanced by the addition of acetone to the solution. This same phenomenon was observed in an investigation of the chemiluminescent oxidation of iron (II) phthalocyanine.[9] The products were identified as iron oxide, phthalimide, and an unidentified complex of iron with organic material.[9] No attempt was made in the present work to determine the nature of the oxidation products.

The carbon-hydrogen-nitrogen analyses of oxomolybdenum (IV) phthalocyanine were low and irregular. This has also been observed with metal derivatives of octaphenylporphrazine complexes.[38] This irregularity could be related to the high thermal stability of these compounds, which is suggested by the fact that they can be sublimed unchanged under atmospheric conditions. The difficulties with octaphenylporphrazine complexes have been corrected by mixing potassium dichromate with the compound to obtain faster and more complete oxidation. This was not tried in the present study due to the inexperience of the university analyst.

D. Spectroscopic Studies of Oxomolybdenum (IV) Phthalocyanine.

The most important infrared absorption bands of oxomolybdenum (IV) phthalocyanine are those at 972 and 896 cm^{-1}. The absorption at 972 cm^{-1} was assigned by Hill and Norgett[12] to the asymmetrical stretching vibration of molybdenum-oxygen, and our results are in agreement with this assignment. The other absorption at 896 cm^{-1} may be assigned to the molybdenum-nitrogen absorption of the isoindole nitrogens in the phthalocyanine compound. This absorption is in the range reported for metal nitrogen vibrations of various metal phthalocyanines.[23]

As an example of the utility of infrared spectroscopy, a strong absorption was observed from 970-980 cm^{-1} in an infrared spectrogram of molybdenum (II) phthalocyanine; this was reported by Buslaev and co-workers.[14] This is the area of absorption which is indicative of the asymmetrical stretching frequency of molybdenum-oxygen moiety in oxomolybdenum (IV) phthalocyanine. Therefore, the experimental procedure for molybdenum (II) phthalocyanine was repeated (Preparation II-B) and the data indicated that the compound was oxomolybdenum (IV) phthalocyanine.

It is well known that phthalocyanine compounds have two intense bands in the ultraviolet and visible spectrum, one generally in the range from 666 to 715 mμ and the other around 355 mμ.[12, 39] These absorptions are thought to arise from $\pi \longrightarrow \pi^*$ transitions.[39] Hill and Norgett[12] have reported the absorption of oxomolybdenum (IV) phthalocyanine at 706 mμ (the compound prepared in this report absorbed at 705 mμ) was comparable to that of other mono- oxophthalocyanine compounds.

Since bivalent metal phthalocyanines generally absorb below 680 mμ, these authors related this shift to lower energy to the higher oxidation state of the metal. However, Lever[39] points out that the lower energy absorption (red band) is almost independent of the central metal ion and that the high energy absorption (Soret or blue band) is the absorption affected by the metal ion. It should be noted that Hill and Norgett do not completely agree with the more detailed investigation of Lever.

E. Attempts to Prepare Other Derivatives.

Because the position trans to the oxygen is vacant in oxomolybdenum (IV) phthalocyanine, an attempt was made to prepare oxopyridinemolybdenum (IV) phthalocyanine in which the pyridine occupies the trans position. This is known to occur in oxomolybdenum (V) tetraphenylporphine where the trans position is occupied by chloro-, hydroxo-, and perhydroxo- ions.[15] Also, in complexes with the vanadium (VO^{2+}) moiety, such as oxobis(acetylacetonato)vanadium (IV), the position trans to the oxygen is readily occupied by a Lewis base, such as pyridine or ammonia.[40] Therefore, oxomolybdenum (IV) phthalocyanine was placed in dry pyridine and the mixture was refluxed for four hours. The effort was unsuccessful as only unreacted starting material was recovered. Since the pyridine reaction is representive of this type of complex formation and since it was unsuccessful, this phase of the project was not pursued further.

The most reasonable explanation for the unavilability of the *trans* position in oxomolybdenum (IV) phthalocyanine is the decreased availability of the d orbitals *trans* to the oxygen moiety. The multiple bond character between the molybdenum-oxygen moiety indicated by the position of the asymmetric molybdenum-oxygen stretching frequency suggests $p_\pi \rightarrow d_\pi$ bonding from the oxygen to the molybdenum. Increased electron density on the molybdenum would decrease the bond order from oxygen to molybdenum resulting in a lower absorption for the molybdenum-oxygen bond. It is therefore possible that the electron resonance in the phenyl groups decreases the electron density in the metal d orbitals, thus increasing the $p_\pi \rightarrow d_\pi$ donation from the terminal oxygen to the metal. This increased bond order of the molybdenum-oxygen moiety (in this case) would decrease the availability of the orbitals *trans* to the oxygen. Both, the increased solubility due to a decrease in molecular interaction and the decreased bond order between molybdenum-oxygen in oxomolybdenum (V) tetraphenylporphine increase the possibility of occupying the position *trans* to the oxygen. These same factors decrease the availability of the orbitals *trans* to the oxygen in the molybdenum phthalocyanine complex.

Further evidence for the strength of the oxygen bond to molybdenum can be shown by the position of the metal-oxygen stretching frequency in the infrared spectra of both compounds. The molybdenum-oxygen absorption in oxomolybdenum (V) tetraphenylporphine complexes was observed from 900 to 941 cm^{-1}, depending on the ligand *trans* to the oxygen, and it was observed at 972 cm^{-1} for oxomolybdenum (IV) phthalocyanine. The higher frequency suggests greater $p_\pi \longrightarrow d_\pi$ bonding from oxygen to molybdenum in the phthalocyanine complex, thus reducing the availability of the orbitals trans to the oxygen.

The insolubility of oxomolybdenum (IV) phthalocyanine in all solvents, except concentrated sulfuric acid, precluded a study of its chemical reactivity. Therefore, an attempt was made to increase the solubility of the compound. The simplest and most common method of increasing the solubility of metal phthalocyanines is by attaching sulfonate groups to the benzene portion of the phthalocyanine ring.[3,5] This can be accomplished by two methods: (1) starting with a sulfonated isoindoline compound, or (2) directly sulfonating the metal phthalocyanine compound using chlorosulfonic acid. In the present work only method two was investigated. The reaction of chlorosulfonic acid and oxomolybdenum (IV) phthalocyanine was unsuccessful because the acid destroyed the molybdenum phthalocyanine compound. An inorganic compound containing molybdenum and sulfate groups was the only product isolated.

II. Attempts to Prepare Dioxomolybdenum (VI) Phthalocyanine.

One stated objective of the project was the preparation of a linear MoO_2^{2+} moiety. The previous reactions involving molybdenum dioxydichloride with organic reagents offered a possibility of obtaining the dioxo- species in small quantities; however, none was obtained. Therefore, an attempt was made to oxidize oxomolybdenum (IV) phthalocyanine. Air oxidation at various temperatures was not only unsuccessful but resulted in decomposition of the phthalocyanine compound. Attempts to find a solvent in which other oxidizing agents could be used were also unsuccessful. The attempted sulfonation of the phthalocyanine complex to increase the solubility resulted in decomposition. Therefore, this phase of the investigation was not pursued further.

In the article by Arzoumanidis and O'Connell [16] on the catalytic oxidation of glucose, the catalyst utilized was reported to be a dioxomolybdenum (VI) phthalocyanine compound. However, no preparation procedure or experimental evidence to justify its formulation was given. In light of the recent theoretical prediction of the nonlinearity of the MoO_2^{2+} moiety, an attempt was made to obtain information on the dioxo-complex from the authors[16] to verify the formulation of their compound as a dioxomolybdenum (VI) phthalocyanine complex. However no reply was received and no further work was carried out.

III. Molybdenum (II) Phthalocyanine.

Because all previous attempts to obtain an oxygen free molybdenum phthalocyanine complex were unsuccessful, it seemed feasible to start with a stable, low oxidation state molybdenum compound. The compound which best satisfied these criteria was molybdenum hexacarbonyl. As an added advantage, this compound was also quite soluble in most organic solvents. Therefore, the reaction of molybdenum hexacarbonyl and 1,3-diiminoisoindoline was carried out in quinoline. The red product obtained was molybdenum (II) phthalocyanine, identified by its infrared spectrum and carbon-hydrogen analyses. The fact that a molybdenum-oxygen absorption was not observed in the infrared spectrum indicates that an oxygen-free molybdenum phthalocyanine compound can be formed and is stable to oxidation.

Formation of an oxygen free molybdenum phthalocyanine indicates two possible sources of oxygen for oxomolybdenum (IV) phthalocyanine. One, the oxygen was present in the other molybdenum reagents and was not detected; or two, the molybdenum reagents with a high oxidation state (plus three or higher) were highly reactive to any available trace of oxygen (impurity or vessel wall). In either case, the source of oxygen in oxomolybdenum (IV) phthalocyanine (Preparation II) has not been completely solved. Therefore, further work in this area is suggested.

The infrared spectrum of molybdenum (II) phthalocyanine (Table IX) was similar to the spectrum of oxomolybdenum (IV) phthalocyanine except in the region from 900 to 980 cm^{-1}. No absorption was observed in the 970 to 980 cm^{-1} range. However, a medium absorption was observed at 957 cm^{-1}. This is indicative of the β modification of metal phthalocyanines,[12,41,42] the most stable form, obtained when the metal phthalocyanine is precipitated from high boiling solvents such as quinoline.

A medium-weak absorption at 1000 cm^{-1} was also observed in the infrared spectrum of the product. This absorption is indicative of a non-metal phthalocyanine, possibly as an impurity in the product. An impurity is suggested by the fact that the elemental analyses for molybdenum (II) phthalocyanine were consistently high (1.0 to 1.5 %).

Evidence for the stability of the compound is obtained from the fact that molybdenum (II) phthalocyanine can be recrystalized from concentrated sulfuric acid. The infrared spectra before and after recrystalization are similar, except for a small-medium absorption at 1720 cm^{-1}. This absorption appeared somewhat lessened when a pulverized sample of the product was placed in an abderhalden for 24 hours at 100°C and 2 mm pressure. At present the source of this absorption is unknown.

The ultraviolet-visible spectrum for molybdenum (II) phthalocyanine (Table XV) is different from the spectrum of oxomolybdenum (IV) phthalocyanine. This difference is related to the reduction in oxidation state of the molybdenum. The red band for molybdenum (II) phthalocyanine is found to absorb at 695 mu, which is in agreement with the metal phthalocyanine series. This absorption is slightly lower than that of the oxo-substituted molybdenum phthalocyanine. This is the general trend followed by low oxidation state metal phthalocyanines versus high oxidation state metal phthalocyanines.

IV. Oxocarbonylmolybdenum (IV) Phthalocyanine.

Previously, it was suggested that urea may have been the source of oxygen in oxomolybdenum (IV) phthalocyanine. Since the reaction of molybdenum hexacarbonyl with 1,3-diiminoisoindoline yielded an oxygen free molybdenum phthalocyanine compound, it was possible to investigate urea as a source of oxygen. Therefore, the reaction of molybdenum hexacarbonyl with phthalonitrile and urea in quinoline was carried out. A brown product was collected and identified from its infrared spectrum and carbon-hydrogen analyses as oxocarbonylmolybdenum (IV) phthalocyanine. Obtaining an oxygen species of molybdenum phthalocyanine in the presence of urea gives supporting evidence that urea can be a source of oxygen.

Two different products, oxocarbonylmolybdenum (IV) phthalocyanine and oxomolybdenum (IV) phthalocyanine, were isolated from this reaction and the yield of each was found to be temperature dependent. When the reaction was carried out at the reflux temperature of quinoline (236°C), oxomolybdenum (IV) phthalocyanine was obtained (40 % yield). When the temperature was reduced to 180-200°C, the same product was obtained, but the yield was diminished (25-30 %). At a reaction temperature of 160-170°C, oxocarbonylmolybdenum (IV) phthalocyanine was obtained. The average yield of two runs was 15 %. Temperatures below 140-150°C did not produce any phthalocyanine complex.

It was reported[43] that phthalonitrile readily combines with metals, such as copper, to form metal phthalocyanine complexes at the reaction temperature of 190°C. The reaction proceeds vigorously at 210°C with the evolution of heat, but does not occur at all at 150°C. While the tendency to form metal phthalocyanines is great, this study indicates that the formation is dependent upon the reaction temperature. The reaction of molybdenum hexacarbonyl with phthalonitrile and urea begins to form a phthalocyanine compound around 160°C, with an increase in yield at elevated temperatures, at the expense of losing the carbonyl ligand. Heating the oxocarbonylmolybdenum (IV) phthalocyanine in the dry state in an abderhalden at 236°C and 2 mm pressure for 16 hours resulted in partial loss of the carbonyl, as evidenced from the reduction of the absorption at 2200 cm^{-1} in the infrared spectrum. This suggests that the loss of the carbonyl ligand is temperature dependent.

The infrared spectrum of oxocarbonylmolybdenum (IV) phthalocyanine (Table XII) is similar to the spectrum obtained for oxomolybdenum (IV) phthalocyanine, except for a medium-weak absorption which was observed at 2200 cm^{-1}. This absorption is assigned to the carbon-oxygen asymmetrical stretching frequency of the carbonyl group. In a study on the interactions of carbonyl stretching modes in metal carbonyl compounds, it was found that the highest intensity absorption (A_1) is normally weak and dependent upon the electronegativity, the π-donating ability, and the polarizability of the metal ion.[44] The A_1 modes of iodopentacarbonylrhenium (I) and bromopentacarbonylrhenium (I) compounds were found to absorb at 2145 and 2150 cm^{-1} respectively.[44] The high energy carbonyl absorptions were attributed to the more electronegative halogens which leave the metal with a lesser amount of electron-donating ability. The presence of a better π-donating ligand on the metal will reverse this trend unless other groups are present (such as carbonyl or amine groups) to absorb the metal electrons. Therefore, the high absorption frequency for the carbonyl in oxocarbonylmolybdenum (IV) phthalocyanine may be due to the isoindole nitrogens backbonding with the molybdenum, which results in a greater dipole in the carbonyl ligand.

The ultraviolet-visible spectrum of oxocarbonylmolybdenum (IV) phthalocyanine (Table XVI) is significantly different from the spectrum of oxomolybdenum (IV) phthalocyanine in the blue band region. This is the region most affected by changes in the metal ion. The presence of the carbonyl ligand would change the electronic environment of the molybdenum ion thereby causing a change in the ultraviolet spectrum.

SUMMARY

The objectives of this research were : (1) to increase the yield of oxomolybdenum (IV) phthalocyanine, (2) to investigate the origin of oxygen in molybdenum phthalocyanine, and (3) to obtain a linear MoO_2^{2+} moiety. The first objective was fully realized. However, the origin of the oxygen was not completely solved. The possibility of obtaining a linear MoO_2^{2+} moiety was found to be in agreement with theoretical predictions. Two new compounds, molybdenum (II) phthalocyanine and oxocarbonylmolybdenum (IV) phthalocyanine, were characterized. In addition, the use of molybdenum phthalocyanine compounds as model compounds for the investigation of the biochemically important molybdenum systems were found to be unsuitable because of insolubility.

The organic precursors possessing the isoindoline skeleton was found to have the largest contribution to the increased yield. The reduction and the configuration of the molybdenum reagent may possibly be a small factor in affecting the yield.

The origin of the oxygen was not solved but the fact that molybdenum (II) phthalocyanine was obtained seems to rule out all possibilities except the molybdenum reagents and atmospheric leakage into the system. Urea was found to be a positive contributor of oxygen.

APPENDIX

The infrared and ultraviolet-visible spectra are given in the following tables. The infrared spectra were obtained as nujol mulls on potassium bromide plates in the range from 400 to 4000 cm^{-1}, and as potassium bromide wafers (KBr) in the range from 250 to 4000 cm^{-1}. The nujol absorbs in the 3000 - 2850 cm^{-1} region, and at 1460 and 1375 cm^{-1}, therefore these absorptions due to nujol were not reported. The relative intensities are given as follows:

shld. - - Shoulder
vw - - Very Weak
w - - Weak
m - - Medium
s - - Strong
vs - - Very Strong
bd - - Broad

Table V. Infrared Absorption Maxima of
1,3 - Diiminoisoindoline (Potassium Bromide Wafer).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3282	s	1017	m
3258	s	983	vw
1693	m	950	vw
1642	s	890	m
1601	s	878	m
1562	shld.	850	m(bd)
1545	vs	817	w
1532	s(bd)	785	m
1470	s	776	s
1460	s	745	m
1440	vs(bd)	708	s
1345	m	695	s
1325	m	663	m
1312	s	642	m
1273	vw	632	s
1262	vs	557	shld.
1176	s	552	m
1156	vs	457	w
1145	vs	408	w
1081	s	350	w(bd)
1068	s	265	vw

Table VI. Infrared Absorption Maxima of 1,3-Diiminoisoindoline (Nujol Mull on Potassium Bromide Plates).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3285	s	1081	s
3260	s	1068	s
1693	m	1017	m
1643	s	983	vw
1601	s	950	vw
1562	shld.	890	m
1545	vs	880	m
1532	s(bd)	850	m(bd)
1470	s	817	w
1460	s	785	m
1440	vs(bd)	776	s
1345	m	745	m
1325	m	708	s
1312	s	695	s
1273	vw	663	m
1262	vs	642	m
1176	s	632	s
1156	vs	557	shld.
1145	vs	552	m

Table VII. Infrared Absorption Maxima of Oxomolybdenum (IV) Phthalocyanine (Potassium Bromide Wafer).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
1720	w(bd)	1005	vw
1610	w	974	s
1496	m	897	m
1478	w	878	w
1460	vw	778	m
1415	m	754	s
1332	vs	731	vs
1290	s	638	w(bd)
1160	m	581	w
1119	vs	514	w
1088	vs	443	w
1064	s	351	vw

Table VIII. Infrared Absorption Maxima of Oxomolybdenum (IV) Phthalocyanine (Nujol Mull on Potassium Bromide Plates).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
1720	w(bd)	972	m
1605	w	895	m
1494	m	875	vw
1422	w	775	w
1330	s	752	m
1287	s	728	s
1158	m	635	vw
1118	s	578	w
1085	s	512	w
1061	m	442	shld.

Table IX. Infrared Absorption Maxima of Molybdenum(II) Phthalocyanine (Potassium Bromide Wafer).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
1720	vw	957	w
1608	w	892	m
1525	w	865	w
1496	m	799	vw
1470	m	766	m
1432	vw	747	s
1406	w	727	shld.
1329	vs	719	vs
1286	m	610	w
1159	m	579	w
1115	vs	504	w
1079	vs	431	m
1059	shld.	396	w
1000	m-w	348	w

Table X. Infrared Absorption Maxima of Molybdenum (II) Phthalocyanine (Nujol Mull on Potassium Bromide Plates).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
1720	vw	957	w
1608	w	892	m
1525	w	865	w
1496	m	799	vw
1406	w	766	m
1329	s	747	m-s
1286	m	727	shld.
1159	m	719	s
1115	s	610	vw
1079	s	579	w
1059	shld.	504	vw
1000	m-w	431	shld.

Table XI. Infrared Absorption Maxima of Molybdenum (II) Phthalocyanine, Recrystalized from Concentrated Sulfuric Acid (Potassium Bromide Wafer).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
1720	m-w	957	w
1608	w	892	w
1525	w	865	w
1496	m-w	799	vw
1470	m	766	m
1432	vw	747	s
1406	w	727	shld.
1329	vs	719	vs
1286	m	610	w
1159	m	579	w
1115	vs	504	w
1079	vs	431	m
1059	shld.	396	w
1000	m-w	348	w

Table XII. Infrared Absorption Maxima of Oxocarbonylmolybdenum (IV) Phthalocyanine (Potassuim Bromide Wafer).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
2200	w	955	shld.
1605	w	892	m
1491	m	869	w
1473	w	795	vw
1435	vw	773	m
1410	m	749	s
1329	vs	725	vs
1283	s	635	vw
1155	m	610	vw
1113	vs	578	w
1083	vs	508	w
1058	s	440	m
1000	m	418	vw
969	s	397	w

Table XIII. Infrared Absorption Maxima of Oxocarbonylmolybdenum (IV) Phthalocyanine (Nujol Mull on Potassium Bromide Plates).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
2200	w	960	shld.
1605	w	892	m
1491	m	869	w
1435	shld.	795	vw
1410	m	773	m
1329	s	747	s
1283	s	725	s
1155	w	718	shld.
1113	s	635	vw
1083	s	610	vw
1058	m	578	vw
1000	w	508	vw
969	m	440	shld.

Table XIV. Ultraviolet-Visible Absorption Maxima and Molar Extinction Coefficient for Oxomolybdenum (IV) Phthalocyanine.*

Wave Length in mμ	Log $\epsilon_{max.}$	Wave Length in mμ	Log $\epsilon_{max.}$
768	3.603	410	4.294
705	4.629	330	4.947
655	4.117	300	5.033
		270	4.987

Table XV. Ultraviolet-Visible Absorption Maxima and Molar Extinction Coefficient for Molybdenum (II) Phthalocyanine.*

Wave length in mμ	Log $\epsilon_{max.}$	Wave length in mμ	Log $\epsilon_{max.}$
775	4.960	445	5.773
695	6.201	335	6.398
660	5.912	310	6.352
638	5.738	295	6.228
598	5.532	250	6.339

Table XVI. Ultraviolet-Visible Absorption Maxima and Molar Extinction Coefficient for Oxocarbonlymolybdenum (IV) Phthalocyanine.*

Wave length in mμ	Log $\epsilon_{max.}$	Wave length in mμ	Log $\epsilon_{max.}$
775	5.925	595	5.722
692	6.544	337	6.626
656	6.253	309	6.568
635	6.057	250	6.616

* Solvent is 1,2,4 - Trichlorobenzene.

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