An Infrared Investigation of Triphenylphosphine, Triphenylphosphine Oxide, and some of their Complexes

Lynne L. Haas

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AN INFRARED INVESTIGATION OF
TRIPHENYLPHOSPHINE, TRIPHENYLPHOSPHINE OXIDE,
AND SOME OF THEIR COMPLEXES

BY

LYNNE L. HAAS

A thesis submitted
in partial fulfillment of the requirements for the
degree Master of Science, Major in
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AN INFRARED INVESTIGATION OF
TRIPHENYLPHOSPHINE, TRIPHENYLPHOSPHINE OXIDE,
AND SOME OF THEIR COMPLEXES

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 requirement for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

/ / Thesis Advisor

Head, Chemistry Department
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INTRODUCTION

The infrared spectra of triphenylphosphine, triphenylphosphine oxide, and their complexes have been studied by several groups of workers. These spectra are helpful in determining the modes of complex formation and elucidating structural aspects of the complexes. Although many of the bands can be attributed to phenyl modes, the areas between 1200 and 1050 cm\(^{-1}\) and between 800 and 700 cm\(^{-1}\) contain bands which arise from bonding within the ligand (phosphorus-phenyl linkages) or bonding of the ligand to a metal ion (phosphorus-metal linkages in triphenylphosphine complexes and oxygen-metal linkages in triphenylphosphine oxide complexes).

Work with triphenylphosphine at South Dakota State University revealed that bands in the 700 cm\(^{-1}\) and 1100 cm\(^{-1}\) region were often present but had received no definitive assignments in previous spectral studies. Some workers preferred to ignore bands in these regions (particularly those in the 700 cm\(^{-1}\) region) even though they often appear as some of the most intense absorption in the spectra. Most simply tried to make sweeping generalizations of structure or bonding to account for the bands. Preliminary work revealed that these generalizations break down when a broad range of complexes is examined. It was also apparent that the intensity of the bands relative to adjacent bands varied
in different types of complexes, and could be related to structure. The aspect of intensity has not been considered by previous studies. Because of the neglect of these aspects of the infrared spectra, this research was undertaken in order to clarify ambiguous assignments and determine the reasons for differences in the characteristic features of triphenylphosphine, triphenylphosphine oxide and various types of complexes involving these ligands.

In addition, a complex obtained from the reaction of triphenylphosphine and indium (III) perchlorate 8-hydrate unexpectedly produced a spectrum quite different from those of other phosphine complexes. This complication led to an investigation of the adducts obtained from the interaction of hydrogen chloride or hydrogen bromide and triphenylphosphine oxide in order to determine the spectral characteristics of hydrogen bonding in these adducts. This information was used to draw conclusions concerning the type of bonding present in certain complexes of transition metal salts.
Phosphorus, like nitrogen, is able to form trivalent compounds, $\text{PH}_3$ or $\text{PR}_3$, where $R = \text{alkyl or aryl}$. These phosphines, as a class, are Lewis bases; they can form complexes with metal derivatives by donation of the non-bonding electron pair on the phosphorus atom to a metal ion. Triaryl phosphines make especially good donors toward transition metal ions. Phosphines can be oxidized to form phosphine oxides, $R_3\text{P}\rightarrow\text{O}$, and these molecules also serve as donors toward metal ions.

The historical section will cover these characteristics of triphenylphosphine, triphenylphosphine complexes, triphenylphosphine oxide, and triphenylphosphine oxide complexes in detail as they are elucidated by their infrared spectra. Background information on the characteristics of hydrogen bonded compounds is also presented. Comments are made on specific complexes only when they exhibit some unique property. No attempt is made to provide a comprehensive history of each complex investigated.

TRIPHENYLPHOSPHINE

The most useful region for infrared study of phosphines is $2000 - 400 \text{ cm}^{-1}$. Phosphine bands between 400 and $200 \text{ cm}^{-1}$ tend to become obscured by the stronger metal-anion bond vibrations which occur in this region.

Whiffen conducted a study of the phenyl vibrational
modes of X-substituted benzenes where X = halogen (1). These assignments can be directly related to the spectrum of triphenylphosphine, with the X-substituent being phosphorus. The C=C skeletal vibrations (k,l,m,n, by Whiffen's notation) appear between 1585 and 1435 cm\(^{-1}\) (2) (3). The C-H in-plane deformation modes (a,c,b) are observed between 1180 and 1023 cm\(^{-1}\). The phenyl breathing mode p occurs as a weak band at 996 cm\(^{-1}\). The C-H out-of-plane deformations f and v appear as strong bands at 746 and 690 cm\(^{-1}\) respectively, and are characteristic of mono-substituted phenyl groups as are weak absorptions between 2000 and 1600 cm\(^{-1}\) (4) (5). The C=C stretching frequency of the ring is expected slightly below 800 cm\(^{-1}\) but does not appear. It is probably shifted below 700 cm\(^{-1}\) due to the electronegativity of the phosphorus atom (6).

There are six vibrational modes of the benzene ring in which a substituent X, in this case the phosphorus
atom, contributes appreciable amplitude. Consequently, the frequencies are sensitive to the mass of X and are designated X-sensitive (i.e., P-sensitive) modes. Whiffen designated these vibrational modes as q, r, t, u, x, y (1).

Modes q, r, t represent C-P-stretching, u is a C-P in-plane deformation, and x, y are out-of-plane deformation modes. The P-sensitive mode q occurs in triphenylphosphine at 1089 cm\(^{-1}\) (5) (7). In alkyl phosphines, other P-sensitive modes can be observed between 455 and 400 cm\(^{-1}\) (6). However, phenyl bands obscure these absorptions in the spectrum of triphenylphosphine. The P-sensitive mode r expected about 700 cm\(^{-1}\) cannot be resolved from the strong phenyl absorption at 690 cm\(^{-1}\). There are no simply phosphorus-carbon stretching modes and bands assigned as such (8) are now recognized as P-sensitive.

It was proposed by Daasch and Smith (9) that bands appearing near 1440 and 1000 cm\(^{-1}\) were characteristic of a phosphorus-phenyl linkage. The former always appears above 1450 cm\(^{-1}\) in hydrocarbons and below 1450 cm\(^{-1}\) in
phosphorus compounds. The latter band always appears at lower frequencies in hydrocarbons. However, later work indicated that these bands appear in the spectra of other Group IVA and VA derivatives as well as phosphorus compounds, and they were reassigned as activated ring vibrations due to the phenyl groups alone (3) (5) (8).

TRIPHENYLPHOSPHINE COMPLEXES

Although phosphorus has a low donor strength in an environment of three phenyl groups, the stability of addition compounds of triphenylphosphine and metal salts is considerable. The stability is ascribed to \( \pi \)-bonding between filled \( d \) orbitals of the metal and vacant \( d \) orbitals of phosphorus. Such \( \pi \)-bonding augments the \( \sigma \)-type coordination bond formed by using the lone pair of electrons on the phosphorus atom (10).

![Diagram of triphenylphosphine complex]

The dative bond formation between metal and phosphorus shifts the P-sensitive modes to slightly higher frequencies (11). In the spectrum of Ni \([(C_6H_5)_3P]_2Cl_2\], mode \( q \) appears at 1094 cm\(^{-1}\). Similar shifts are observed for cobalt, copper, and indium complexes. Bands which are slightly shifted from their positions in the spectrum of triphenylphosphine in the region 433 - 423 cm\(^{-1}\) have also
been assigned to the formation of phosphorus-metal bonds (P-sensitive mode t) (6). The majority of bands above 500 cm$^{-1}$ are due to the ligand, and remain stable from one complex to the next.

For the Ni [(C$_6$H$_5$)$_3$P]$_2$Cl$_2$ complex, a tetrahedral, rather than square planar, structure has been confirmed by x-ray crystal studies (12). The weaker the field, the more favored a tetrahedral configuration becomes. Here, the weakening is induced by the electron withdrawing power of the ring and the ability of d orbitals of phosphorus to interact with ring orbitals. This causes a strengthening of phosphorus-phenyl bonds with concomitant weakening of nickel-phosphorus bonds.

The triphenylphosphine derivative of indium(III) perchlorate contains four-coordinate indium(III), the usual coordination number for indium(III) with phosphorus ligands. The bonding involves the overlap of filled 4d indium orbitals with empty d orbitals of phosphorus (13).

**TRIPHENYLPHOSPHINE OXIDE**

Comparisons of the spectrum of triphenylphosphine oxide to that of benzene revealed that all the characteristic phenyl modes were present. In addition, Holmann and Pinchas observed a band at 1121 cm$^{-1}$ (14) which they attributed to an in-plane ring deformation shifted from the position of the analogous band in the spectrum of benzene (1157 cm$^{-1}$). They ascribed the shift to weak in-
teractions between the ring $\pi$-electrons and the positively charged phosphorus atom. This interaction could then give rise to resonance structures such as

![Resonance structures](image)

thereby weakening C-H bonds, accounting for the lower frequency. The band was later reassigned to the P-sensitive mode $q$ indicative of a phosphorus-phenyl linkage (8).

Holmann and Pinchas were also concerned with determining the frequency of the P-O stretch by comparing the spectra of normal triphenylphosphine oxide with the $^{18}O$ labeled compound (14). They found a band at $1172 \text{ cm}^{-1}$ in the spectrum of $(\text{C}_6\text{H}_5)_3\text{PO}^{18}$ which had no analog in the spectrum of normal triphenylphosphine oxide. It was reasonable that the greater oxygen mass would cause a downward shift of a band at $1190 \text{ cm}^{-1}$. This was then assigned as the P-O stretching frequency.

Studies of other organophosphorus compounds indicated that the position of the P-O stretching frequency was dependent on the electronegativity of the substituents (9). For $\text{F}_3\text{PO}$, at one extreme, the P-O stretch was found near $1414 \text{ cm}^{-1}$, while it appeared at $1177 \text{ cm}^{-1}$ in the spectrum of $(\text{CH}_3)_3\text{PO}$, at the other extreme (2) (15). The effect of electronegativity changes became even more apparent when the P-O
stretching frequency for triphenylphosphine oxide ($1190 \text{ cm}^{-1}$) was compared with that of C$_{6}$H$_{5}$Cl PO which absorbs near $1275 \text{ cm}^{-1}$ (9). Cotton, et al., (16) and Sheldon and Tyree (17) utilized this data to postulate that the P-O bond in phosphine oxides involved first a coordinate covalent bond ($P^+\rightarrow O^-$) and secondly some backbonding ($P^-\rightarrow O^+$) resulting from the overlap of filled $p$ $\pi$-orbitals of oxygen with empty $d$ $\pi$-orbitals of phosphorus. If only a $\sigma$-bond were involved, the greater electronegativity of the substituents would weaken the $P^+\rightarrow O^-$ bond and would lower its stretching frequency. However, increasing the electronegativity increases the amount of backbonding, increasing the bond order and frequency.

Sheldon and Tyree have shown that when triphenylphosphine oxide becomes coordinated to a metal ion, the donor atom is oxygen and not one of the other substituents (17). Examining POC$_3$Cl, they pointed out that donation by chlorine would have an opposite effect on the P-O stretching frequency as donation by the oxygen. Chlorine donation would encourage backbonding ($P^-\rightarrow O^+$), increasing the frequency, while oxygen donation would inhibit it.

P-sensitive modes $q$ and $r$ in triphenylphosphine oxide occur as strong bands at $1125 \text{ cm}^{-1}$ and $720 \text{ cm}^{-1}$ respectively (11). The band at $1125 \text{ cm}^{-1}$ is highly sensitive to the electronegativity of the substituents of the central
atom as evidenced by its shift from 1089 cm\(^{-1}\) for triphenylphosphine.

A weak band near 1095 cm\(^{-1}\) has been ascribed to an overtone (2\(v\)) of a strong band near 540 cm\(^{-1}\) (11).

**TRIPHENYLPHOSPHINE OXIDE COMPLEXES**

The complex Co\(\{\text{C}_6\text{H}_5\text{Po}\}\)_2(NO\(_3\))\(_2\) was originally assigned a tetrahedral structure (18). However, the crystal structure of Co\(\{\text{CH}_3\text{Po}\}\)_2(NO\(_3\))\(_2\) showed it to have an irregular configuration which contained six coordinated oxygen atoms, the nitrate ions thus acting as bidentate ligands. The spectral similarities of the compound to the triphenylphosphine oxide derivative led researchers to accept a similar configuration for the aryl derivative (19). Cotton et al., pointed out that nitrate ions acting as monodentate ligands could not be distinguished from those functioning as bidentate ligands through the use of their infrared absorptions alone. The absorptions arising from the triphenylphosphine oxide ligand were similar to those of the uncoordinated molecule except for the downward shift of the P-O stretch to 1155 cm\(^{-1}\). Other first row transition metal nitrate derivatives which contain triphenylphosphine oxide have nearly identical spectra except for slight shifts in the P-O stretch even though they contain monodentate nitrate ions with four coordinate metal ions (18).

The shifted P-O band is sometimes broadened or split
into a doublet. The complex Ni \([(C_6H_5)_3PO]_4(CIO_4)_2\) for example, absorbs at 1145 cm\(^{-1}\) and 1170 cm\(^{-1}\). It has been suggested that this effect is caused by the existence of nonequivalent ligands in the crystal which would vary more or less in their vibrational frequencies (16). The perchlorate anion has negligible donor properties and is not incorporated into the coordination sphere. Ionic perchlorate bands appear at 620 and 1100 cm\(^{-1}\). The latter is broadened by crystalline field effects and may blur the P-O absorption.

It was originally thought that the coordinated triphenylphosphine oxide groups had to be linear and that the \([\text{Ni} \cdot [(C_6H_5)_3PO]_4]^2+\) cation would thus have to assume a tetrahedral configuration in order to accommodate such an arrangement even though ultraviolet data suggested that the cation was square planar. Later investigations however, showed that Ni-O bond distances as short as 2 Å were still possible with a Ni-O-P angle of less than or equal to 160° with two trans ligands bent upward and two downward. Under these conditions, the NiO\(_4\) groups could be nearly planar. The \([M[(C_6H_5)_3PO]_4]^2+\) cations for metals like cobalt(II), normally forming tetrahedral complexes would be tetrahedral in this case as well with linear M-O-P groups forced by steric considerations (20) (21).

The complex In \([(C_6H_5)_3PO]_4(CIO_4)_3\) is unusual in
that it contains four coordinate indium(III) while it was shown that with nitrogen and sulfur donors and oxygen donors other than triphenylphosphine oxide, indium(III) has a coordination number of six (22). The lowering of the coordination number may be due to steric effects. Another explanation is that four coordinate indium(III) only occurs with ligands that can form both σ- and τ-bonds to the metal (13). Since the charge of the cation causes contraction of the d orbitals, the negative charge of strongly electronegative ligands is not easily transferred to the positive ion, and τ-bonding with the d orbital is unlikely. With less electronegative ligands, the reduction of the positive charge is more probable, the d orbitals are less contracted and τ-bonding is feasible provided the weakly electronegative ligand can also form τ-bonds. The overlap involves unfilled 5d orbitals of indium and the filled p orbitals of oxygen. The P-O stretch is found at 1140 cm$^{-1}$.

Besides triphenylphosphine oxide complexes, strong bands near 1100 and 720 cm$^{-1}$ also appear in the spectra of triphenylphosphonium salts, (C$_6$H$_5$)$_3$PRX, where R = alkyl, aryl, or hydrogen, and X = halogen or other anion. The band at 1110 - 1114 cm$^{-1}$ has been assigned to the X-sensitive mode q shifted from 1090 cm$^{-1}$ for triphenylphosphine on coordination (2) (23) or to a four coordinate phosphorus atom (4) (24). The strong band at 720 cm$^{-1}$
has also been ascribed by several workers to a four coordinate phosphorus atom (4) (10) (24). It has also been considered as further splitting of the \( f \) mode near 750 cm\(^{-1} \) or as the \( X \)-sensitive vibration \( r \) (2).

HYDROGEN BONDED COMPOUNDS

In inorganic chemistry there are very few compounds whose structures depend on hydrogen bonding alone. The triatomic \( HX_2^- \) anion where \( X = \) halide, pseudohalide, or oxyanion, provides a simple framework in which to study the characteristics of the hydrogen bond (25).

Several models have been proposed to explain the energy relationships of hydrogen bonds. When the chemical environments of both atoms bonded to the hydrogen are the same, the bond may be represented by potential functions (26).

Figure I. Qualitative potential functions and energy levels for the \( XHX \) bond.
Figure I-a represents two positions of minimum energy which the hydrogen atom can occupy separated by a high potential energy barrier. This situation would be most likely to arise when the X···X distance is relatively long, making it difficult for the proton to gain the energy necessary to move from one position to the other. When the X atoms are equivalent, X-H···X and X···H-X are equally probable and the bond is asymmetrical. As the distance between the two minima decreases, the separating barrier is reduced (Figure I-b), and the rate of interconversion of these two species increases. With sufficiently low potential barriers, "tunneling" between the two minimum energy positions produces a splitting of the vibrational levels of the ground state which can be detected in the infrared spectra. In the limiting case, the potential barrier vanishes (Figure I-c) leaving only one stable position of the hydrogen atom, centrally located between the two X atoms.

Although asymmetrical hydrogen bonds should show three infrared active modes (Figure I-b) while symmetrical hydrogen bonds give rise to only one vibrational mode, the type of hydrogen bond is difficult to classify on the basis of the infrared spectra. The low energy transition resulting from the resonance split in the ground state energy level may be beyond the range of far infrared instruments. Often the remaining two modes are close together. Since bands
attributable to hydrogen bonding are usually of great width, it is often difficult to distinguish one band from two superimposed bands.

Of all the $\text{H(halogen)}_2^-$ anions, hydrogen bifluoride is the most stable, with the strongest, shortest hydrogen bond. Peterson and Levy (27) determined by neutron diffraction that the hydrogen atom is at the midpoint of the $\text{F} \cdots \text{F}$ system. Infrared bands at 1225 and 1450 cm$^{-1}$ have been assigned to $\nu_2$, the bending mode, and $\nu_3$, the asymmetric stretching mode respectively (25) (28). The absence of any band which could be assigned to $\nu_1$, the symmetric stretching mode, supports the symmetrical structure.

X-ray investigations of hydrogen bichloride showed linear $\text{ClHCl}$ groups with a Cl$\cdots$Cl distance of 3.14 Å. Waddington (29) proposed a symmetrically located hydrogen atom on the basis of the similarity in the infrared bands arising from HF$_2^-$ and HCl$_2^-$. However, later studies of ammonium salts revealed that the spectra fell into two distinct groups (30). Type I salts (containing the cations Cs$^+$, (CH$_3$)$_4$N$^+$, (C$_4$H$_9$)$_4$N$^+$, and [(C$_{16}$H$_{33}$)(CH$_3$)$_3$]N$^+$) produce spectra with three recurring bands: $\nu_3$ between 1520 and 1670 cm$^{-1}$, $\nu_2$ near 1200 cm$^{-1}$, and a far infrared band near 200 cm$^{-1}$ assigned to $\nu_1$. Thus, the spectra suggest that these salts have linear but asymmetrical hydrogen bonds ascribed to nonequivalence of the chlorine atoms in the crystal lattice. Type II salts (with cations (C$_2$H$_5$)$_4$N$^+$,
(C₃H₇)₄N⁺, and (C₅H₁₁)₄N⁺) produce spectra with a broad asymmetrical absorption between 600 and 1300 cm⁻¹. Two maxima occur within this region, one centered between 700 and 800 cm⁻¹ (ν₃), and one between 1050 and 1100 cm⁻¹ (ν₂), consistent with a symmetrical, single minimum potential well structure.

It was concluded that the type of hydrogen bond formed in these tetraalkylammonium salts depends on the equivalence or independence of the chlorine atoms in the lattice since the distribution among the cations is random. However, later infrared studies of cesium bihalide salts at low temperatures (31) determined that the proton is not centrosymmetric in Type I salts and that the anions have either Cᵥᵥᵥ or Cₛ symmetry. The anions of Type II salts may have Dᵥᵥᵥ or Cᵥᵥᵥ structures although Cᵥᵥᵥ is favored because of the appearance of ν₁ near 210 cm⁻¹.

Hydrogen bonded oxyanions also show spectral features dependent on the position of the hydrogen atom in the bond. The infrared spectra of Type A acid salts (characterized by symmetrical, single minimum hydrogen bonds in which the two X atoms are crystallographically equivalent and linked by the acidic hydrogen) show hydroxyl frequencies far below the usual 3500 cm⁻¹ region, a wide plateau of absorption spreading for several hundred wave numbers between 700 and 1000 cm⁻¹, and an absorption "window" near 900 cm⁻¹ (32) (33). X-ray structural investigations of
[(C₆H₅)₄As]H(NO₃)₂ showed monodentate, coplanar nitrate ions linked across a center of symmetry by a very short hydrogen bond (2.54 Å). The spectrum exhibits a very strong broad band centered near 800 cm⁻¹ and an hydroxyl band near 1600 cm⁻¹. Most monocarboxylic acid salts also fall within this category (33) (34).

Type B acid salts with the two X atoms readily distinguishable crystallographically, contain asymmetrical hydrogen bonds (32). Type B spectra approximate the superposition of the spectra of the salt and free acid, each taken separately (33). Most hydrogen phosphates, arsenates, periodates, and phthalates of metals and ammonium fall into this group. Calcium and barium hydrogen phosphate as representatives of Type B salts exhibit two hydroxyl stretching frequencies near 2800 and 2360 cm⁻¹ resulting from the split in the ground state energy levels caused by the tunneling effect (35).

Many adducts of triphenylphosphine oxide also contain hydrogen bonds. One of the first reports of such compounds examined the adduct of triphenylphosphine oxide with hydrochloric acid. Two possible structures were formulated:

\[(\text{C}_6\text{H}_5)_3\text{P} \rightleftharpoons ^\ddagger\text{OH}^{\text{Cl}} \quad \text{or} \quad (\text{C}_6\text{H}_5)_3\text{P} = ^\ddagger\text{H}^{\text{Cl}}\]

Both were rejected in favor of the hydrogen bonded structure: \((\text{C}_6\text{H}_5)_3\text{PO}\cdots\text{HCl}\) (36).

Hadzi later made a study of adducts of triphenyl-
phosphine oxide with several strong acids (nitric, trichloracetic, hydrochloric and hydrobromic) to determine the degree of proton transfer in the adducts (37). The spectrum of \((\text{C}_6\text{H}_5\)\)_3\text{PO} \cdot \text{HNO}_3\) showed bands arising from the hydrogen nitrate molecule indicating that proton transfer did not occur. Otherwise, nitrate ion bands at 381, 815, and 738 cm\(^{-1}\) would have appeared instead. Diffuse absorption in the higher frequency regions made it impossible to locate the hydroxyl frequency. The spectrum of \((\text{C}_6\text{H}_5\)\)_3\text{PO} \cdot \text{HOOCCCl}_3\) contained two hydroxyl stretching frequencies at 1850 and 2250 cm\(^{-1}\) attributed to a double minimum potential for the hydrogen. All the adducts showed enhanced bands between 1050 and 1160 cm\(^{-1}\) and a shifted \(\text{P-O}\) stretching band, sometimes observed only as a shoulder on the intense aromatic band near 1120 cm\(^{-1}\). Only \((\text{C}_6\text{H}_5\)\)_3\text{PO} \cdot \text{HBr}\) had spectral features which could be ascribed to proton transfer. A very broad, strong band observed at 1780 cm\(^{-1}\) was assigned to the \(\text{POH}\) stretching mode, appearing very low compared to usual hydroxyl frequencies. This was ascribed to the formation of a strong hydrogen bond. A band at 1480 cm\(^{-1}\) was assigned to an hydroxyl deformation mode, again indicative that proton transfer had taken place. A strong band at 982 cm\(^{-1}\) was taken as evidence of a strongly modified \(\text{P-O}\) group.

Three possible structures have been proposed for the hydrate of triphenylphosphine oxide, \([\text{(C}_6\text{H}_5\)\)_3\text{PO}]_2 \cdot \text{H}_2\text{O}\) (14).
The bridging structure II-a was based on dipole moment studies which determined that the P-O group is very polar. The phosphonium hydroxide structure II-b also was proposed to account for the polar nature of the hydrate. Structure II-c was based on the premise that the P-O bond is essentially a double bond and the water adds across it. It accounts for the short P-O bond length observed. Holmann and Pinchas discounted structure II-c by refluxing triphenylphosphine oxide with $^{18}$O$_2$. Upon recovering and drying the triphenylphosphine oxide, it was found to not have become enriched with heavy oxygen as would result if the oxygens were equivalent. The spectrum of triphenylphosphine oxide was little affected by the addition of the water molecule, also ruling out structure II-c. The only differences in the spectrum of the hydrate were a band at 3410 cm$^{-1}$ assigned to the hydroxyl stretching frequency and a decrease of 4 cm$^{-1}$ in the C-H stretching frequency. Both of these
features suggest that the hydrate is held together more by interactions between the phenyl ring and water molecule than by hydrogen bonding to the phosphoryl group.

On the other hand, the complex \([\text{(C}_6\text{H}_5)_3\text{PO}]_2\cdot\text{H}_2\text{O}_2\) appears to be a simple adduct of two triphenylphosphine oxide groups linked by a bridging peroxide molecule. The hydroxyl frequency is found at 3200 cm\(^{-1}\), and the P-O stretching frequency is shifted to 1180 cm\(^{-1}\). A lack of absorption between 1600 and 1700 cm\(^{-1}\) confirms that the compound is not a hydrate (38).
EXPERIMENTAL

Infrared Spectra

The spectra of all complexes were obtained as nujol mulls on potassium bromide plates or as potassium bromide wafers. The region from 4000 to 400 cm⁻¹ was observed with a model 521 Perkin-Elmer grating spectrophotometer.

Reagents

Triphenylphosphine was obtained from Alfa Inorganics, Inc., and from Eastman Organic Chemicals. It was used as received.

Triphenylphosphine oxide was obtained from M and T Chemicals, Inc., and was used as received.

Indium(III) chloride and indium(III) perchlorate 8-hydrate were used as received from Alpha Inorganics, Inc.

The following chemicals were used as received from Fischer Scientific Co.:

Copper(II) chloride 2-hydrate
Cobalt(II) chloride 6-hydrate
Sodium iodide
Copper(II) nitrate 3-hydrate
47% hydriodic acid
Anhydrous diethyl ether

The following reagents were used as received from J. T. Baker Chemical Co.:

Nickel(II) chloride 6-hydrate
Mercury(II) chloride
Nickel(II) carbonate
47% hydrobromic acid
Cobalt(II) nitrate 6-hydrate was used as received from Merck and Co., Inc.
Ethyl acetate and nickel(II) 6-hydrate were used as received from Matheson, Coleman, and Bell, Inc.
Copper(II) perchlorate was obtained from G. Frederick Smith Chemical Co.
Cobalt(II) carbonate was obtained from Allied Chemical Corporation.
Lithium nitrate was obtained from Mallinckrodt Chemical Works.
Dry hydrogen bromide gas was produced by the dropwise addition of bromine to 1,2,3,4-tetrahydronaphthalene. The gas was passed through 1,2,3,4-tetrahydronaphthalene to remove traces of free bromine.
Dry hydrogen chloride gas was prepared by the dropwise addition of concentrated sulfuric acid to solid sodium chloride. The gas was bubbled through concentrated sulfuric acid and a drying tube filled with calcium chloride to remove traces of water.
Pure dry ethanol was prepared by the method of Lund and Bjerrum (39). For procedures not requiring dry ethanol, the reagent was obtained from U. S. Industrial Chemicals.
Nickel(II) bromide, cobalt(II) iodide, nickel(II)
iodide, and cobalt(II) bromide were prepared by the method of Brauer (40).

Copper(I) chloride and copper(I) bromide were prepared by standard methods (41).

Copper(I) iodide was prepared by the method of Mellor (42).

1,2,3,4-tetrahydronaphthalene was obtained from Eastman Organic Chemicals.

Analyses

Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., and by the analysts at South Dakota State University.

Indium was determined qualitatively as indium(III) hydroxide (43). The sample was dissolved in a mixture of concentrated hydrochloric acid and concentrated nitric acid. After boiling to dispel excess nitric acid, the solution was filtered and the filtrate added to a solution of concentrated aqueous ammonia containing ammonium chloride. A white precipitate indicated the presence of indium.

The only syntheses included in this section are those for compounds obtained with indium salts. The procedures for the preparation of the remaining complexes are listed as references with the respective infrared spectrum of each complex.

Dichlorobis(triphenylphosphine oxide)indium(III) Chloride.
When 0.54 g. indium(III) chloride in 10 ml. hot ethanol was added to 3.8 g. triphenylphosphine oxide in 10 ml. hot ethanol, a precipitate formed immediately. The product was isolated by filtration, washed with benzene, and dried to give 1.05 g. (56.5%) of white crystals. See appendix for infrared spectrum.

**Anal.** Calcd for C$_{36}$H$_{30}$P$_2$InO$_2$Cl$_3$: C, 55.70; H, 3.80;

Found: C, 55.54; H, 3.87.

Infrared data indicated that an identical product was obtained from the reaction of 0.50 g. indium(III) chloride with 2.4 g. triphenylphosphine in 15 ml. of a 1:1 mixture of ethanol and carbon tetrachloride. After concentrating to half-volume by boiling and standing in an ice bath, the solution yielded a white solid which was isolated by filtration, washed with cold ethanol, and dried to give 0.83 g. (44.6%) of white crystals.

**Anal.** Found: C, 55.31; H, 3.90.

**Tetrakis(triphenylphosphine oxide)indium(III) Perchlorate.**

This complex was prepared by a modification of the procedure of Carty and Tuck (13). To 2.0 g. triphenylphosphine oxide in 15 ml. carbon tetrachloride was added 1.3 g. indium(III) perchlorate 8-hydrate in 10 ml. methanol. The solution was refluxed for six hours followed by the addition of diethyl ether until turbidity persisted. After vigorous shaking and standing overnight, the solution yielded a white precipitate which was isolated by filtration, washed
with methanol and dried to give 0.33 g. (9.4%) of white crystals. See appendix for infrared spectrum.

**Anal.** Calcd for \(\text{C}_{72} \text{H}_{60} \text{P}_{4} \text{InO}_{16} \text{Cl}_3\): C, 56.66; H, 3.97; Found: C, 57.37; H, 4.15

The infrared spectrum was identical for a product obtained by adding 2.0 g. triphenylphosphine oxide in 15 ml. carbon tetrachloride to 1.3 g. indium(III) perchlorate 8-hydrate in 10 ml. methanol. The solution was concentrated by boiling and diethyl ether added until turbidity persisted. After several hours, the solution was again concentrated and more diethyl ether was added. After twenty-four hours, the viscous solution was again treated with ether, shaken vigorously, and left to stand. After several hours, a precipitate formed which was isolated by filtration, washed with benzene and methanol, and dried to yield 2.5 g. (71.4%) of white crystals.

**Reactions of Triphenylphosphine with Indium(III) Perchlorate 8-hydrate.**

No product was obtained when 0.5 g. indium(III) perchlorate 8-hydrate and 1.5 g. triphenylphosphine were refluxed in 20 ml. dry ethanol for twelve hours followed by the addition of 20 ml. cyclohexane. The solution was then concentrated to a volume of 10 ml. by boiling and 2 ml. cyclohexane added. A precipitate formed which was isolated by filtration, washed with methanol, and air dried to give 0.36 g. of white solid.
The infrared spectrum of the compound contained only bands characteristic of triphenylphosphine. No bands characteristic of the perchlorate ion were present. 

**Anal.** Calcd for $C_{18}H_{15}P$: C, 82.35; H, 5.76; 
Found: C, 80.92; H, 5.90.

When 1.0 g. indium(III) perchlorate 8-hydrate in 10 ml. ethyl acetate was added to an excess of triphenylphosphine (2.8 g.) in 10 ml. of the same solvent, a precipitate formed immediately. Isolation by filtration yielded 0.31 g. of white crystals. The infrared spectrum indicated that only triphenylphosphine was recovered.

**Bis(triphenylphosphine oxide) Hydrogen Perchlorate.**

A solution of 0.5 g. indium(III) perchlorate 8-hydrate and 1.5 g. triphenylphosphine in 20 ml. of a 1:1 mixture of ethanol and carbon tetrachloride was concentrated to half-volume by boiling. The addition of a small amount of diethyl ether resulted in the formation of a white precipitate. The product weighed 1.18 g. (87.4%). The infrared spectrum contains broad bands at 900 and 1235 cm$^{-1}$ characteristic of hydrogen bonds as well as bands characteristic of triphenylphosphine oxide. 

**Anal.** Calcd for $C_{36}H_{31}P_2O_6Cl$: C, 65.75; H, 4.63; 
Found: C, 65.46; H, 4.73.

A solution of 1.5 g. triphenylphosphine and 0.5 g. indium(III) perchlorate 8-hydrate in 20 ml. of a 1:1 mixture of ethanol and carbon tetrachloride was refluxed for six
hours and subsequently concentrated to half-volume by boiling. After several hours in an ice bath, a precipitate formed. Isolation by filtration yielded 1.2 g. (87.6%) of white crystals. Recrystallization from ethanol yielded 1.06 g. (77.4%) of product.

The infrared spectrum of this compound was identical to that of the preceding one and identified it as bis-(triphenylphosphine oxide) hydrogen perchlorate.

Triphenylphosphonium Perchlorate.

A solution of 1.2 g. indium(III) perchlorate 8-hydrate in 10 ml. hot ethyl acetate was added dropwise to 2.0 g. triphenylphosphine in 10 ml. of the same solvent. A precipitate formed immediately and was isolated by filtration after standing in an ice bath for two hours. Washing with methanol and diethyl ether followed by drying yielded 0.88 g. (38.3%) of white crystals. The infrared spectrum contained bands near 2400 and 930 cm\(^{-1}\) indicative of a P-H bond. Bands characteristic of the perchlorate ion were also present.

Anal. Calcd for C\(_{18}\)H\(_{16}\)PO\(_4\)Cl: C, 57.16; H, 4.28; Found: C, 58.64; H, 4.34.

An attempt to recrystallize the compound from a mixture of ethanol and ethyl acetate yielded only triphenylphosphine. The infrared spectrum indicated that the compound had decomposed as the characteristic bands of the perchlorate ion were no longer present and only frequencies associated with triphenylphosphine were observed.
Reactions of Triphenylphosphine Oxide with Hydrogen Bromide.

Hydrogen bromide gas was bubbled through a solution of 2.0 g. triphenylphosphine oxide in 10 ml. 95% ethanol for 15 minutes. The solution was concentrated by boiling until a solid formed. The yellow product weighed 0.56 g. The infrared spectrum showed a medium intensity band at 1150 cm\(^{-1}\) and a strong band at 1120 cm\(^{-1}\) characteristic of coordinated triphenylphosphine oxide.

Hydrogen bromide gas was bubbled through a solution of 5.0 g. triphenylphosphine oxide in 10 ml. 95% ethanol for 30 minutes. The solution was concentrated by boiling until a solid formed. The light brown solid weighed 0.34 g. The infrared spectrum showed very strong bands at 1190 and 1121 cm\(^{-1}\) indicating that only triphenylphosphine oxide is present.

Hydrogen bromide gas was bubbled through a solution of 2.0 g. triphenylphosphine oxide in 25 ml. 95% ethanol. The solution was partially evaporated under a vacuum for several hours and then left to evaporate in air for two weeks. Dark purple crystals were isolated which weighed 0.85 g. The infrared spectrum contained bands indicative of coordinated triphenylphosphine oxide.

Reactions of Triphenylphosphine Oxide with Hydrogen Chloride.

A solution of 5.0 g. triphenylphosphine oxide in 20 ml. of a 1:1 mixture of hot ethanol and concentrated hydrochloric
acid was left to evaporate in air for twenty-four hours and then placed in an ice bath. A white precipitate formed, was isolated by filtration, and dried to give 1.45 g. of product. The infrared spectrum contained the characteristic frequencies of coordinated triphenylphosphine oxide.

Hydrogen chloride gas was bubbled through a solution of 2.0 g. triphenylphosphine oxide in 25 ml. dry ethanol for one and one-half hours. The solvent was then evaporated under a vacuum until nearly dry. Overnight, a slight crop of brown crystals formed. The product weighed 0.75 g. The infrared spectrum showed bands indicative of coordinated triphenylphosphine oxide.

When the preceding reaction was carried out in 95% ethanol, 0.63 g. of crystals were isolated. The infrared spectrum was identical to that of the preceding product.

**Anal. Calcd for C\textsubscript{18}H\textsubscript{16}POCl: C, 68.83; H, 5.13;**

**Found: C, 70.90; H, 5.38.**
DISCUSSION OF RESULTS

Prior to the beginning of this investigation, work with triphenylphosphine, triphenylphosphine oxide and their complexes was being conducted at South Dakota State University. When an attempt was made to identify structural aspects of several unknown compounds through the use of their infrared spectra, it was discovered that no comprehensive study of triphenylphosphine and triphenylphosphine oxide spectral characteristics existed. One unknown compound, which was later found to be \( \text{[CH}_3\text{COCH}_2\text{C(CH}_3\text{)}_2\text{P(C}_6\text{H}_5\text{)}_3\text{]}_2\text{ReCl}_6 \), had a sharp strong band at 1098 cm\(^{-1}\) while another, \( \text{[CH}_3\text{COCH}_2\text{C(CH}_3\text{)}_2\text{P(C}_6\text{H}_5\text{)}_3\text{]}\text{ReCl}_5\text{P(C}_6\text{H}_5\text{)}_3 \), showed a band at 1100 cm\(^{-1}\) and a shoulder at 1087 cm\(^{-1}\). Both showed a band of medium intensity at 720 cm\(^{-1}\). It was not possible to determine from the literature whether these bands arose from P-O, P-M, or P-H bonds. The literature was no more definitive than that the bands perhaps were the result of a four coordinate phosphorus atom. No reference was made to specific substituents of the phosphorus atom or what effect they had on the strength and position of different bands.

At the same time, Majumdar and Bhattacharyya (23) reported the spectra of several triphenylphosphine oxide and triphenylphosphonium salts. They assigned a strong band at 1125 cm\(^{-1}\) as being characteristic of a four coordinate phosphorus atom in triphenylphosphine oxide complexes. No men-
tion was made of absorption in the 720 cm$^{-1}$ region. This omission seemed unusual as a very strong band had been observed near 720 cm$^{-1}$ in the spectra of all triphenylphosphine oxide complexes previously studied.

Triphenylphosphonium salts also have spectra showing a medium intensity band near 720 cm$^{-1}$. However, only tentative assignments of this band had been made and intensity had never been discussed (2) (24).

Work at South Dakota State University with yttrium complexes produced compounds with the formulation $Y[(C_6H_5)_3PO]_xCl_3$, where $X = 3$ or $4$. The spectra of these complexes contained strong bands at 720 and 1148 cm$^{-1}$, and a medium intensity band at 1181 cm$^{-1}$. The latter was of special interest as it is in the same region as the P-O stretching frequency of uncoordinated triphenylphosphine oxide. It was thought that a band in this region might then be of diagnostic utility in distinguishing coordinated from uncomplexed triphenylphosphine oxide.

Since the present investigation was undertaken, Deacon and Green (11) have published an in-depth survey of the spectral characteristics of triphenylphosphine and triphenylphosphine oxide which has answered some of the questions this investigation set out to probe. However, the results presented here contradict some of those reported by Deacon and Green, and cover a broader range of compounds.

Derivatives of metal chloride salts were prepared first
as they are most common. The spectra of these were then compared to those of complexes prepared from the reaction of triphenylphosphine or triphenylphosphine oxide with metal bromides and metal iodides to determine the effect of changing the anion. Then the effect of replacing the halide anion by an oxyanion, nitrate or perchlorate, was studied. Several different types of metals were used: the first row transition metals, nickel, cobalt, and copper, to compare the spectra of side-by-side elements; indium; mercury; and the alkali metals, sodium and lithium, to study the effects of non-transition metals. Nearly all of these complexes have been made previously. However, explanations of the entire spectra are lacking in the literature. Only single bands or small sections of the spectra have been reported in most cases, and no detailed study of the influence of all the above aspects on the band positions has been reported. Results previously obtained for mononuclear rhenium and molybdenum have been included along with the results of trinuclear clusters of rhenium(III).

TRIPHENYLPHOSPHINE OXIDE COMPLEXES

The spectra of all triphenylphosphine oxide complexes are remarkably similar to each other. The main difference is in the position of the P-O stretching frequency.
### Table II. Characteristic Frequencies of Triphenylphosphine Complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\delta$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(C_6H_5)_3P = (L)$</td>
<td>1089 m$^a$</td>
<td>---</td>
</tr>
<tr>
<td>InL$_2$Cl$_3$</td>
<td>1091 s</td>
<td>705 m</td>
</tr>
<tr>
<td>CuL$_3$Cl$_2$</td>
<td>1091 s</td>
<td>705 shld.</td>
</tr>
<tr>
<td>CoL$_2$Cl$_2$</td>
<td>1091 s</td>
<td>705 m</td>
</tr>
<tr>
<td>NiL$_2$Cl$_2$</td>
<td>1092 s</td>
<td>705 m</td>
</tr>
<tr>
<td>HgL$_2$Cl$_2$</td>
<td>1095 s</td>
<td>710 m</td>
</tr>
<tr>
<td>CuL$_3$Br$_3$</td>
<td>1089 m</td>
<td>709 shld.</td>
</tr>
<tr>
<td>CoL$_2$Br$_2$</td>
<td>1092 s</td>
<td>709 m</td>
</tr>
<tr>
<td>NiL$_2$Br$_2$</td>
<td>1091 s</td>
<td>710 m</td>
</tr>
<tr>
<td>CuL$_3$I$_3$</td>
<td>1089 s</td>
<td>---</td>
</tr>
<tr>
<td>CoL$_2$I$_2$</td>
<td>1089 m</td>
<td>708 w</td>
</tr>
<tr>
<td>NiL$_2$I$_2$</td>
<td>1089 m</td>
<td>705 shld.</td>
</tr>
<tr>
<td>CuL$_4$(ClO$_4$)$_2$</td>
<td>1081 vs</td>
<td>---</td>
</tr>
<tr>
<td>CuL$_2$(NO$_3$)$_2$</td>
<td>1089 s</td>
<td>705 m</td>
</tr>
<tr>
<td>CoL$_2$(NO$_3$)$_2$</td>
<td>1089 m</td>
<td>---</td>
</tr>
<tr>
<td>NiL$_2$(NO$_3$)$_2$</td>
<td>1088 m</td>
<td>---</td>
</tr>
</tbody>
</table>

$^a$relative intensities: shld. = shoulder, vw = very weak, w = weak, m = medium, s = strong, vs = very strong
to the phenyl mode ν alone and have been assigned to r. The splitting may be the result of solid state effects (11).)
Upon coordination of the phosphorus atom to a metal ion, the r mode shifts to higher frequencies. For most of the complexes, it is observed between 705 and 710 cm$^{-1}$ (see Table II).

The perchlorate and nitrate derivatives all contain weak to medium bands between 1115 and 1120 cm$^{-1}$ and weak bands at 720 cm$^{-1}$ indicative of coordinated triphenylphosphine oxide. Carty and Tuck (51) reported that triphenylphosphine is oxidized to triphenylphosphine oxide when triphenylphosphine complexes are recrystallized from ethanol-ether mixtures or if an ethanol-ether solution of the complex is left open to the atmosphere for several days. Their results suggested that the oxygen incorporated into the complex comes from either atmospheric oxygen or moisture in the solvent, not from the solvent itself. Thus, since water was present in the solvents used to prepare the nitrate and perchlorate derivatives, it is reasonable that small quantities of triphenylphosphine were oxidized to triphenylphosphine oxide.

The bromide and iodide complexes with triphenylphosphine also contain weak bands near 1120 cm$^{-1}$ and very weak bands or shoulders at 720 cm$^{-1}$. These features are weaker than those of the perchlorate and nitrate spectra and indicate little conversion of the phosphine to the oxide. Very
weak nujol bands are sometimes observed in the 720 cm\(^{-1}\) region, but assigning this band to the \(r\) mode of triphenylphosphine oxide is more reasonable since the \(q\) mode is also present. The moisture for the oxidation may have come from the solvent or it may be that the anhydrous metal iodides and bromides used as starting materials were not completely dry.

**COMPARISON OF TRIPHENYLPHOSPHINE AND TRIPHENYLPHOSPHINE OXIDE SPECTRA**

Triphenylphosphine oxide complexes can be distinguished from triphenylphosphine complexes by observing the regions between 1200 to 1050 cm\(^{-1}\) and 750 to 700 cm\(^{-1}\). Triphenylphosphine oxide complexes are characterized by P-O stretching frequencies between 1160 and 1125 cm\(^{-1}\). The \(q\) mode is observed between 1120 and 1115 cm\(^{-1}\), and the \(r\) mode near 720 cm\(^{-1}\). Triphenylphosphine complexes contain the \(q\) mode near 1090 cm\(^{-1}\) and the \(r\) mode between 705 and 710 cm\(^{-1}\).

The position of the \(q\) mode is dependent on the electronegativity of the substituent of the phosphorus atom. Thus, the frequency of the \(q\) mode decreases in the order 
\[
(C_6H_5)_3PO > (C_6H_5)_3PR^+ > (C_6H_5)_3PM > (C_6H_5)_3P.
\]

The intensity of the \(q\) mode of triphenylphosphine complexes distinguishes this band from the 2\(y\) overtone band of triphenylphosphine oxide complexes in this region. If a band at 1120 cm\(^{-1}\) is also present, the 1090 cm\(^{-1}\) band will be stronger in triphenylphosphine complexes, and the 1120 cm\(^{-1}\) will be stronger
in triphenylphosphine oxide complexes.

The triphenylphosphine complexes in which a band appears at 720 cm\(^{-1}\) due to triphenylphosphine oxide contamination are readily distinguished by the intensity of this band. In the spectra of triphenylphosphine oxide complexes, the \( \nu \) mode occurs as a strong band, and is always more intense than the phenyl modes on either side near 740 and 690 cm\(^{-1}\). However, in complexes containing triphenylphosphine, this band is much weaker than the adjacent phenyl bands. Similarly, triphenylphosphonium salts always contain a band near 720 cm\(^{-1}\) whose intensity is weaker than the adjacent phenyl bands. The intensity of the 720 cm\(^{-1}\) band for these types of compounds appears to decrease in the order \((C_6H_5)_3PO\) > \((C_6H_5)_3PR^+\) > \((C_6H_5)_3PM\).

The phenyl breathing mode \( \rho \) appears consistently as a sharp band at 995 ± 1 cm\(^{-1}\). Therefore it was used to calibrate the band positions for both triphenylphosphine and triphenylphosphine oxide spectra.

It is now possible to make assignments for the bands in the spectra of the triphenylphosphine derivatives of rhenium(IV) mentioned earlier. The complex

\[
[\text{CH}_3\text{COCH}_2\text{C(CH}_3)_2\text{P(C}_6\text{H}_5)_3]\text{ReCl}_6
\]

contained a band at 1098 cm\(^{-1}\) which is assigned to the \( q \) mode of coordinated triphenylphosphine. The complex \([\text{CH}_3\text{COCH}_2\text{C(CH}_3)_2\text{P(C}_6\text{H}_5)_3]\text{ReCl}_5\text{P(C}_6\text{H}_5)_3\) contains two triphenylphosphine molecules in different
environments, thus giving rise to a shoulder and a band in the region of the \( q \) mode of triphenylphosphine. Both spectra contain medium bands at 720 cm\(^{-1} \) characteristic of triphenylphosphonium salts.

**INDIUM(III) COMPLEXES WITH TRIPHENYLPHOSPHINE AND TRIPHENYLPHOSPHINE OXIDE.**

The distinguishing spectral characteristics of triphenylphosphine and triphenylphosphine oxide have been used to determine the composition of several complexes of indium(III) salts.

The spectrum of the compound obtained from a mixture of indium(III) chloride and triphenylphosphine oxide in ethanol conformed to those of other oxide derivatives. However, the spectrum of the product obtained by the reaction of indium(III) chloride and triphenylphosphine in an ethanol-carbon tetrachloride mixture was identical to that of the oxide derivative, and did not contain the distinctive phosphine bands. It is proposed that the reaction proceeds via an ylid mechanism in which the carbon tetrachloride first attacks the triphenylphosphine molecule, creating a site for oxygen substitution:

\[
\text{CCl}_4 + (\text{C}_6\text{H}_5)_3\text{P} \rightarrow (\text{C}_6\text{H}_5)_3\text{P} = \text{CCl}_2 + (\text{C}_6\text{H}_5)_3\text{PCl}_2
\]

Triphenylphosphine oxide is then the attacking ligand in these reactions (52).
Carty and Tuck (13) reported that the four coordinate complex $\text{In}[(\text{C}_6\text{H}_5)_3\text{P}]_3(\text{ClO}_4)_3$ was prepared by refluxing indium(III) perchlorate 8-hydrate with triphenylphosphine in an ethanol-carbon tetrachloride mixture. Our results indicate that once again the triphenylphosphine was oxidized to triphenylphosphine oxide. However, the spectra of the products obtained with triphenylphosphine and triphenylphosphine oxide were not identical as they were with indium(III) chloride. The spectrum of the product obtained from the reaction of indium(III) perchlorate 8-hydrate and triphenylphosphine oxide conformed to those of other oxide derivatives and there is no question that the complex is the expected $\text{In}[(\text{C}_6\text{H}_5)_3\text{PO}]_4(\text{ClO}_4)_3$. However, the spectrum of the product obtained from triphenylphosphine and indium(III) perchlorate 8-hydrate in ethanol and carbon tetrachloride showed anomalous bands not observed in any other spectrum. The conversion of triphenylphosphine to triphenylphosphine oxide was confirmed by the presence of intense absorption at 720 cm$^{-1}$ (the $r$ mode for coordinated triphenylphosphine oxide) and at 1115 cm$^{-1}$ (the $q$ mode). A strong band centered at 1100 cm$^{-1}$ indicated that perchlorate ions were present. However, the spectrum also contained broad bands centered at 900 and 1235 cm$^{-1}$.

Absorption in these regions has been observed in basic salts containing hydrogen bonds. These salts are produced
by the reaction of a base (B) and a strong acid (HY) and
can be formulated as \([BHB]^+\ Y^-\) analogous to the acid salts
\(M^+[XHX]^-\). Although basic salts contain the hydrogen bond in
the cation, the spectra do not differ significantly from those
of the \(HX_2^-\) anions.

Cook investigated several basic salts of pyridine-1-
oxide and hydrogen hexafluoroarsenate(V) and found broad,
strong bands at 1280 and 890 cm\(^{-1}\) which he assigned to \(\nu_2\)
and \(\nu_3\) respectively. These features are indicative of short,
strong hydrogen bonds formulated as \([C\ H\ NO\cdots\ H\cdots\ ONC\ H_5^5]^-\)\(^53\). An X-ray crystal study of \(Q_2\ HA_sF_6\) where \(Q = 1\)-methyl-
2-quinolone showed that the hydrogen bond \([Q\cdots\ H\cdots\ Q]^+\) is
short but does not lie across a symmetry element. However,
the infrared spectrum shows the features associated with
symmetric, short hydrogen bonds (broad bands centered at
1200 and 800 cm\(^{-1}\)) ascribed to "accidental" symmetry in the
complex. The structure is thus described as a pseudo-A type
\(54\).

The product obtained with triphenylphosphine and indi-
dium(III) perchlorate 8-hydrate is thus not a coordinated
metal complex at all but rather the basic salt bis(triphenyl-
phosphine oxide) hydrogen perchlorate
\([\{C\ H_6^5\}_3\ PO\cdots\ H\cdots\ OP(C\ H_6^5)^3\}^+\ ClO_4^-\). This formulation is sup-
ported by carbon and hydrogen analyses and a qualitative
test for indium which was negative.
The degree of proton transfer can be related to differences in electronic energy between the free and protonated molecules, \((\text{C}_6\text{H}_5)_3\text{PO}\) and \((\text{C}_6\text{H}_5)_3\text{POH}\). The main contribution to the electronic energy is the amount of back donation from p electrons of oxygen to vacant d orbitals of phosphorus (55). Thus hydrogen bonding predominates over protonation partly because the destruction of backbonding is less and also because protonation removes some negative charge on the oxygen which counterbalances positive charge on the phosphorus. It is even possible that some positive charge may be brought into the vicinity, resulting in repulsion.

\[
(\text{C}_6\text{H}_5)_3\text{P}^{4+}\text{O}^- \ + \ \text{H}^+ \rightarrow (\text{C}_6\text{H}_5)_3\text{P}^{4+}\text{O}^{4+}\text{H}
\]

Hadzi reported that proton transfer can occur only when the vacant proton level of the base is below the occupied level of the acid (37). In his studies, only hydrobromic acid was strong enough to meet these requirements. The formulation of the complex with hydrogen perchlorate as containing a very strong, short hydrogen bond coincides with Hadzi's results since perchloric acid is even stronger than hydrobromic acid. (The excessive amount of water present in indium(III) perchlorate makes it probable that a fairly large amount of perchloric acid is present.)

Because the reactions of triphenylphosphine with both indium(III) chloride and indium(III) perchlorate 8-hydrate in ethanol and carbon tetrachloride failed to produce a
triphenylphosphine indium(III) complex, procedures using different solvents were tried. The reaction product of indium(III) chloride and triphenylphosphine in ethyl acetate (51) showed a spectrum containing bands at 1094 and 705 cm\(^{-1}\), recognized as the \(q\) and \(r\) modes of triphenylphosphine. No bands characteristic of triphenylphosphine oxide were observed. Carbon and hydrogen analyses supported the conclusion that the complex was \(\text{In}[(\text{C}_6\text{H}_5\text{)}_3\text{P}]_2\text{Cl}_3\).

Carty and Tuck listed two methods of preparation of \(\text{In}[(\text{C}_6\text{H}_5\text{)}_3\text{P}]_4(\text{ClO}_4)_3\) (13), neither of which succeed. When ethyl acetate was used as the solvent, the spectrum of the resulting compound contained a medium intensity band at 2400 cm\(^{-1}\) indicative of \(\text{P-H}\) stretching, a strong band at 860 cm\(^{-1}\) assigned to the \(\text{P-H}\) bending mode, and a medium intensity band at 721 cm\(^{-1}\) assigned to the \(r\) mode characteristic of triphenylphosphonium salts. A strong band at 1110 cm\(^{-1}\) is ascribed to the asymmetric stretching mode of the perchlorate ion and hides the \(q\) mode of triphenylphosphonium salts in this region. (The presence of the perchlorate ion is further substantiated by a medium intensity band at 930 cm\(^{-1}\), the symmetric stretching mode; a very strong band at 623 cm\(^{-1}\), the asymmetric bending mode; and a very weak band at 460 cm\(^{-1}\), the symmetric bending mode of the perchlorate ion (56).) On the basis of its spectrum and carbon, hydrogen, and indium analyses, the compound appears to be triphenylphosphonium
perchlorate $\left[\left(\text{C}_6\text{H}_5\right)_3\text{PH}\right]^+\text{ClO}_4^-$. 

Recrystallization of this salt was attempted but only a small amount of sample could be recovered. The spectrum of this product showed no perchlorate bands and no bands near 1110 or 720 cm$^{-1}$. These observations indicated that recrystallization decomposed the original complex and only triphenylphosphine was recovered. Carbon and hydrogen analyses matched with the calculated percentages of triphenylphosphine.

Carty and Tuck also reported that $\text{In}\left[\left(\text{C}_6\text{H}_5\right)_3\text{P}\right]_4\text{(ClO}_4\right)_3$ could be prepared by refluxing the metal perchlorate and ligand in ethanol for twelve hours and precipitating the product with cyclohexane (13). This procedure also yielded a product which could be identified by its spectrum and an indium test (negative) as triphenylphosphine. Similarly, when an excess of triphenylphosphine was reacted with indium(III) perchlorate 8-hydrate in ethyl acetate, only triphenylphosphine was isolated.

**REACTIONS OF HYDROGEN CHLORIDE AND HYDROGEN BROMIDE WITH TRIPHENYLPHOSPHINE OXIDE**

Attempts by Eastland (66) to reproduce Hadzi's adduct $\left(\text{C}_6\text{H}_5\right)_3\text{PO} \cdot \text{HBr}$ (37) once resulted in a product which gave a spectrum containing a strong, broad absorption plateau between 850 and 1030 cm$^{-1}$ with two maxima occurring at 930 cm$^{-1}$ and 1005 cm$^{-1}$. These features suggest the presence of a short, symmetrical hydrogen bond such as $\left[\left(\text{C}_6\text{H}_5\right)_3\text{PO} \cdot \text{H} \cdot \cdot \cdot \text{OP(} \text{C}_6\text{H}_5\right)_3\right]^+\text{Br}^-$. However, no further proof
of the structure is available.

Repeated attempts to reproduce the work of Eastland and Hadzi were unsuccessful. All of the products obtained from the reaction of triphenylphosphine oxide with hydrogen bromide or hydrogen chloride were impure and could not be recrystallized without decomposing. The spectra of the crude products did not conform to those reported by Hadzi (37). No broad bands were observed at 1780, 1480, or 982 cm\(^{-1}\), the characteristic frequencies of \((C_6H_5)PO\cdot HBr\).

The spectra of the reaction products of triphenylphosphine oxide with hydrogen chloride or hydrogen bromide are nearly identical. Both contain strong bands at 1150 cm\(^{-1}\) and a very strong band between 1115 and 1120 cm\(^{-1}\). These features indicate that the triphenylphosphine oxide is coordinated in some way. However, no broad bands characteristic of hydrogen bonds were observed. Qualitative tests for chlorine and bromine were inconclusive, but the carbon and hydrogen analyses indicated the possibility of the complex \((C_6H_5)_3PO\cdot HCl\). Hadzi reported a melting point of 120\(^{\circ}\) C for \((C_6H_5)PO\cdot HCl\) while we observed a melting point of 146 - 148° C for the product of the reaction of triphenylphosphine oxide and hydrogen chloride.

The only significant feature in the spectrum of this product is the presence of two broad weak bands at 2500 and 2170 cm\(^{-1}\) which may be the hydroxyl frequencies of an asymmetrical, double-minimum type hydrogen bond analogous to the
spectra of calcium and barium hydrogen phosphate (35).

Hadzi also reported that the 1:1 adducts are unstable and gradually give off hydrogen chloride or hydrogen bromide, finally resulting in the formation of the hemihydrohalide. The products we obtained are stable, and give identical spectra even after several weeks.

Much more work needs to be done in this area. It is clear that much more strenuous conditions are necessary to prepare these adducts than Hadzi cites. The spectra of the reaction products of both hydrogen bromide and hydrogen chloride contain bands near 3400 and 1700 cm\(^{-1}\) showing the presence of water in the products. It may be that the reaction is very sensitive to the presence of moisture.
SUMMARY

The results of this thesis clearly distinguish the distinctive frequencies of triphenylphosphine and triphenylphosphine oxide complexes. Strong bands between 1115 and 1120 cm$^{-1}$ and near 720 cm$^{-1}$ are characteristic of triphenylphosphine oxide complexes, while bands near 1090 cm$^{-1}$ and between 705 and 710 cm$^{-1}$ are characteristic of triphenylphosphine complexes. The intensity of these bands is also indicative of the ligand.

The spectra of indium(III) complexes with triphenylphosphine showed that triphenylphosphine was oxidized to triphenylphosphine oxide when a mixture of ethanol and carbon tetrachloride was used as the solvent. The reaction product of indium(III) perchlorate 8-hydrate and triphenylphosphine from ethanol and carbon tetrachloride was identified as bis(triphenylphosphine oxide) hydrogen perchlorate. The reaction product of indium(III) perchlorate and triphenylphosphine from ethyl acetate was identified as triphenylphosphonium perchlorate.

Attempts to prepare adducts of triphenylphosphine oxide with hydrogen chloride and hydroger bromide were unsuccessful.
APPENDIX

The infrared absorption spectra are given in the following tables. The spectra were obtained as nujol mulls on potassium bromide plates unless otherwise indicated. The relative intensities are given as follows:

- shld. = shoulder
- vw = very weak
- w = weak
- m = medium
- s = strong
- vs = very strong

Peaks due to nujol appearing at 2950, 1460 and 1375 cm\(^{-1}\) were not reported.
Table III. Infrared Absorption Maxima of Triphenylphosphine (potassium bromide wafer).

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Intensity</th>
<th>Frequency (cm(^{-1}))</th>
<th>Intensity</th>
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<tbody>
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<td>3050</td>
<td>w</td>
<td>1025</td>
<td>m</td>
</tr>
<tr>
<td>1950</td>
<td>vw</td>
<td>995</td>
<td>w</td>
</tr>
<tr>
<td>1890</td>
<td>vw</td>
<td>910</td>
<td>vw</td>
</tr>
<tr>
<td>1810</td>
<td>vw</td>
<td>845</td>
<td>w</td>
</tr>
<tr>
<td>1580</td>
<td>w</td>
<td>750</td>
<td>s</td>
</tr>
<tr>
<td>1480</td>
<td>s</td>
<td>745</td>
<td>shld.</td>
</tr>
<tr>
<td>1440</td>
<td>s</td>
<td>739</td>
<td>vs</td>
</tr>
<tr>
<td>1435</td>
<td>s</td>
<td>690</td>
<td>vs</td>
</tr>
<tr>
<td>1375</td>
<td>shld.</td>
<td>615</td>
<td>w</td>
</tr>
<tr>
<td>1320</td>
<td>vw</td>
<td>545</td>
<td>vs</td>
</tr>
<tr>
<td>1308</td>
<td>w</td>
<td>515</td>
<td>m</td>
</tr>
<tr>
<td>1275</td>
<td>w(broad)</td>
<td>500</td>
<td>s</td>
</tr>
<tr>
<td>1175</td>
<td>w</td>
<td>495</td>
<td>s</td>
</tr>
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<td>1150</td>
<td>w</td>
<td>430</td>
<td>w</td>
</tr>
<tr>
<td>1089</td>
<td>m</td>
<td>415</td>
<td>w</td>
</tr>
<tr>
<td>1068</td>
<td>w</td>
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Table IV. Infrared Absorption Maxima of Dichlorobis-(triphenylphosphine)cobalt(II) (58).

<table>
<thead>
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<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
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<tbody>
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<td>vw</td>
<td>1155</td>
<td>w</td>
</tr>
<tr>
<td>1880</td>
<td>vw</td>
<td>1091</td>
<td>s</td>
</tr>
<tr>
<td>1810</td>
<td>vw</td>
<td>1065</td>
<td>vw</td>
</tr>
<tr>
<td>1660</td>
<td>vw</td>
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<td>m</td>
</tr>
<tr>
<td>1580</td>
<td>vw</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1570</td>
<td>vw</td>
<td>970</td>
<td>w</td>
</tr>
<tr>
<td>1480</td>
<td>s</td>
<td>920</td>
<td>w</td>
</tr>
<tr>
<td>1430</td>
<td>vs</td>
<td>850</td>
<td>w</td>
</tr>
<tr>
<td>1330</td>
<td>vw</td>
<td>740</td>
<td>s</td>
</tr>
<tr>
<td>1300</td>
<td>vw</td>
<td>705</td>
<td>m</td>
</tr>
<tr>
<td>1260</td>
<td>vw</td>
<td>689</td>
<td>s</td>
</tr>
<tr>
<td>1220</td>
<td>vw</td>
<td>611</td>
<td>vw</td>
</tr>
<tr>
<td>1179</td>
<td>w</td>
<td>521</td>
<td>s</td>
</tr>
<tr>
<td>1160</td>
<td>w</td>
<td>499</td>
<td>s</td>
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</table>
Table V. Infrared Absorption Maxima of Dichlorobis-(triphenylphosphine)nickel(II) (59).

<table>
<thead>
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<th>Frequency (cm⁻¹)</th>
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<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
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</thead>
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<td>1070</td>
<td>vw</td>
</tr>
<tr>
<td>1900</td>
<td>vw</td>
<td>1025</td>
<td>m</td>
</tr>
<tr>
<td>1810</td>
<td>vw</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1585</td>
<td>w</td>
<td>970</td>
<td>vw</td>
</tr>
<tr>
<td>1570</td>
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<td>vw</td>
</tr>
<tr>
<td>1480</td>
<td>s</td>
<td>850</td>
<td>w</td>
</tr>
<tr>
<td>1435</td>
<td>vs</td>
<td>741</td>
<td>m</td>
</tr>
<tr>
<td>1330</td>
<td>vw</td>
<td>738</td>
<td>m</td>
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<tr>
<td>1300</td>
<td>vw</td>
<td>705</td>
<td>m</td>
</tr>
<tr>
<td>1280</td>
<td>shld.</td>
<td>690</td>
<td>s</td>
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<tr>
<td>1171</td>
<td>vw</td>
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<td>m</td>
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<td>1162</td>
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<td>m</td>
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<td>vw</td>
<td>440</td>
<td>w</td>
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<tr>
<td>1092</td>
<td>s</td>
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</table>
Table VI. Infrared Absorption Maxima of Dichlorobis-(triphenylphosphine)indium(III) Chloride (51).

<table>
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<th>Intensity</th>
<th>Frequency (cm(^{-1}))</th>
<th>Intensity</th>
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<tbody>
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<td>w</td>
<td>1025</td>
<td>m</td>
</tr>
<tr>
<td>1880</td>
<td>w</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1810</td>
<td>w</td>
<td>970</td>
<td>vw</td>
</tr>
<tr>
<td>1660</td>
<td>w</td>
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<td>vw</td>
</tr>
<tr>
<td>1580</td>
<td>w</td>
<td>840</td>
<td>w</td>
</tr>
<tr>
<td>1565</td>
<td>vw</td>
<td>770</td>
<td>w</td>
</tr>
<tr>
<td>1480</td>
<td>s</td>
<td>741</td>
<td>vs</td>
</tr>
<tr>
<td>1435</td>
<td>vs</td>
<td>705</td>
<td>m</td>
</tr>
<tr>
<td>1330</td>
<td>w</td>
<td>690</td>
<td>vs</td>
</tr>
<tr>
<td>1310</td>
<td>w</td>
<td>613</td>
<td>vw</td>
</tr>
<tr>
<td>1280</td>
<td>shld.</td>
<td>542</td>
<td>vw</td>
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<td>1180</td>
<td>w</td>
<td>523</td>
<td>m</td>
</tr>
<tr>
<td>1160</td>
<td>vw</td>
<td>504</td>
<td>m</td>
</tr>
<tr>
<td>1155</td>
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<td>495</td>
<td>m</td>
</tr>
<tr>
<td>1091</td>
<td>s</td>
<td>445</td>
<td>shld.</td>
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<td>1069</td>
<td>vw</td>
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Table VII. Infrared Absorption Maxima of Chlorotris-
(triphenylphosphine)copper(I) (57).

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
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<tbody>
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<td>1950</td>
<td>w</td>
<td>1025</td>
<td>m</td>
</tr>
<tr>
<td>1900</td>
<td>w</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1810</td>
<td>w</td>
<td>970</td>
<td>vw</td>
</tr>
<tr>
<td>1585</td>
<td>w</td>
<td>910</td>
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</tr>
<tr>
<td>1570</td>
<td>vw</td>
<td>850</td>
<td>vw</td>
</tr>
<tr>
<td>1480</td>
<td>s</td>
<td>750</td>
<td>s</td>
</tr>
<tr>
<td>1435</td>
<td>vs</td>
<td>741</td>
<td>vs</td>
</tr>
<tr>
<td>1325</td>
<td>vw</td>
<td>705</td>
<td>shld.</td>
</tr>
<tr>
<td>1310</td>
<td>w</td>
<td>689</td>
<td>vs</td>
</tr>
<tr>
<td>1180</td>
<td>w</td>
<td>611</td>
<td>w</td>
</tr>
<tr>
<td>1150</td>
<td>w</td>
<td>527</td>
<td>s</td>
</tr>
<tr>
<td>1091</td>
<td>s</td>
<td>502</td>
<td>s</td>
</tr>
<tr>
<td>1070</td>
<td>vw</td>
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Table VIII. Infrared Absorption Maxima of Dichlorobis-(triphenylphosphine)mercury(II) (60).

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<th>Intensity</th>
<th>Frequency (cm(^{-1}))</th>
<th>Intensity</th>
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</thead>
<tbody>
<tr>
<td>1950</td>
<td>vw</td>
<td>1065</td>
<td>vw</td>
</tr>
<tr>
<td>1900</td>
<td>vw</td>
<td>1025</td>
<td>m</td>
</tr>
<tr>
<td>1810</td>
<td>vw</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1580</td>
<td>w</td>
<td>970</td>
<td>w</td>
</tr>
<tr>
<td>1565</td>
<td>vw</td>
<td>920</td>
<td>w</td>
</tr>
<tr>
<td>1480</td>
<td>s</td>
<td>840</td>
<td>w</td>
</tr>
<tr>
<td>1430</td>
<td>vs</td>
<td>759</td>
<td>w</td>
</tr>
<tr>
<td>1330</td>
<td>w</td>
<td>749</td>
<td>m</td>
</tr>
<tr>
<td>1300</td>
<td>w</td>
<td>740</td>
<td>m</td>
</tr>
<tr>
<td>1260</td>
<td>vw</td>
<td>710</td>
<td>m</td>
</tr>
<tr>
<td>1180</td>
<td>w</td>
<td>689</td>
<td>s</td>
</tr>
<tr>
<td>1155</td>
<td>w</td>
<td>522</td>
<td>s</td>
</tr>
<tr>
<td>1095</td>
<td>s</td>
<td>502</td>
<td>s</td>
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</table>
Table IX. Infrared Absorption Maxima of Bromotris-(triphenylphosphine)copper(I) (57).

<table>
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<th>Intensity</th>
<th>Frequency (cm(^{-1}))</th>
<th>Intensity</th>
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</thead>
<tbody>
<tr>
<td>1960</td>
<td>vw</td>
<td>1025</td>
<td>m</td>
</tr>
<tr>
<td>1900</td>
<td>vw</td>
<td>995</td>
<td>w</td>
</tr>
<tr>
<td>1810</td>
<td>vw</td>
<td>965</td>
<td>shld.</td>
</tr>
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<td>1573</td>
<td>vw</td>
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<td>shld.</td>
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<tr>
<td>1568</td>
<td>vw</td>
<td>845</td>
<td>vw</td>
</tr>
<tr>
<td>1480</td>
<td>s</td>
<td>740</td>
<td>s</td>
</tr>
<tr>
<td>1438</td>
<td>vs</td>
<td>731</td>
<td>m</td>
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<td>w</td>
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<td>vw</td>
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<td>shld.</td>
<td>690</td>
<td>vs</td>
</tr>
<tr>
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<td>w</td>
<td>618</td>
<td>w</td>
</tr>
<tr>
<td>1153</td>
<td>w</td>
<td>545</td>
<td>m</td>
</tr>
<tr>
<td>1118</td>
<td>w</td>
<td>520</td>
<td>s</td>
</tr>
<tr>
<td>1089</td>
<td>m</td>
<td>510</td>
<td>s</td>
</tr>
<tr>
<td>1065</td>
<td>vw</td>
<td>490</td>
<td>m</td>
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</table>
Table X. Infrared Absorption Maxima of Dibromobis-(triphenylphosphine)cobalt(II) (58).

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
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<tbody>
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<td>1025</td>
<td>m</td>
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<tr>
<td>1900</td>
<td>vw</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1800</td>
<td>vw</td>
<td>970</td>
<td>w</td>
</tr>
<tr>
<td>1580</td>
<td>vw</td>
<td>840</td>
<td>vw</td>
</tr>
<tr>
<td>1570</td>
<td>shld.</td>
<td>741</td>
<td>s</td>
</tr>
<tr>
<td>1480</td>
<td>s</td>
<td>721</td>
<td>vw</td>
</tr>
<tr>
<td>1440</td>
<td>vs</td>
<td>709</td>
<td>m</td>
</tr>
<tr>
<td>1310</td>
<td>shld.</td>
<td>691</td>
<td>vs</td>
</tr>
<tr>
<td>1179</td>
<td>w</td>
<td>550</td>
<td>w</td>
</tr>
<tr>
<td>1155</td>
<td>w</td>
<td>528</td>
<td>s</td>
</tr>
<tr>
<td>1117</td>
<td>w</td>
<td>503</td>
<td>s</td>
</tr>
<tr>
<td>1092</td>
<td>s</td>
<td>441</td>
<td>w</td>
</tr>
<tr>
<td>1070</td>
<td>vw</td>
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Table XI. Infrared Absorption Maxima of Dibromobis-(triphenylphosphine)nickel(II) (59).

<table>
<thead>
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<th>Frequency (cm⁻¹)</th>
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<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
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<td>m</td>
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<tr>
<td>1900</td>
<td>vw</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1810</td>
<td>vw</td>
<td>970</td>
<td>w</td>
</tr>
<tr>
<td>1650</td>
<td>vw</td>
<td>850</td>
<td>w</td>
</tr>
<tr>
<td>1585</td>
<td>w</td>
<td>741</td>
<td>vs</td>
</tr>
<tr>
<td>1570</td>
<td>w</td>
<td>721</td>
<td>vVw</td>
</tr>
<tr>
<td>1480</td>
<td>s</td>
<td>710</td>
<td>m</td>
</tr>
<tr>
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<td>vs</td>
<td>690</td>
<td>vs</td>
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<td>w</td>
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<tr>
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<td>vw</td>
<td>550</td>
<td>w</td>
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<tr>
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<td>491</td>
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<td>s</td>
<td>448</td>
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<td>shld.</td>
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<td>Intensity</td>
<td>Frequency (cm⁻¹)</td>
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<td>-----------</td>
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</tr>
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<td>w</td>
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<td>m</td>
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<tr>
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<td>w</td>
<td>1025</td>
<td>m</td>
</tr>
<tr>
<td>1810</td>
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<td>w</td>
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<td>vw</td>
</tr>
<tr>
<td>1580</td>
<td>m</td>
<td>910</td>
<td>w</td>
</tr>
<tr>
<td>1570</td>
<td>w</td>
<td>850</td>
<td>w</td>
</tr>
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<td>1480</td>
<td>s</td>
<td>740</td>
<td>vs</td>
</tr>
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<td>1430</td>
<td>vs</td>
<td>720</td>
<td>shld.</td>
</tr>
<tr>
<td>1310</td>
<td>w</td>
<td>690</td>
<td>vs</td>
</tr>
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<td>615</td>
<td>w</td>
</tr>
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<td>1210</td>
<td>w</td>
<td>546</td>
<td>m</td>
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<tr>
<td>1180</td>
<td>w</td>
<td>519</td>
<td>vs</td>
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<tr>
<td>1150</td>
<td>w</td>
<td>510</td>
<td>vs</td>
</tr>
<tr>
<td>1115</td>
<td>w</td>
<td>490</td>
<td>shld.</td>
</tr>
<tr>
<td>1089</td>
<td>s</td>
<td>440</td>
<td>vw</td>
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Table XIII. Infrared Absorption Maxima of Diodobis-(triphenylphosphine)cobalt(II) (58).

<table>
<thead>
<tr>
<th>Frequency (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Intensity</th>
<th>Frequency (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Intensity</th>
</tr>
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<tbody>
<tr>
<td>1950</td>
<td>vw</td>
<td>1025</td>
<td>w</td>
</tr>
<tr>
<td>1880</td>
<td>vw</td>
<td>995</td>
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</tr>
<tr>
<td>1800</td>
<td>vw</td>
<td>920</td>
<td>shld.</td>
</tr>
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<td>vw</td>
<td>850</td>
<td>vw</td>
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<td>vw</td>
<td>745</td>
<td>w</td>
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<td>s</td>
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<td>s</td>
<td>721</td>
<td>vw</td>
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<td>w</td>
<td>708</td>
<td>w</td>
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<td>shld.</td>
<td>691</td>
<td>vs</td>
</tr>
<tr>
<td>1180</td>
<td>shld.</td>
<td>550</td>
<td>w</td>
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<td>w</td>
<td>525</td>
<td>s</td>
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<td>500</td>
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<td>m</td>
<td>489</td>
<td>w</td>
</tr>
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<td>shld.</td>
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Table XIV. Infrared Absorption Maxima of Diiodobis-(triphenylphosphine)nickel(II) (59).

<table>
<thead>
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<th>Intensity</th>
<th>Frequency (cm(^{-1}))</th>
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</thead>
<tbody>
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<td>vw</td>
<td>995</td>
<td>w</td>
</tr>
<tr>
<td>1900</td>
<td>vw</td>
<td>965</td>
<td>shld.</td>
</tr>
<tr>
<td>1810</td>
<td>vw</td>
<td>850</td>
<td>w</td>
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<td>1580</td>
<td>w</td>
<td>755</td>
<td>m</td>
</tr>
<tr>
<td>1565</td>
<td>w</td>
<td>749</td>
<td>m</td>
</tr>
<tr>
<td>1480</td>
<td>s</td>
<td>741</td>
<td>m</td>
</tr>
<tr>
<td>1430</td>
<td>vs</td>
<td>739</td>
<td>m</td>
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<tr>
<td>1310</td>
<td>w</td>
<td>720</td>
<td>w</td>
</tr>
<tr>
<td>1280</td>
<td>s</td>
<td>705</td>
<td>shld.</td>
</tr>
<tr>
<td>1180</td>
<td>w</td>
<td>690</td>
<td>s</td>
</tr>
<tr>
<td>1152</td>
<td>w</td>
<td>548</td>
<td>m</td>
</tr>
<tr>
<td>1115</td>
<td>w</td>
<td>521</td>
<td>s</td>
</tr>
<tr>
<td>1089</td>
<td>m</td>
<td>499</td>
<td>m</td>
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<tr>
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<td>485</td>
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<td>1025</td>
<td>w</td>
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Table XV. Infrared Absorption Maxima of Tetrakis(triphenylphosphine) copper(II) Perchlorate (61).

<table>
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<th>Frequency (cm⁻¹)</th>
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<td>vs</td>
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<tr>
<td>1900</td>
<td>vw</td>
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<td>shld.</td>
</tr>
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<td>1800</td>
<td>vw</td>
<td>1025</td>
<td>m</td>
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<tr>
<td>1580</td>
<td>w</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1570</td>
<td>shld.</td>
<td>920</td>
<td>shld.</td>
</tr>
<tr>
<td>1480</td>
<td>s</td>
<td>850</td>
<td>vw</td>
</tr>
<tr>
<td>1435</td>
<td>vs</td>
<td>742</td>
<td>s</td>
</tr>
<tr>
<td>1330</td>
<td>shld.</td>
<td>721</td>
<td>m</td>
</tr>
<tr>
<td>1310</td>
<td>m</td>
<td>692</td>
<td>vs</td>
</tr>
<tr>
<td>1280</td>
<td>shld.</td>
<td>621</td>
<td>m</td>
</tr>
<tr>
<td>1180</td>
<td>w</td>
<td>549</td>
<td>s</td>
</tr>
<tr>
<td>1163</td>
<td>m</td>
<td>519</td>
<td>s</td>
</tr>
<tr>
<td>1119</td>
<td>m</td>
<td>505</td>
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Table XVI. Infrared Absorption Maxima of Dinitratobis-(triphenylphosphine)copper(II) (61).

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<th>Frequency (cm(^{-1}))</th>
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<td>m</td>
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<tr>
<td>1900</td>
<td>vw</td>
<td>970</td>
<td>w</td>
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<tr>
<td>1810</td>
<td>vw</td>
<td>920</td>
<td>vw</td>
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<td>1750</td>
<td>vw</td>
<td>810</td>
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<tr>
<td>1580</td>
<td>w</td>
<td>750</td>
<td>m</td>
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<tr>
<td>1570</td>
<td>w</td>
<td>740</td>
<td>s</td>
</tr>
<tr>
<td>1480</td>
<td>s</td>
<td>720</td>
<td>m</td>
</tr>
<tr>
<td>1440</td>
<td>vs</td>
<td>705</td>
<td>m</td>
</tr>
<tr>
<td>1330</td>
<td>w</td>
<td>691</td>
<td>vs</td>
</tr>
<tr>
<td>1310</td>
<td>w</td>
<td>631</td>
<td>w</td>
</tr>
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<td>s</td>
<td>621</td>
<td>w</td>
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<tr>
<td>1180</td>
<td>w</td>
<td>612</td>
<td>w</td>
</tr>
<tr>
<td>1155</td>
<td>m</td>
<td>548</td>
<td>m</td>
</tr>
<tr>
<td>1115</td>
<td>m</td>
<td>525</td>
<td>m</td>
</tr>
<tr>
<td>1089</td>
<td>s</td>
<td>506</td>
<td>m</td>
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<tr>
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<td>shld.</td>
<td>495</td>
<td>m</td>
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<tr>
<td>1020</td>
<td>m</td>
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Table XVII. Infrared Absorption Maxima of Dinitratobis-(triphenylphosphine)cobalt(II) (61).

<table>
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<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
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<td>1025</td>
<td>m</td>
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<td>1880</td>
<td>vw</td>
<td>995</td>
<td>m</td>
</tr>
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<td>vw</td>
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</tr>
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<td>w</td>
<td>920</td>
<td>w</td>
</tr>
<tr>
<td>1440</td>
<td>s</td>
<td>850</td>
<td>w</td>
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<tr>
<td>1325</td>
<td>vw</td>
<td>744</td>
<td>vs</td>
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<td>w</td>
<td>720</td>
<td>m</td>
</tr>
<tr>
<td>1280</td>
<td>w</td>
<td>690</td>
<td>vs</td>
</tr>
<tr>
<td>1175</td>
<td>vw</td>
<td>612</td>
<td>vw</td>
</tr>
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<td>1155</td>
<td>w</td>
<td>545</td>
<td>m</td>
</tr>
<tr>
<td>1120</td>
<td>w</td>
<td>515</td>
<td>m</td>
</tr>
<tr>
<td>1089</td>
<td>m</td>
<td>499</td>
<td>s</td>
</tr>
<tr>
<td>1070</td>
<td>w</td>
<td>491</td>
<td>s</td>
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</table>
Table XVIII. Infrared Absorption Maxima of Dinitratobis-
(triphenylphosphine)nickel(II) (59).

<table>
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<th>Frequency (cm⁻¹)</th>
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<td>w</td>
<td>1025</td>
<td>m</td>
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<tr>
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<td>w</td>
<td>995</td>
<td>m</td>
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<td>1810</td>
<td>w</td>
<td>970</td>
<td>shld.</td>
</tr>
<tr>
<td>1650</td>
<td>w</td>
<td>910</td>
<td>w</td>
</tr>
<tr>
<td>1580</td>
<td>m</td>
<td>850</td>
<td>w</td>
</tr>
<tr>
<td>1570</td>
<td>shld.</td>
<td>750</td>
<td>shld.</td>
</tr>
<tr>
<td>1480</td>
<td>s</td>
<td>740</td>
<td>vs</td>
</tr>
<tr>
<td>1435</td>
<td>s</td>
<td>720</td>
<td>m</td>
</tr>
<tr>
<td>1320</td>
<td>vw</td>
<td>690</td>
<td>vs</td>
</tr>
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<td>1305</td>
<td>w</td>
<td>631</td>
<td>w</td>
</tr>
<tr>
<td>1280</td>
<td>w</td>
<td>621</td>
<td>w</td>
</tr>
<tr>
<td>1175</td>
<td>w</td>
<td>612</td>
<td>w</td>
</tr>
<tr>
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<td>vw</td>
<td>549</td>
<td>m</td>
</tr>
<tr>
<td>1115</td>
<td>w</td>
<td>519</td>
<td>s</td>
</tr>
<tr>
<td>1088</td>
<td>m</td>
<td>500</td>
<td>s</td>
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<td>1067</td>
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Table XIX. Infrared Absorption Maxima of Triphenylphosphine Oxide.

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<td>w</td>
<td>994</td>
<td>m</td>
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<tr>
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<td>w (broad)</td>
<td>980</td>
<td>w</td>
</tr>
<tr>
<td>1820</td>
<td>w (broad)</td>
<td>970</td>
<td>w</td>
</tr>
<tr>
<td>1670</td>
<td>w</td>
<td>922</td>
<td>w</td>
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<td>m</td>
<td>862</td>
<td>w</td>
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<td>1565</td>
<td>vw</td>
<td>842</td>
<td>w</td>
</tr>
<tr>
<td>1480</td>
<td>m</td>
<td>753</td>
<td>s</td>
</tr>
<tr>
<td>1435</td>
<td>s</td>
<td>748</td>
<td>s</td>
</tr>
<tr>
<td>1310</td>
<td>m</td>
<td>721</td>
<td>vs</td>
</tr>
<tr>
<td>1270</td>
<td>w</td>
<td>693</td>
<td>vs</td>
</tr>
<tr>
<td>1190</td>
<td>vs</td>
<td>618</td>
<td>vw</td>
</tr>
<tr>
<td>1160</td>
<td>shld.</td>
<td>542</td>
<td>vs</td>
</tr>
<tr>
<td>1121</td>
<td>vs</td>
<td>510</td>
<td>m</td>
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<tr>
<td>1093</td>
<td>w</td>
<td>460</td>
<td>w</td>
</tr>
<tr>
<td>1082</td>
<td>m</td>
<td>445</td>
<td>vw</td>
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<tr>
<td>1024</td>
<td>w</td>
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Table XX. Infrared Absorption Maxima of Dichlorobis(triphenylphosphine oxide)indium(III) Chloride (potassium bromide wafer).

<table>
<thead>
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<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
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<td>m</td>
<td>1155</td>
<td>vs</td>
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<td>2960</td>
<td>m</td>
<td>1115</td>
<td>s</td>
</tr>
<tr>
<td>2920</td>
<td>w</td>
<td>1088</td>
<td>m</td>
</tr>
<tr>
<td>1960</td>
<td>w(broad)</td>
<td>1066</td>
<td>w</td>
</tr>
<tr>
<td>1900</td>
<td>w(broad)</td>
<td>1020</td>
<td>w</td>
</tr>
<tr>
<td>1820</td>
<td>w(broad)</td>
<td>994</td>
<td>m</td>
</tr>
<tr>
<td>1630</td>
<td>w</td>
<td>920</td>
<td>vw</td>
</tr>
<tr>
<td>1585</td>
<td>m</td>
<td>845</td>
<td>vw</td>
</tr>
<tr>
<td>1480</td>
<td>m</td>
<td>740</td>
<td>m</td>
</tr>
<tr>
<td>1432</td>
<td>vs</td>
<td>719</td>
<td>s</td>
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<tr>
<td>1380-90</td>
<td>w(broad)</td>
<td>688</td>
<td>s</td>
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<tr>
<td>1330</td>
<td>w</td>
<td>610</td>
<td>w</td>
</tr>
<tr>
<td>1310</td>
<td>w</td>
<td>543</td>
<td>vs</td>
</tr>
<tr>
<td>1260</td>
<td>vw</td>
<td>520</td>
<td>shld.</td>
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<tr>
<td>1180</td>
<td>shld.</td>
<td>455</td>
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<td></td>
<td></td>
<td>440</td>
<td>w</td>
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Table XXI. Infrared Absorption Maxima of Dichlorobis-(triphenylphosphine oxide)copper(II) (62).

<table>
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<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
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</thead>
<tbody>
<tr>
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<td>1068</td>
<td>m</td>
</tr>
<tr>
<td>1900</td>
<td>vw</td>
<td>1020</td>
<td>w</td>
</tr>
<tr>
<td>1820</td>
<td>vw</td>
<td>994</td>
<td>m</td>
</tr>
<tr>
<td>1585</td>
<td>w</td>
<td>970</td>
<td>w</td>
</tr>
<tr>
<td>1480</td>
<td>w</td>
<td>920</td>
<td>vw</td>
</tr>
<tr>
<td>1440</td>
<td>s</td>
<td>845</td>
<td>vw(broad)</td>
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<td>m</td>
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<tr>
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<td>w</td>
<td>745</td>
<td>m</td>
</tr>
<tr>
<td>1182</td>
<td>vw</td>
<td>719</td>
<td>vs</td>
</tr>
<tr>
<td>1165</td>
<td>shld.</td>
<td>690</td>
<td>s</td>
</tr>
<tr>
<td>1138</td>
<td>s</td>
<td>545</td>
<td>vs</td>
</tr>
<tr>
<td>1115</td>
<td>s</td>
<td>541</td>
<td>vs</td>
</tr>
<tr>
<td>1080</td>
<td>m</td>
<td>465</td>
<td>vw</td>
</tr>
<tr>
<td></td>
<td></td>
<td>440</td>
<td>vs</td>
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</table>
Table XXII. Infrared Absorption Maxima of Dichlorobis-(triphenylphosphine oxide)cobalt(II) (63).

<table>
<thead>
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<th>Frequency (cm(^{-1}))</th>
<th>Intensity</th>
<th>Frequency (cm(^{-1}))</th>
<th>Intensity</th>
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<td>1020</td>
<td>w</td>
</tr>
<tr>
<td>1900</td>
<td>vw</td>
<td>996</td>
<td>w</td>
</tr>
<tr>
<td>1820</td>
<td>vw</td>
<td>850</td>
<td>vw</td>
</tr>
<tr>
<td>1585</td>
<td>w</td>
<td>756</td>
<td>m</td>
</tr>
<tr>
<td>1480</td>
<td>w</td>
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<td>m</td>
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<td>s</td>
<td>721</td>
<td>vs</td>
</tr>
<tr>
<td>1340</td>
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<td>691</td>
<td>s</td>
</tr>
<tr>
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<td>w</td>
<td>549</td>
<td>vs</td>
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<td>s</td>
<td>541</td>
<td>vs</td>
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<td>1119</td>
<td>s</td>
<td>521</td>
<td>w</td>
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<td>1090</td>
<td>m</td>
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<td>vw</td>
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Table XXIII. Infrared Absorption Maxima of Dichlorobis-(triphenylphosphine oxide)nickel(II) (64).

<table>
<thead>
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<tr>
<td>1970</td>
<td>w(broad)</td>
<td>1090</td>
<td>shld.</td>
</tr>
<tr>
<td>1900</td>
<td>w(broad)</td>
<td>1029</td>
<td>w</td>
</tr>
<tr>
<td>1830</td>
<td>w(broad)</td>
<td>996</td>
<td>m</td>
</tr>
<tr>
<td>1620</td>
<td>w(broad)</td>
<td>975</td>
<td>shld.</td>
</tr>
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<td>w</td>
<td>940</td>
<td>vw</td>
</tr>
<tr>
<td>1480</td>
<td>w</td>
<td>850</td>
<td>w(broad)</td>
</tr>
<tr>
<td>1440</td>
<td>s</td>
<td>750</td>
<td>w</td>
</tr>
<tr>
<td>1310</td>
<td>w</td>
<td>745</td>
<td>m</td>
</tr>
<tr>
<td>1280</td>
<td>vw</td>
<td>719</td>
<td>s</td>
</tr>
<tr>
<td>1189</td>
<td>s</td>
<td>691</td>
<td>s</td>
</tr>
<tr>
<td>1155</td>
<td>m</td>
<td>545</td>
<td>vs</td>
</tr>
<tr>
<td>1118</td>
<td>s</td>
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Table XXIV. Infrared Absorption Maxima of Dichlorobis-
(triphenylphosphine oxide)mercury(II) (36).

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</tr>
<tr>
<td>1900</td>
<td>w (broad)</td>
<td>930</td>
<td>w</td>
</tr>
<tr>
<td>1830</td>
<td>w (broad)</td>
<td>920</td>
<td>w</td>
</tr>
<tr>
<td>1590</td>
<td>w</td>
<td>755</td>
<td>w</td>
</tr>
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<td>s</td>
<td>720</td>
<td>vs</td>
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<td>w</td>
<td>691</td>
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<tr>
<td>1155</td>
<td>s</td>
<td>615</td>
<td>vw</td>
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<td>1115</td>
<td>s</td>
<td>549</td>
<td>vs</td>
</tr>
<tr>
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<td>m</td>
<td>500</td>
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Table XXV. Infrared Absorption Maxima of Dibromobis-(triphenylphosphine oxide)copper(II) (62).

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<tr>
<td>1900</td>
<td>w</td>
<td>1071</td>
<td>m</td>
</tr>
<tr>
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<td>w</td>
<td>1029</td>
<td>m</td>
</tr>
<tr>
<td>1710</td>
<td>w</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1590</td>
<td>w</td>
<td>925</td>
<td>vw</td>
</tr>
<tr>
<td>1480</td>
<td>m</td>
<td>920</td>
<td>shld.</td>
</tr>
<tr>
<td>1435</td>
<td>s</td>
<td>850</td>
<td>w</td>
</tr>
<tr>
<td>1330</td>
<td>vw</td>
<td>746</td>
<td>m</td>
</tr>
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<td>1300</td>
<td>vw</td>
<td>722</td>
<td>s</td>
</tr>
<tr>
<td>1175</td>
<td>s</td>
<td>691</td>
<td>s</td>
</tr>
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<td>shld.</td>
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<td>vw</td>
</tr>
<tr>
<td>1140</td>
<td>s</td>
<td>542</td>
<td>vs</td>
</tr>
<tr>
<td>1120</td>
<td>s</td>
<td>442</td>
<td>w</td>
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</table>
Table XXVI. Infrared Absorption Maxima of Dibromobis-(triphenylphosphine oxide) cobalt(II) (63).

<table>
<thead>
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<th>Intensity</th>
<th>Frequency (cm(^{-1}))</th>
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<tr>
<td>1960</td>
<td>shld.</td>
<td>1025</td>
<td>w</td>
</tr>
<tr>
<td>1900</td>
<td>vw</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1815</td>
<td>vw</td>
<td>970</td>
<td>shld.</td>
</tr>
<tr>
<td>1590</td>
<td>w</td>
<td>920</td>
<td>shld.</td>
</tr>
<tr>
<td>1570</td>
<td>shld.</td>
<td>850</td>
<td>vw</td>
</tr>
<tr>
<td>1480</td>
<td>m</td>
<td>745</td>
<td>m</td>
</tr>
<tr>
<td>1440</td>
<td>vs</td>
<td>690</td>
<td>s</td>
</tr>
<tr>
<td>1335</td>
<td>w</td>
<td>611</td>
<td>shld.</td>
</tr>
<tr>
<td>1310</td>
<td>w</td>
<td>541</td>
<td>vs</td>
</tr>
<tr>
<td>1280</td>
<td>shld.</td>
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<td>w</td>
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<tr>
<td>1086</td>
<td>s</td>
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Table XXVII. Infrared Absorption Maxima of Dibromobis-(triphenylphosphine oxide)nickel(II) (64).

<table>
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<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
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<tr>
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<td>1025</td>
<td>w</td>
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<td>1810</td>
<td>vw</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
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<td>w(broad)</td>
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<td>shld.</td>
</tr>
<tr>
<td>1590</td>
<td>w</td>
<td>920</td>
<td>shld.</td>
</tr>
<tr>
<td>1480</td>
<td>shld.</td>
<td>850</td>
<td>vw</td>
</tr>
<tr>
<td>1440</td>
<td>s</td>
<td>745</td>
<td>m</td>
</tr>
<tr>
<td>1330</td>
<td>shld.</td>
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<td>s</td>
</tr>
<tr>
<td>1310</td>
<td>w</td>
<td>690</td>
<td>s</td>
</tr>
<tr>
<td>1280</td>
<td>shld.</td>
<td>615</td>
<td>shld.</td>
</tr>
<tr>
<td>1180</td>
<td>shld.</td>
<td>541</td>
<td>vs</td>
</tr>
<tr>
<td>1145</td>
<td>s</td>
<td>510</td>
<td>shld.</td>
</tr>
<tr>
<td>1115</td>
<td>s</td>
<td>445</td>
<td>w</td>
</tr>
<tr>
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<td>m</td>
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Table XXVIII. Infrared Absorption Maxima of Diiodobis-(triphenylphosphine oxide)cobalt(II) (63).

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<th>Frequency (cm⁻¹)</th>
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<td>1068</td>
<td>w</td>
</tr>
<tr>
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<td>vw</td>
<td>1025</td>
<td>m</td>
</tr>
<tr>
<td>1770</td>
<td>vw</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1590</td>
<td>w</td>
<td>970</td>
<td>shld.</td>
</tr>
<tr>
<td>1570</td>
<td>shld.</td>
<td>920</td>
<td>shld.</td>
</tr>
<tr>
<td>1480</td>
<td>m</td>
<td>850</td>
<td>vw</td>
</tr>
<tr>
<td>1440</td>
<td>s</td>
<td>745</td>
<td>m</td>
</tr>
<tr>
<td>1330</td>
<td>w</td>
<td>721</td>
<td>s</td>
</tr>
<tr>
<td>1310</td>
<td>w</td>
<td>689</td>
<td>s</td>
</tr>
<tr>
<td>1280</td>
<td>shld.</td>
<td>611</td>
<td>vw</td>
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<td>sh</td>
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<td>vs</td>
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<td>vw</td>
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<td>1117</td>
<td>s</td>
<td>442</td>
<td>w</td>
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<td>m</td>
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Table XXIX. Infrared Absorption Maxima of Diodobis-
(triphenylphosphine oxide)nickel(II) (64).

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<th>Frequency (cm(^{-1}))</th>
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<td>vw</td>
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<td>m</td>
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<tr>
<td>1710</td>
<td>vw</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1590</td>
<td>w</td>
<td>970</td>
<td>w</td>
</tr>
<tr>
<td>1440</td>
<td>s</td>
<td>920</td>
<td>shld.</td>
</tr>
<tr>
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<td>shld.</td>
<td>850</td>
<td>w</td>
</tr>
<tr>
<td>1310</td>
<td>w</td>
<td>750</td>
<td>w</td>
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<td>shld.</td>
<td>722</td>
<td>s</td>
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<tr>
<td>1185</td>
<td>shld.</td>
<td>692</td>
<td>s</td>
</tr>
<tr>
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<td>m</td>
<td>550</td>
<td>vs</td>
</tr>
<tr>
<td>1120</td>
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Table XXX. Infrared Absorption Maxima of Iodopentakis(triphenylphosphine oxide)lithium (65).

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<th>Frequency (cm(^{-1}))</th>
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<tr>
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<td>m</td>
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<tr>
<td>1810</td>
<td>vw</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1590</td>
<td>w</td>
<td>920</td>
<td>shld.</td>
</tr>
<tr>
<td>1570</td>
<td>shld.</td>
<td>850</td>
<td>vw</td>
</tr>
<tr>
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<td>m</td>
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<td>s</td>
<td>747</td>
<td>m</td>
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<tr>
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<td>shld.</td>
<td>720</td>
<td>s</td>
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<tr>
<td>1310</td>
<td>w</td>
<td>690</td>
<td>s</td>
</tr>
<tr>
<td>1280</td>
<td>shld.</td>
<td>615</td>
<td>w</td>
</tr>
<tr>
<td>1185</td>
<td>m</td>
<td>549</td>
<td>s</td>
</tr>
<tr>
<td>1155</td>
<td>shld.</td>
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<td>s</td>
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<td>469</td>
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<td>vw</td>
<td>440</td>
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Table XXXI. Infrared Absorption Maxima of Iodopentakis-(triphenylphosphine oxide)sodium (65).

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<th>Frequency (cm$^{-1}$)</th>
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<tbody>
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</tr>
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<td>1900</td>
<td>w</td>
<td>1029</td>
<td>m</td>
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<tr>
<td>1830</td>
<td>w</td>
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<td>m</td>
</tr>
<tr>
<td>1610</td>
<td>vw</td>
<td>975</td>
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<td>m</td>
<td>925</td>
<td>vw</td>
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<tr>
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<td>w</td>
</tr>
<tr>
<td>1480</td>
<td>m</td>
<td>754</td>
<td>m</td>
</tr>
<tr>
<td>1440</td>
<td>vs</td>
<td>720</td>
<td>vs</td>
</tr>
<tr>
<td>1330</td>
<td>w</td>
<td>691</td>
<td>s</td>
</tr>
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<td>m</td>
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<td>vw</td>
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<tr>
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<td>vw</td>
</tr>
<tr>
<td>1210</td>
<td>m</td>
<td>550</td>
<td>vs</td>
</tr>
<tr>
<td>1185</td>
<td>s</td>
<td>510</td>
<td>w</td>
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<td>w</td>
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Table XXXII. Infrared Absorption Maxima of Tetrakis-(triphenylphosphine oxide)indium(III) Perchlorate.

<table>
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<th>Frequency (cm⁻¹)</th>
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<td>s(broad)</td>
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<td>1900</td>
<td>w(broad)</td>
<td>1085</td>
<td>vs(broad)</td>
</tr>
<tr>
<td>1820</td>
<td>w(broad)</td>
<td>1022</td>
<td>w</td>
</tr>
<tr>
<td>1780</td>
<td>w(broad)</td>
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<td>m</td>
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<td>1590</td>
<td>m</td>
<td>920</td>
<td>w</td>
</tr>
<tr>
<td>1481</td>
<td>m</td>
<td>850</td>
<td>vw</td>
</tr>
<tr>
<td>1440</td>
<td>vs</td>
<td>747</td>
<td>m</td>
</tr>
<tr>
<td>1335</td>
<td>w</td>
<td>721</td>
<td>vs</td>
</tr>
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<td>1312</td>
<td>w</td>
<td>690</td>
<td>s</td>
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<td>1181</td>
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<td>shld.</td>
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<td>1115</td>
<td>vs(broad)</td>
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<td>vs</td>
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Table XXXIII. Infrared Absorption Maxima of Tetrakis-(triphenylphosphine oxide)copper(II) Perchlorate (21).

<table>
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<td>w</td>
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<td>m</td>
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<tr>
<td>1820</td>
<td>w</td>
<td>995</td>
<td>s</td>
</tr>
<tr>
<td>1770</td>
<td>w</td>
<td>970</td>
<td>w</td>
</tr>
<tr>
<td>1680</td>
<td>w</td>
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<td>w</td>
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<tr>
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<td>w</td>
<td>850</td>
<td>w</td>
</tr>
<tr>
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<td>s</td>
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<td>m</td>
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<td>745</td>
<td>m</td>
</tr>
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<td>s</td>
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<td>620</td>
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<td>w</td>
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<td>sh</td>
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<td>1105</td>
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<td>w</td>
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<tr>
<td>1090</td>
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<td>435</td>
<td>m</td>
</tr>
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<td>1071</td>
<td>w</td>
</tr>
<tr>
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<td>1029</td>
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</tr>
<tr>
<td>1890</td>
<td>w</td>
<td>1010</td>
<td>s</td>
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<tr>
<td>1810</td>
<td>w</td>
<td>996</td>
<td>w</td>
</tr>
<tr>
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<td>w</td>
<td>925</td>
<td>w</td>
</tr>
<tr>
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<td>w</td>
<td>850</td>
<td>w</td>
</tr>
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<td>w</td>
<td>759</td>
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<td>w</td>
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<td>s</td>
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<td>1485</td>
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<td>721</td>
<td>vs</td>
</tr>
<tr>
<td>1440</td>
<td>vs</td>
<td>690</td>
<td>s</td>
</tr>
<tr>
<td>1280</td>
<td>s</td>
<td>615</td>
<td>w</td>
</tr>
<tr>
<td>1181</td>
<td>s</td>
<td>542</td>
<td>vs</td>
</tr>
<tr>
<td>1155</td>
<td>s</td>
<td>455</td>
<td>shld.</td>
</tr>
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<td>1119</td>
<td>vs</td>
<td>445</td>
<td>w</td>
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<tr>
<td>1092</td>
<td>m</td>
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Table XXXV. Infrared Absorption Maxima of Dinitratobis-
(triphenylphosphine oxide)cobalt(II) (63).

<table>
<thead>
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<th>Intensity</th>
<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
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<td>1070</td>
<td>m</td>
</tr>
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<td>w</td>
<td>1020</td>
<td>s</td>
</tr>
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<td>1890</td>
<td>w</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1810</td>
<td>w</td>
<td>930</td>
<td>w</td>
</tr>
<tr>
<td>1760</td>
<td>w</td>
<td>920</td>
<td>w</td>
</tr>
<tr>
<td>1710</td>
<td>w</td>
<td>850</td>
<td>w</td>
</tr>
<tr>
<td>1610</td>
<td>w</td>
<td>758</td>
<td>m</td>
</tr>
<tr>
<td>1590</td>
<td>m</td>
<td>745</td>
<td>s</td>
</tr>
<tr>
<td>1570</td>
<td>w</td>
<td>720</td>
<td>vs</td>
</tr>
<tr>
<td>1490</td>
<td>s (broad)</td>
<td>689</td>
<td>s</td>
</tr>
<tr>
<td>1480</td>
<td>shld.</td>
<td>631</td>
<td>vw</td>
</tr>
<tr>
<td>1440</td>
<td>s</td>
<td>621</td>
<td>vw</td>
</tr>
<tr>
<td>1330</td>
<td>w</td>
<td>611</td>
<td>vw</td>
</tr>
<tr>
<td>1280</td>
<td>vs</td>
<td>541</td>
<td>vs</td>
</tr>
<tr>
<td>1180</td>
<td>s</td>
<td>515</td>
<td>shld.</td>
</tr>
<tr>
<td>1155</td>
<td>s</td>
<td>455</td>
<td>shld.</td>
</tr>
<tr>
<td>1119</td>
<td>vs</td>
<td>442</td>
<td>w</td>
</tr>
<tr>
<td>1091</td>
<td>m</td>
<td></td>
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</table>
Table XXXVI. Infrared Absorption Maxima of Dinitrato-
bis(triphenylphosphine oxide)nickel(II)
(63).

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
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</thead>
<tbody>
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<td>w</td>
<td>1069</td>
<td>w</td>
</tr>
<tr>
<td>1900</td>
<td>w</td>
<td>1020</td>
<td>s</td>
</tr>
<tr>
<td>1820</td>
<td>w</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1770</td>
<td>w</td>
<td>925</td>
<td>w</td>
</tr>
<tr>
<td>1710</td>
<td>w</td>
<td>850</td>
<td>w</td>
</tr>
<tr>
<td>1610</td>
<td>w</td>
<td>755</td>
<td>m</td>
</tr>
<tr>
<td>1589</td>
<td>w</td>
<td>740</td>
<td>m</td>
</tr>
<tr>
<td>1570</td>
<td>w</td>
<td>720</td>
<td>vs</td>
</tr>
<tr>
<td>1480</td>
<td>vs (broad)</td>
<td>690</td>
<td>s</td>
</tr>
<tr>
<td>1440</td>
<td>vs</td>
<td>631</td>
<td>vw</td>
</tr>
<tr>
<td>1335</td>
<td>w</td>
<td>621</td>
<td>vw</td>
</tr>
<tr>
<td>1280</td>
<td>s</td>
<td>611</td>
<td>vw</td>
</tr>
<tr>
<td>1175</td>
<td>s</td>
<td>541</td>
<td>vs</td>
</tr>
<tr>
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<td>m</td>
<td>452</td>
<td>shld.</td>
</tr>
<tr>
<td>1115</td>
<td>s</td>
<td>442</td>
<td>w</td>
</tr>
<tr>
<td>1091</td>
<td>w</td>
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Table XXXVII. Infrared Absorption Maxima of Nitrato-pentakis(triphenylphosphine oxide)-lithium (65).

<table>
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<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
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<tbody>
<tr>
<td>1900</td>
<td>w</td>
<td>1029</td>
<td>w</td>
</tr>
<tr>
<td>1820</td>
<td>w</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1590</td>
<td>w</td>
<td>930</td>
<td>vw</td>
</tr>
<tr>
<td>1570</td>
<td>shld.</td>
<td>850</td>
<td>vw</td>
</tr>
<tr>
<td>1480</td>
<td>m</td>
<td>750</td>
<td>m</td>
</tr>
<tr>
<td>1440</td>
<td>s</td>
<td>740</td>
<td>w</td>
</tr>
<tr>
<td>1340</td>
<td>m(broad)</td>
<td>721</td>
<td>s</td>
</tr>
<tr>
<td>1310</td>
<td>shld.</td>
<td>691</td>
<td>s</td>
</tr>
<tr>
<td>1280</td>
<td>shld.</td>
<td>618</td>
<td>w</td>
</tr>
<tr>
<td>1190</td>
<td>s</td>
<td>550</td>
<td>vs</td>
</tr>
<tr>
<td>1160</td>
<td>shld.</td>
<td>456</td>
<td>m</td>
</tr>
<tr>
<td>1119</td>
<td>s</td>
<td>440</td>
<td>shld.</td>
</tr>
<tr>
<td>1071</td>
<td>m</td>
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Table XXXVIII. Infrared Absorption Maxima of Bis(tri-triphenylphosphine oxide) Hydrogen Perchlorate.

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<th>Frequency (cm(^{-1}))</th>
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<td>1980</td>
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<td>995</td>
<td>w</td>
</tr>
<tr>
<td>1900</td>
<td>vw</td>
<td>970</td>
<td>vw</td>
</tr>
<tr>
<td>1810</td>
<td>vw</td>
<td>925-870</td>
<td>m (v. br)</td>
</tr>
<tr>
<td>1581</td>
<td>m</td>
<td>765</td>
<td>w</td>
</tr>
<tr>
<td>1570</td>
<td>shld.</td>
<td>745</td>
<td>m</td>
</tr>
<tr>
<td>1480</td>
<td>m</td>
<td>720</td>
<td>s</td>
</tr>
<tr>
<td>1431</td>
<td>vs</td>
<td>685</td>
<td>s</td>
</tr>
<tr>
<td>1330</td>
<td>shld.</td>
<td>619</td>
<td>s</td>
</tr>
<tr>
<td>1305</td>
<td>w</td>
<td>540</td>
<td>vs</td>
</tr>
<tr>
<td>1250-1220</td>
<td>w (broad)</td>
<td>470</td>
<td>m</td>
</tr>
<tr>
<td>1179</td>
<td>w</td>
<td>435</td>
<td>w</td>
</tr>
<tr>
<td>1115</td>
<td>s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1080</td>
<td>vs (broad)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1025</td>
<td>w</td>
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Table XXXIX. Infrared Absorption Maxima of Triphenylphosphonium Perchlorate.

<table>
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<th>Frequency (cm$^{-1}$)</th>
<th>Intensity</th>
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<td>2405</td>
<td>m</td>
<td>930</td>
<td>w</td>
</tr>
<tr>
<td>1980</td>
<td>vw</td>
<td>910</td>
<td>m</td>
</tr>
<tr>
<td>1925</td>
<td>vw</td>
<td>870</td>
<td>s</td>
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<tr>
<td>1800</td>
<td>vw</td>
<td>860</td>
<td>shld.</td>
</tr>
<tr>
<td>1700</td>
<td>vw</td>
<td>835</td>
<td>vw</td>
</tr>
<tr>
<td>1581</td>
<td>s</td>
<td>765</td>
<td>s</td>
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<tr>
<td>1571</td>
<td>shld.</td>
<td>750</td>
<td>m</td>
</tr>
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<td>1480</td>
<td>s</td>
<td>735</td>
<td>vs</td>
</tr>
<tr>
<td>1440</td>
<td>vs</td>
<td>721</td>
<td>m</td>
</tr>
<tr>
<td>1405</td>
<td>shld.</td>
<td>715</td>
<td>s</td>
</tr>
<tr>
<td>1330</td>
<td>w</td>
<td>695</td>
<td>vs</td>
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<tr>
<td>1310</td>
<td>vw</td>
<td>680</td>
<td>vs</td>
</tr>
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<td>1280</td>
<td>vw</td>
<td>623</td>
<td>vs</td>
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<td>w</td>
<td>615</td>
<td>s</td>
</tr>
<tr>
<td>1165</td>
<td>w</td>
<td>515</td>
<td>vs</td>
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<tr>
<td>1160</td>
<td>vs</td>
<td>492</td>
<td>vs</td>
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<tr>
<td>1110</td>
<td>vs</td>
<td>460</td>
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</tr>
<tr>
<td>1070</td>
<td>vs (broad)</td>
<td>425</td>
<td>m</td>
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<tr>
<td>995</td>
<td>m</td>
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Table XL. Infrared Absorption Maxima of the Reaction Product of Triphenylphosphine Oxide and Hydrogen Bromide.

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<th>Frequency (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Intensity</th>
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<td>vs</td>
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<td>w(broad)</td>
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<td>vw</td>
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<td>w(broad)</td>
<td>1060</td>
<td>m(broad)</td>
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<td>vw</td>
<td>1021</td>
<td>w</td>
</tr>
<tr>
<td>1680</td>
<td>w(broad)</td>
<td>995</td>
<td>m</td>
</tr>
<tr>
<td>1590</td>
<td>w</td>
<td>970</td>
<td>shld.</td>
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<tr>
<td>1481</td>
<td>w</td>
<td>925</td>
<td>shld.</td>
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<td>s</td>
<td>845</td>
<td>shld.</td>
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<td>w</td>
<td>755</td>
<td>w</td>
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<td>shld.</td>
<td>721</td>
<td>vs</td>
</tr>
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<td>1310</td>
<td>vw</td>
<td>691</td>
<td>s</td>
</tr>
<tr>
<td>1270</td>
<td>shld.</td>
<td>612</td>
<td>w</td>
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<td>vw</td>
<td>550</td>
<td>vs</td>
</tr>
<tr>
<td>1150</td>
<td>s</td>
<td>455</td>
<td>w</td>
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Table XLI. Infrared Absorption Maxima of the Reaction Product of Triphenylphosphine Oxide and Hydrogen Chloride.

<table>
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</tr>
<tr>
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<td>w(broad)</td>
<td>1021</td>
</tr>
<tr>
<td>1650</td>
<td>w(broad)</td>
<td>995</td>
</tr>
<tr>
<td>1585</td>
<td>w</td>
<td>925</td>
</tr>
<tr>
<td>1480</td>
<td>shld.</td>
<td>840</td>
</tr>
<tr>
<td>1435</td>
<td>m</td>
<td>745</td>
</tr>
<tr>
<td>1375</td>
<td>m</td>
<td>735</td>
</tr>
<tr>
<td>1335</td>
<td>shld.</td>
<td>719</td>
</tr>
<tr>
<td>1310</td>
<td>vw</td>
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</tr>
<tr>
<td>1150</td>
<td>s</td>
<td>610</td>
</tr>
<tr>
<td>1115</td>
<td>vs</td>
<td>545</td>
</tr>
<tr>
<td>1080</td>
<td>shld.</td>
<td>448</td>
</tr>
</tbody>
</table>
REFERENCES


48. A. K. Majumdar and R. G. Bhattacharyya, private communication.


