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THE COORDINATION PROPERTIES OF TERTIARY PHOSPHINE SULFIDE AND SELENIDES.

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THE COORDINATION PROPERTIES OF
TERTIARY PHOSPHINE SULFIDE AND SELENIDES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

William Earl Slinkard, B.S.

* * * * * *

The Ohio State University
1969

Approved by

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Adviser
Department of Chemistry
ACKNOWLEDGEMENTS

I would like to thank Dr. Devon W. Meek for his interest and encouragement during the course of this investigation and to especially thank my wife, Virginia, for her help in preparing this dissertation and for her patience and consideration during these years of graduate study. I would also like to thank the National Institutes of Health (Grant No. ROI ES 00170) for financial support which allowed me to devote full time to research (1967-1969).
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"The Coordination Properties of Tris(dimethylamino)phosphine Sulfide",

FIELDS OF STUDY

Major Field: Inorganic Chemistry

Studies in Coordination Chemistry. Professor Devon W. Meek
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<td>Electronic Spectrum of Ni(SP₂S)Br₂•1/2THF, CH₃NO₂ Solution.</td>
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<td>24</td>
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<tr>
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INTRODUCTION

Phosphine Oxides

The coordination properties of tertiary phosphine oxides have been studied extensively and these compounds have been found to be excellent ligands. A summary of the work in this area from 1861 to 1962 reports complexes of triphenyl-, tribenzyl-, trimethyl-, triethyl-, and tricyclohexylphosphine oxides with 23 different elements including both metals and non-metals in various oxidation states. The popularity of phosphine oxides as ligands has not diminished in the last few years. Since 1962, as shown in Tables 1 and 2, 47 articles describing complexes of triphenyl- andtrialkylphosphine oxides have appeared. More exotic mono- and bidentate phosphine oxides such as hexamethylphosphoramide, bis(diisopropoxyphosphinyl)methane, bis(di-n-butyl-phosphinyl) methanee, octamethylpyrophosphoramide, nonamethylimidodiphosphoramide, octamethylmethylenediphosphoramide, and imido bis(diphenylphosphine) dioxide have been reported recently and are being studied.

Phosphine oxides also have been used extensively as extractants for various metal ions in analytical chemistry. The efficiency of phosphine oxides to extract metal ions from aqueous solutions follows the same trend as their basicities as measured with
TABLE X
TRIPHENYLPHOSPHINE OXIDE COMPLEXES REPORTED SINCE 1962

<table>
<thead>
<tr>
<th>Lewis Acid</th>
<th>Reference</th>
<th>Lewis Acid</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(I)</td>
<td>2</td>
<td>Re(III)</td>
<td>16</td>
</tr>
<tr>
<td>Na(I)</td>
<td>2</td>
<td>Fe(II)</td>
<td>3</td>
</tr>
<tr>
<td>Mg(II)</td>
<td>3</td>
<td>Fe(III)</td>
<td>3,17</td>
</tr>
<tr>
<td>Ti(IV)</td>
<td>4,5</td>
<td>Co(II)</td>
<td>18</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>6</td>
<td>Cu(II)</td>
<td>19</td>
</tr>
<tr>
<td>V(IV)</td>
<td>6</td>
<td>Ag(I)</td>
<td>2</td>
</tr>
<tr>
<td>Nb(V)</td>
<td>5,7</td>
<td>Zn(II)</td>
<td>3</td>
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<tr>
<td>Ta(V)</td>
<td>5,7</td>
<td>Cd(II)</td>
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<tr>
<td>Cr(II)</td>
<td>8</td>
<td>Hg(I)</td>
<td>20</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>3</td>
<td>Hg(II)</td>
<td>3</td>
</tr>
<tr>
<td>Mo(0)</td>
<td>9,10</td>
<td>Al(III)</td>
<td>3,5</td>
</tr>
<tr>
<td>Mo(IV)</td>
<td>11</td>
<td>Ga(III)</td>
<td>3</td>
</tr>
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<td>Mo(V)</td>
<td>12,13</td>
<td>In(III)</td>
<td>3,21</td>
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<td>W(0)</td>
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<td>Tl(III)</td>
<td>3,22,23</td>
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<td>W(V)</td>
<td>14</td>
<td>Sn(IV)</td>
<td>3,24,25,26</td>
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<td>W(VI)</td>
<td>6,14</td>
<td>Pb(IV)</td>
<td>27</td>
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<tr>
<td>Re(I)</td>
<td>15</td>
<td>Sb(III)</td>
<td>3</td>
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</table>
TABLE 2
TRIALKYLPHOSPHINE\textsuperscript{a} OXIDE COMPLEXES REPORTED SINCE 1962

<table>
<thead>
<tr>
<th>Lewis Acid</th>
<th>Reference</th>
<th>Lewis Acid</th>
<th>Reference</th>
<th>Lewis Acid</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>Mn(II)</td>
<td>41</td>
<td>Cu(II)</td>
<td>41</td>
<td>Si(IV)</td>
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<tr>
<td>Fe(II)</td>
<td>41</td>
<td>Al(III)</td>
<td>42, 45, 46</td>
<td>U(IV)</td>
<td>33, 34</td>
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<tr>
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<td>17, 42</td>
<td>Ga(III)</td>
<td>42, 46</td>
<td>U(V)</td>
<td>35</td>
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<tr>
<td>Co(II)</td>
<td>41, 43</td>
<td>In(III)</td>
<td>46</td>
<td>U(VI)</td>
<td>33, 38, 39, 47, 48</td>
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<tr>
<td>Ni(II)</td>
<td>41</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

\textsuperscript{a}Alkyl = methyl, ethyl, n-butyl, cyclohexyl, or n-octyl.

phenol\textsuperscript{74} or trimethylsilane:\textsuperscript{75} \( (\text{CH}_3\text{O})_3\text{PO} < (\text{C}_6\text{H}_5)_3\text{PO} < (\text{CH}_3)_3\text{PO} < < [(\text{CH}_3)_2\text{N}]_3\text{PO} \). However, bidentate organophosphorous compounds of the type \( R_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})R_2 \) are much more powerful extractants, often by several orders of magnitude, than the corresponding monodentate phosphine oxides.\textsuperscript{73, 76, 77} There is no evidence to indicate delocalization of electrons in the chelate ring. Moreover, chelate ring formation does not involve ionization of a proton from an enol form of the complexes as in the case of \( \beta \)-diketones.\textsuperscript{73} As suggested for other related bidentate phosphine oxides,\textsuperscript{62, 67} it appears that these types of ligands exert a very strong chelating effect.

After studying the extensive and voluminous work with phosphine oxides, one wonders about the analogous phosphine sulfides and selenides. What are their coordination properties? How do they compare
with phosphine oxides? Perhaps before the work done with phosphorous-
sulfur and -selenium ligands is presented, it is advisable to review
the differences and similarities of phosphine chalcogenides themselves.
It is of particular interest to discuss the bonding between the
phosphorous and chalcogenide, as well as oxygen, sulfur, and selenium
ligands in general.

The Nature of the Phosphorous-Chalcogenide Bond

The nature of the bonding between the phosphorous and
chalcogenide in phosphine oxides, sulfides, and selenides has been the
subject of considerable conjecture, especially the role of d-orbitals
in \( \pi \)-bonding.\(^78\) The two extremes of bonding may be represented by forms
I and II, where form I represents a single coordinate bond and form II
represents a \( \sigma \)- and at least one \( \pi \)-bond. \( \pi \pi \)-d\( \pi \) bonding would arise

\[
R_3P^+X^- \leftrightarrow R_3P=X
\]

I II

from the donation of the non-bonding p-electrons of the chalcogenide
into vacant 3d orbitals of phosphorous. This is quite possible on the
basis of symmetry arguments\(^79\) and considerable experimental evidence
also points to a degree of \( \pi \pi \)-d\( \pi \) bonding in the P-X bond.

The bond lengths of some phosphorous chalcogenide compounds
are given in Tables 3 and 4. For comparison the sum of the single bond
covalent radii for the P-X bond is 1.76, 2.14, and 2.27\( \text{Å} \) for oxygen,
sulfur, and selenium respectively.\(^80\) Similarly, the P=S and P=Se
double bonds are 1.94 and 2.07\( \text{Å} \) respectively. The marked
TABLE 3
P-X BOND LENGTHS OF SOME PHOSPHOROUS-CHALCOGENIDE COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Length (Å)</th>
<th>Ref.</th>
<th>Compound</th>
<th>Bond Length (Å)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P₄O₁₀</td>
<td>1.39a</td>
<td>81</td>
<td>(C₂H₅)₃PS</td>
<td>1.864</td>
<td>85</td>
</tr>
<tr>
<td>(CH₃)₃PO</td>
<td>1.48</td>
<td>82</td>
<td>(C₂H₅)₂P(S)P(S)(C₂H₅)₂</td>
<td>1.94</td>
<td>86</td>
</tr>
<tr>
<td>P₄S₅</td>
<td>1.94a</td>
<td>83</td>
<td>CH₃(C₆H₅)P(S)P(S)CH₃(C₆H₅)</td>
<td>1.98</td>
<td>87</td>
</tr>
<tr>
<td>P₄S₇</td>
<td>1.95a</td>
<td>84</td>
<td>(C₂H₅)₃PSe</td>
<td>1.963</td>
<td>85</td>
</tr>
<tr>
<td>P₄S₁₀</td>
<td>1.95a</td>
<td>84</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

aExocyclic P-X bond only.

contraction of the P-X bond from that of the calculated single bond
to the bond length of the N-O bond in trimethylamine oxide, where
no π-bonding is expected, is 1.36Å compared to a calculated single
bond value of 1.36Å.

The infrared and Raman spectra of a number of phosphine oxides shows that as the electronegativity of the substituents on phosphorous increases, the P-O stretching frequency also increases. This is in good agreement with the effects of π-δ bonding. As phosphorous becomes more electropositive in character, the amount of phosphorous-oxygen π-bonding should increase, thus increasing the bond order of
the P-O bond. The linear relationship between the stretching frequency and electronegativity is not as obvious with the P-S bond. However, a normal coordinate analysis has been performed\(^90\) on the \(Z_3^PS\) molecules (\(Z = \text{halogen}\)) and shows that the P-S stretching frequency is strongly influenced by mechanical coupling and that there is appreciable double bonding in the P-S bond. Although the P-S stretching frequency does not show it, the calculated bond orders do show an increase in bond order with an increase in electronegativity of the \(Z\) substituents, as expected for \(p\pi-d\pi\) bonding. These results as well as those for the analogous \(Z_3^PO\) molecules are presented in Table 4. The bond lengths are also included and may be compared with values presented in Table 3. However, the bond lengths of the \(Z_3^PX\) molecules were not determined as accurately as those in the solid \(R_3^PX\) molecules.

### Table 4

**Bond Orders and Lengths for the P-X Bond in \(Z_3^PX\) Molecules**

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v_{P-X}(\text{cm}^{-1}))</th>
<th>Ref.</th>
<th>Bond Order</th>
<th>Ref.</th>
<th>Bond Length (Å)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F_3^PS)</td>
<td>695</td>
<td>91</td>
<td>1.7</td>
<td>90</td>
<td>1.86</td>
<td>95</td>
</tr>
<tr>
<td>(Cl_3^PS)</td>
<td>770</td>
<td>91</td>
<td>1.6</td>
<td>90</td>
<td>1.85</td>
<td>96</td>
</tr>
<tr>
<td>(Br_3^PS)</td>
<td>726</td>
<td>92</td>
<td>1.5</td>
<td>90</td>
<td>1.89</td>
<td>97</td>
</tr>
<tr>
<td>(F_3^PO)</td>
<td>1,415</td>
<td>93</td>
<td>2.22</td>
<td>94</td>
<td>1.45</td>
<td>97</td>
</tr>
<tr>
<td>(Cl_3^PO)</td>
<td>1,290</td>
<td>93,89</td>
<td>1.95</td>
<td>94</td>
<td>1.45</td>
<td>97</td>
</tr>
<tr>
<td>(Br_3^PO)</td>
<td>1,261</td>
<td>89</td>
<td>1.92</td>
<td>94</td>
<td>1.41</td>
<td>97</td>
</tr>
</tbody>
</table>
The bond strength of the P-O bond in various phosphine oxides is between 128 and 156 kcal/mole and the P-S bond strength is around 90 kcal/mole. In contrast, the bond strength of the N-O bond, a single coordinate bond, is between 50 and 70 kcal/mole. Although differences in ionization potentials and interelectronic repulsion may account for small differences in bond energy, the large difference between the P-O and N-O bonds indicates some multiple bonding in the P-O bond. The degree of π-δπ bonding in the P-S bond is less than that of the P-O bond.

The low values of the dipole moments of phosphine chalcogenides compared to amine oxides suggests that some of the negative charge on the chalcogenide has been displaced toward the phosphorous via π-δπ bonding. The amine oxide would have the lowest dipole moment, if the bonds were strictly coordinate, since nitrogen is more electronegative than phosphorous and the N-O single bond is shorter than the P-X single bond. In addition, the estimated value of the P-O coordinate bond is 4.25D, which is considerably greater than that calculated for the P-O unit from experimental data, 2.7D and 2.88D, the P-S unit in phosphine sulfides, 3.1D, or the P-Se unit in phosphine selenides, 3.2D. Without accurate bond lengths, it is impossible to determine whether the increase in dipole moments from oxide to selenide is due primarily to a decrease in the π-δπ bonding or to the increasing length of the P-X bond.

Nuclear magnetic resonance, both 1H and 31P, has been used to show the effects of π-δπ bonding in the P-X bond. The 13C-H coupling
constants of some methyl substituted phosphorous compounds shows that the phosphorous atom in trimethylphosphine oxide more closely resembles a neutral $P$ rather than a $P^+$ so that the $P-O$ bond must have considerable multiple bond character.\textsuperscript{101}

An ASP-LCAO-MO quantum mechanical calculation of $^{31}P$ chemical shifts has been made using $s$, $p$, and $d$ orbitals and allowing full latitude in $\pi$-bonding.\textsuperscript{102} The calculations show that the $^{31}P$ chemical shift may be used to estimate the amount of $p\pi-d\pi$ bonding to phosphorous. The number of $\pi$-electrons indicated on phosphorous (see Table 5) is the total number and does not indicate the distribution among the various bonds. However, for the alkyl and probably the aryl substituents, the $\pi$-electrons will be localized in the $P-X$ bond. It is apparent, then, that there is some multiple bonding in the $P-X$ bond, with the amount of $p\pi-d\pi$ bonding decreasing from oxygen to selenium. Even though the distribution of $\pi$-electrons among the various bonds between phosphorous and substituents having lone pair electrons cannot be determined, nevertheless the total number of $\pi$-electrons does decrease from oxygen to selenium, which is consistent with decreasing $p\pi-d\pi$ bonding in the same sequence.

Proton NMR has also been used to determine the basicity of phosphine oxides and sulfides by measuring the chemical shift of the methyl group bonded to phosphorous as a function of sulfuric acid concentration.\textsuperscript{103} As shown in Table 6, the phosphine chalcogenides are about $10^6$\textsuperscript{-}10\textsuperscript{8} less basic than amine oxides. The large difference in
TABLE 5
π-BONDS TO PHOSPHOROUS IN $Z_3PX$ COMPOUNDS

<table>
<thead>
<tr>
<th>Z</th>
<th>$Z_3$PO</th>
<th>$Z_3$PS</th>
<th>$Z_3$PSe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-$ C$_6$H$_5$</td>
<td>0.40</td>
<td>0.18</td>
<td>$-$</td>
</tr>
<tr>
<td>$-$ CH$_3$</td>
<td>0.35</td>
<td>0.21</td>
<td>$-$</td>
</tr>
<tr>
<td>$-$ SCH$_3$</td>
<td>0.56</td>
<td>0.47</td>
<td>0.30</td>
</tr>
<tr>
<td>$-$ N(CH$_3$)$_2$</td>
<td>1.03</td>
<td>0.93</td>
<td>0.76</td>
</tr>
<tr>
<td>$-$ O$_3$C$_6$H$_5$</td>
<td>1.54</td>
<td>1.22</td>
<td>0.98</td>
</tr>
<tr>
<td>$-$ OCH$_3$</td>
<td>1.63</td>
<td>1.31</td>
<td>1.15</td>
</tr>
</tbody>
</table>

TABLE 6
BASICITIES OF SOME PHOSPHINE CHALCOGENIDES AND SOME RELATED COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>pKa</th>
<th>Compound</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$(C$_6$H$_5$)$_2$PS</td>
<td>$-$4.5</td>
<td>(CH$_3$)$_3$AsO</td>
<td>3.8</td>
</tr>
<tr>
<td>(CH$_3$)$_2$C$_6$H$_5$PS</td>
<td>$-$4.5</td>
<td>(CH$_3$)$_3$NO</td>
<td>4.7</td>
</tr>
<tr>
<td>CH$_3$(C$_6$H$_5$)$_2$PO</td>
<td>$-$3.3</td>
<td>(CH$_3$)$_3$SbO</td>
<td>5.4</td>
</tr>
<tr>
<td>(CH$_3$)$_2$C$_6$H$_5$PO</td>
<td>$-$2.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
basicity may be interpreted on the basis that the lone pair electrons on oxygen or sulfur are used in $p\pi-d\pi$ bonding, whereas in amine oxides, the bond is a coordinate bond, so that electron density is concentrated on the oxygen atom, thereby making it very basic.

In conclusion, the experimental evidence as well as symmetry arguments clearly indicate that there is an appreciable amount of $p\pi-d\pi$ bonding in the phosphorous-chalcogenide bond. The bonding may be represented as being intermediate between form I and II, becoming more like form II as the substituents on phosphorous become more electronegative. Moreover, for the same substituents on phosphorous, the extent of $p\pi-d\pi$ bonding decreases from oxygen to selenium.

Oxygen, Sulfur, and Selenium Ligands in General

Ahrland, Chatt, and Davis have made an extensive survey of the relative affinity of ligands toward metal ions. They have found that

1. There is a considerable difference between the coordinating affinity of the first and second element of each Group of ligand atoms in the periodic table. 2. The acceptor metal atoms may be classified as being in class (a) if they form their most stable complexes with the first ligand atom of each Group or class (b) with some ligand atom other than the first member of the Group. Most metal ions are in class (a), whereas class (b) acceptors generally are the same metal ions which also form stable olefin and iodide complexes. Thus, the relative order of affinity of oxygen, sulfur, and selenium ligands is $O>S>Se$ for class (a) acceptors and $O<S-Se$ for class (b) acceptors. The order of $S$ and $Se$
ligands with class (b) acceptors varies with the acceptor, that is, for some class (b) acceptors the order is S>Se while for others the order may be reversed.

Pearson has extended this classification system considerably to include Lewis acids in general, not just metal ions, and to include Lewis bases.\textsuperscript{106,107} They have been divided into two categories, "soft" and "hard", based mainly on polarizability. The general principle of related affinities of acids and bases has been stated by Pearson as "hard" acids prefer to associate with "hard" bases and "soft" acids prefer to associate with "soft" bases. A "soft" base is defined as one in which the donor atom is of high polarizability and low electronegativity and is easily oxidized or is associated with empty, low-lying orbitals, whereas a "hard" base has the opposite properties, low polarizability and high electronegativity, is hard to reduce, and is associated with empty orbitals of high energy and hence inaccessible. Sulfur and selenium ligands then are classified as "soft" bases whereas oxygen ligands are "hard" bases. Similar definitions based on polarizability apply to "soft" and "hard" acids, which correspond generally to class (a) and (b) metal ions. For later reference, "soft" and borderline metal ions are listed in Table 7, the remaining metal ions are considered "hard" metals.

The preferred interaction of hard-hard and soft-soft acids and bases has been explained\textsuperscript{106,107} using basically two different theories, the ionic-covalent theory\textsuperscript{108,109} and $\pi$-bonding theory,\textsuperscript{110} although other factors such as London forces\textsuperscript{111} and solvation effects\textsuperscript{112} may also be
involved. The ionic-covalent theory states briefly that "hard" acids bind to bases by ionic bonding whereas "soft" acids bind to bases by covalent bonding.

TABLE 7
"SOFT" AND BORDERLINE METAL IONS

<table>
<thead>
<tr>
<th>&quot;Soft&quot;</th>
<th>Borderline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu⁺</td>
<td>Fe²⁺</td>
</tr>
<tr>
<td>Hg⁺</td>
<td>Cu²⁺</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>Sb³⁺</td>
</tr>
<tr>
<td>Pt⁴⁺</td>
<td>Os²⁺</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>Co²⁺</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>Pb²⁺</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>Bi³⁺</td>
</tr>
<tr>
<td>Au⁺</td>
<td>Ni²⁺</td>
</tr>
<tr>
<td>Pd⁴⁺</td>
<td>Sn²⁺</td>
</tr>
<tr>
<td>Tl³⁺</td>
<td>Ir³⁺</td>
</tr>
<tr>
<td>Pt²⁺</td>
<td>Zn²⁺</td>
</tr>
<tr>
<td>Au³⁺</td>
<td>Rh³⁺</td>
</tr>
<tr>
<td>Tl⁺</td>
<td>Ru²⁺</td>
</tr>
</tbody>
</table>

The π-bonding theory of Chatt attributes the main characteristic of class (b) metals to the availability of loosely held outer d-orbital electrons which can form π-bonds with suitable ligands. Suitable ligands would be those in which the basic atom has low-lying empty orbitals such as phosphorous, sulfur, or selenium. In contrast, class (a) metals would have tightly held outer electrons but low-lying orbitals. Class (a) ligands could then form π-bonds in the opposite direction, by donating electrons from the ligand to the empty orbitals of the metal. This would have a repulsive effect with class (b) metals.
Phosphorous-Sulfur and -Selenium Containing Ligands

In general, the bulk of the experimental investigations with phosphorous-sulfur and -selenium ligands has been with thio- and selenophosphinic acids and phosphates of the formula $R_2P(X)Y^-$ and $(RO)_2P(X)Y^-$ ($R = \text{alkyl or aryl group}, X = S \text{ or Se}, \text{and } Y = O, S, \text{ or Se}$). These ligands have been used extensively in industry as intermediates in the synthesis of insecticides, fungicides, and bactericides,\textsuperscript{113,114} as flotation reagents with nonferrous heavy metals,\textsuperscript{115} as oil additives,\textsuperscript{114,115} as vulcanization additives,\textsuperscript{116} and as color additives to plastics.\textsuperscript{117} The coordination properties of these phosphates and phosphinic acids have been studied extensively and have been reviewed several times,\textsuperscript{118-122} however, these reviews are not inclusive as some references have been overlooked. These "soft" ligands can form complexes with a wide variety of metals, both "soft" and "hard", and can act as bidentate ligands by either bridging or forming four-membered chelate rings, or as monodentate ligands.

The ethyl derivatives have been the ligands most extensively studied and with "hard" or borderline metals such as Cr(III), Rh(III), and Ir(III), the diethyldithiophosphate, $(\text{EtO})_2PS_2^-$, was more basic than diethyldithiophosphinic acid, $\text{Et}_2PS_2^-$.\textsuperscript{122} However, with the "soft" metal, Hg(II), the order was reversed.\textsuperscript{123} The ligand field strength of both ligands was comparable to the chloride anion while in a nephelauxetic series both ligands were more covalent than iodide with the dithiophosphate showing a slightly greater effect than the dithiophosphinic acid.\textsuperscript{120,122} When compared to the analogous diseleno derivative, the
Dithiophosphates showed a slightly greater ligand field strength but were less covalent.

The relative order of diethylidithiophosphate (dtp) in a spectrochemical series with related anionic bidentate sulfur ligands such as diethylidithiocarbamate, \( \text{Et}_2\text{NCS}_2^- \) (dtc), ethylthioxanthate, \( \text{Et}_2\text{SCS}_2^- \) (etx), and ethylxanathate, \( \text{Et}_2\text{OCS}_2^- \) (ex) is: dtp < dtc < etx < ex. Jorgensen has proposed an interesting theory to explain this series based on the premise that as the number of lone pairs on sulfur decreases, the difference between the \( \sigma \)-antibonding and \( \pi \)-antibonding effects, \( \Delta \), increases. In order to place dtp at the low end of the series, the P-S bond was assumed to be nearly a single bond so that the maximum number of electron lone pairs would be localized on sulfur. This assumption seems to be in error as the measured P-S bond length in \( (\text{CH}_3\text{O})_2\text{PSS}^-\text{K}^+ \) is 1.96\( \text{Å} \), very close to the calculated P=S double bond length (1.94\( \text{Å} \)) and very much contracted from the calculated P-S single bond length (2.14\( \text{Å} \)). The variations in ligand field strength of sulfur ligands would seem to be a bit more complicated than the estimated number of electron lone pairs on the basic sulfur atom.

In contrast to the extensive research on phosphine oxides and on thio- and selenophosphates and phosphinic acids, it was 1960 before any complexes of phosphine sulfides and selenides were reported, other than a brief mention of a triethylphosphine sulfide complex of Hg(II). Analytical data was presented to show that triphenylphosphine
sulfide formed a complex with Pd(II) and triphenylphosphine selenide
formed complexes with Pd(II) and Sn(IV). Attempts to prepare complexes
of the phosphine sulfide with Co(II), Cu(II), Hg(II), and Sn(IV) were
unsuccessful. No other data was given and ligands of this type were
dismissed as rather poor donors.121,128

In contrast to this generally negative work by coordination
chemists, analytical chemists had shown129,133 that phosphine
sulfides were quite good extractants for "soft" metal ions such as
Cu⁺, Ag⁺, Pd²⁺, Pt²⁺, Hg²⁺, and Au³⁺. In addition, phosphine
sulfides and selenides134,135 formed stable complexes with halogens
and interhalogens similar to phosphine oxides. It is not surprising
then that phosphine sulfides and selenides were soon reinvestigated
as potential ligands.

The first thorough investigation of phosphine sulfides and
selenides as ligands was done in this laboratory.136,138 Soon after, a
large number of complexes of trialkyl- and triphenylphosphine
sulfide,⁵,139-143 tetraalkyldiphosphine disulfide,¹³⁹,¹⁴⁴ and
triphenylphosphine selenide,¹⁴³ were soon reported (Tables 8, 9, and 10).
The work with phosphine sulfides and selenides reveals some
very interesting results and anomalies. Triphenylphosphine sulfide,
which forms complexes with both "hard" and "soft" metals, does not form
complexes with borderline metals such as Co(II), Ni(II), or
Zn(II)⁵,138,¹⁴³ or with the "soft" metal, cadmium(II).¹³⁸ Likewise,
trimethylphosphine sulfide forms complexes with "soft" metals, a "hard"
metal, Sn(IV), and a borderline metal, Zn(II), but not with other
borderline metals such as Co(II) or Ni(II). Tetraalkyldiphosphine

disulfides, $\text{R}_2\text{P(S)P(S)}\text{R}_2$, and tertiary phosphine selenides, however,
form complexes only with "soft" metals except for Zn(II). In addition,
triaalkylphosphine sulfides and tetraalkyldiphosphine disulfides
spontaneously reduce Cu(II) and Cu(I)\textsuperscript{136,138} and Au(III) to Au(I).\textsuperscript{143}
no oxidized species was isolated in these studies.

TABLE 8
TRIPHENYLPHOSPHINE SULFIDE COMPLEXES

<table>
<thead>
<tr>
<th>Compound\textsuperscript{a}</th>
<th>$\nu_{\text{P=S}}$ (cm$^{-1}$)\textsuperscript{b}</th>
<th>Reference</th>
<th>Compound</th>
<th>$\nu_{\text{P=S}}$ (cm$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{L(TiCl}_4\text{)}_2$</td>
<td>575</td>
<td>5</td>
<td>$\text{[AgL}_2\text{]}\text{ClO}_4$</td>
<td>605,595</td>
<td>138</td>
</tr>
<tr>
<td>$\text{LTiBr}_4$</td>
<td>530</td>
<td>5</td>
<td>$\text{LAuCl}$</td>
<td>590</td>
<td>141,140,143</td>
</tr>
<tr>
<td>$\text{LNbCl}_5$</td>
<td>570</td>
<td>5</td>
<td>$\text{LAuCl}_3$</td>
<td>589,596</td>
<td>143,140</td>
</tr>
<tr>
<td>$\text{LTaCl}_5$</td>
<td>570</td>
<td>5</td>
<td>$\text{LHgCl}_2$</td>
<td>593</td>
<td>138,5,142,143</td>
</tr>
<tr>
<td>$\text{L}_2\text{PdCl}_2$</td>
<td>591</td>
<td>138,127,143</td>
<td>$\text{LHgBr}_2$</td>
<td>593</td>
<td>138,128,142,143</td>
</tr>
<tr>
<td>$\text{L}_2\text{PdBr}_2$</td>
<td>587</td>
<td>138</td>
<td>$\text{LHgI}_2$</td>
<td>591</td>
<td>138,142,143</td>
</tr>
<tr>
<td>$\text{L}_2\text{PtCl}_2$</td>
<td>592</td>
<td>138,143</td>
<td>$\text{LA1Br}_3$</td>
<td>576</td>
<td>5</td>
</tr>
<tr>
<td>$\text{[CuL}_4\text{]}\text{ClO}_4$</td>
<td>604</td>
<td>138</td>
<td>$\text{L}_2\text{SnCl}_4$</td>
<td>577</td>
<td>5</td>
</tr>
<tr>
<td>$\text{LCuCl}$</td>
<td>604</td>
<td>142</td>
<td>$\text{LsbCl}_5$</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>$\text{LCuBr}$</td>
<td>602,592</td>
<td>142</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}$\text{L = (C}_6\text{H}_5\text{)}_3\text{PS, } \nu_{\text{P=S}} = 640$ cm$^{-1}$.

\textsuperscript{b}$\nu_{\text{P=S}}$ stretching frequency taken from first reference if more than one reference appears.
TABLE 9
TRIALKYLPHOSPHINE SULFIDE AND TETRAALKYLDIPHOSPHINE DISULFIDE COMPLEXES

<table>
<thead>
<tr>
<th>Compound a, b</th>
<th>vP=S(cm⁻¹)</th>
<th>Reference</th>
<th>Compound</th>
<th>vP=S(cm⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>L_ETiCl₄</td>
<td>-</td>
<td>144</td>
<td>(L_A)₂CdI₂</td>
<td>538</td>
<td>136</td>
</tr>
<tr>
<td>L_ETiBr₄</td>
<td>-</td>
<td>144</td>
<td>L_DCdI₂</td>
<td>588,511</td>
<td>138</td>
</tr>
<tr>
<td>(L_A)₂PdCl₂</td>
<td>527</td>
<td>138</td>
<td>L_ECdI₂</td>
<td>583,531</td>
<td>138</td>
</tr>
<tr>
<td>(L_A)₂PdBr₂</td>
<td>523</td>
<td>138</td>
<td>(L_A)₂HgI₂</td>
<td>528</td>
<td>136</td>
</tr>
<tr>
<td>(L_A)₂PtCl₂</td>
<td>526</td>
<td>138</td>
<td>L_DHgI₂</td>
<td>588,550</td>
<td>138</td>
</tr>
<tr>
<td>[Cu(L_D)₂]ClO₄</td>
<td>598,563</td>
<td>138,136</td>
<td>L_EHgI₂</td>
<td>584,534</td>
<td>138</td>
</tr>
<tr>
<td>[Cu(L_E)₂]ClO₄</td>
<td>590,543</td>
<td>138,136</td>
<td>(L_B)₂SnCl₄</td>
<td>-</td>
<td>139</td>
</tr>
<tr>
<td>[Cu(L_F)₂]ClO₄</td>
<td>596,570</td>
<td>138</td>
<td>(L_C)₂SnCl₄</td>
<td>-</td>
<td>139</td>
</tr>
<tr>
<td>[Ag(L_D)₂]ClO₄</td>
<td>595,559</td>
<td>138</td>
<td>L_GSnCl₄</td>
<td>-</td>
<td>139</td>
</tr>
<tr>
<td>[Ag(L_E)₂]ClO₄</td>
<td>594,547</td>
<td>138</td>
<td>(L_B)₂SnBr₄</td>
<td>-</td>
<td>139</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Zn(L_A)₄</a>₂</td>
<td>537</td>
<td>138</td>
<td>L_GSnBr₄</td>
<td>-</td>
<td>139</td>
</tr>
<tr>
<td>L_DZnCl₂</td>
<td>-</td>
<td>145</td>
<td>L_HSnBr₄</td>
<td>-</td>
<td>139</td>
</tr>
<tr>
<td>(L_A)₂ZnI₂</td>
<td>535</td>
<td>136</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a L_A = (CH₃)₃PS, vP=S = 565 cm⁻¹.
L_B = R₃PS, R = CH₃, C₂H₅, or n-C₃H₇.
L_C = (n-C₄H₉)₃PS.
L_D = (CH₃)₂P(S)P(S)(CH₃)₂, vP=S = 568 cm⁻¹.
L_E = (C₂H₅)₂P(S)P(S)(C₂H₅)₂, vP=S = 549 cm⁻¹.
L_F = (n-C₃H₇)₂P(S)P(S)(n-C₃H₇)₂, vP=S = 583 cm⁻¹.
L_G = RR'P(S)P(S)RR', R=R'=CH₃ or C₂H₅; R = CH₃, R' = C₆H₅.
L_H = (n-C₄H₉)₂P(S)P(S)(n-C₄H₉)₂.

b Because of a lack of sufficient chemical proof (except the Zn complex) tetraalkyldiphosphine disulfide complexes mentioned in ref. 145 are not included.
TABLE 10
TERTIARY PHOSPHINE SELENIDE COMPLEXES

<table>
<thead>
<tr>
<th>Compound</th>
<th>vP=Se(cm⁻¹)</th>
<th>Reference</th>
<th>Compound</th>
<th>vP=Se(cm⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(LA)₂PdCl₂</td>
<td>546</td>
<td>138,143</td>
<td>[Ag(LA)₂ClO₄</td>
<td>551,542</td>
<td>137</td>
</tr>
<tr>
<td>(LB)₂PdCl₂</td>
<td>558</td>
<td>137</td>
<td>(LD)₂CdI₂</td>
<td>480</td>
<td>137</td>
</tr>
<tr>
<td>(LC)₂PdCl₂</td>
<td>528</td>
<td>138</td>
<td>(LA)₂HgCl₂</td>
<td>545</td>
<td>138,143</td>
</tr>
<tr>
<td>(LA)₂PdBr₂</td>
<td>543</td>
<td>138</td>
<td>(LA)₂HgBr₂</td>
<td>545</td>
<td>138,143</td>
</tr>
<tr>
<td>(LA)₂PtCl₂</td>
<td>544</td>
<td>137,143</td>
<td>(LA)₂HgI₂</td>
<td>542</td>
<td>137,143</td>
</tr>
</tbody>
</table>

\[a_{LA} = (C₆H₅)₃PSe, \ \text{vP=Se} = 562 \ \text{cm}^{-1}.
\[L_B = (m-C₇H₇)₃PSe, \ \text{vP=Se} = 574 \ \text{cm}^{-1}.
\[L_C = (p-C₇H₇)₃PSe, \ \text{vP=Se} = 544 \ \text{cm}^{-1}.
\[L_D = (n-C₄H₉)₃PSe, \ \text{vP=Se} = 495 \ \text{cm}^{-1}.

b\text{P=Se stretching frequency taken from first reference if more than one reference appears.}

Unfortunately it is impossible to compare these ligands directly with each other or with other ligands such as phosphine oxides in regard to ligand field strength, covalency of bonding, or other parameters, since all the complexes so far reported have been diamagnetic and, except for Pd(II) and Pt(II), have no visible spectrum. The position of the first band in the visible spectrum has been suggested as a means of comparing the ligand field strength of various ligands toward palladium (II).\textsuperscript{138,146} However, this is only a
qualitative measure at best and comparison to phosphine oxides and other related "hard" bases is not possible.

**Statement of the Research Problem**

Although a number of complexes of phosphine sulfides and a few phosphine selenides have been reported, these complexes did not allow an accurate evaluation of the coordination properties of these ligands to be made or permit a direct comparison of a complete series of these phosphine chalcogenides. Since ligand field theory has been adequately developed for first row transition metals, complexes of these metals would permit much more meaningful information to be obtained. Thus the basis for the research in this dissertation was to obtain a series of first row transition metal complexes with phosphine sulfides and selenides. A comprehensive investigation of the "soft" donor properties of these ligands could then be undertaken with electronic spectra and magnetism. In addition, the oxidation-reduction reactions with certain metals was of interest.
EXPERIMENTAL

**Purchased Chemicals**

All chemicals were reagent grade and used without further purification unless otherwise stated. The following chemicals were freshly distilled under nitrogen before use: phosphorous trichloride, bp 75-76° (lit. value\textsuperscript{147} 75-76°), thiophosphoryl chloride, bp 122-124° (lit. value\textsuperscript{147} 125°), diphenylchlorophosphine, bp\textsubscript{1.0} 124-128° (lit. value\textsuperscript{148} 111-112° at 0.3mm), and tetramethylethylenediamine (TMEDA) from sodium, bp 119-120° (lit. value\textsuperscript{149} 120°). Sulfur was recrystallized at least once from benzene. Grignard and lithium reagents were purchased from commercial sources. All metal salts used were anhydrous unless stated otherwise.

Solvents were anhydrous-reagent grade and were used without further purification unless stated otherwise. Benzene and toluene were dried over sodium wire. Ether (diethyl) used in Grignard or lithium reactions was dried over sodium wire. Tetrahydrofuran (THF) was fractionally distilled from lithium aluminum hydride (bp 65-66°). Dichloromethane and acetonitrile were refluxed over calcium hydride overnight and then fractionally distilled (bp 38-40° and 80-81°, respectively). Nitromethane was washed with 5% sodium bicarbonate, 5% sulfuric acid, dried over calcium chloride, and fractionally distilled from calcium sulfate (bp 100-101°).
Tetramethyldiphosphine disulfide and triphenylphosphine sulfide were purchased from Orgmet, Inc. and M & T Chemicals, Inc. respectively. Bis(diphenylphosphino) methane was first prepared as shown in the experimental section and later purchased from Strem Chemicals, Inc. These chemicals were used without further purification.

**Intermediates**

\[
\text{Me}_2\text{P(S)Br.}^{150}
\]

To a cooled slurry of 43.0g (0.23 mole) of \[\text{Me}_2\text{P(S)P(S)Me}_2\] in 200ml of \(\text{CCl}_4\) was added dropwise 37.8g (0.23 mole) of bromine in 200ml of \(\text{CCl}_4\) with stirring under nitrogen.

\[
\text{Me}_2\text{P(S)P(S)Me}_2 + \text{Br}_2 \rightarrow 2\text{Me}_2\text{P(S)Br} \quad (1)
\]

After stirring the solution an additional hour at room temperature, the \(\text{CCl}_4\) was stripped off under nitrogen, and the residue was vacuum distilled to yield 74.7g (0.43 mole), 92% yield, of dimethylphosphinodithioic bromide, \(\text{bp}^{150}_{1.0} 69-70^\circ\) (lit. value\(^{150}\) 87-88° at 14mm). The compound solidified on standing at room temperature.

\[
\text{(Me}_2\text{N)}_3\text{P.}^{151}
\]

Phosphorous trichloride, 96g (0.70 mole) in 200ml of ether, was added dropwise to a well-stirred solution of 219g (4.9 moles) of \(\text{Me}_2\text{NH}\) in 1000ml of ether which was cooled to \(-15^\circ\) by a butanol-dry ice bath under nitrogen. The white amine hydrochloride

\[
\text{PCl}_3 + 6\text{Me}_2\text{NH} \rightarrow (\text{Me}_2\text{N)}_3\text{P} + 3\text{Me}_2\text{NH}_2\text{Cl} \quad (2)
\]

formed immediately as the \(\text{PCl}_3\) was added. After stirring the mixture overnight at room temperature under nitrogen, the amine hydrochloride
was removed by filtration, the ether stripped off, and the residue vacuum distilled to yield 61.8g (0.38 mole), 54% yield, of tris(dimethylamino)phosphine, $\text{bp}_{15} 56-58^\circ$ (lit. value$^{151}$ 51-52$^\circ$ at 15mm).

**Ph$_2$PNMe$_2$**. To 300g (6.7 moles) of Me$_2$NH in 100ml of ether was added dropwise 220g (1.0 mole) of Ph$_2$PCl under nitrogen at -15$^\circ$ with vigorous stirring. The amine hydrochloride precipitated immediately as the Ph$_2$PCl was being added. After the mixture had stood overnight at room temperature, the amine hydrochloride was removed by filtration, the ether was stripped off, and the residue was vacuum distilled to yield 175g (0.76 mole), 76% yield, of dimethylaminodiphenylphosphine, $\text{bp}_{1.0} 116-120^\circ$ (lit. value$^{152}$ 112$^\circ$ at 2mm).

**Ph$_2$PMe**. Methylmagnesium bromide, 0.75 mole in 250ml of ether, was added dropwise to a well-stirred solution of 132g (0.60 mole) of Ph$_2$PCl in 200ml of ether under nitrogen with cooling. The reaction

\[
\text{Ph}_2\text{PCl} + \text{MeMgBr} \rightarrow \text{Ph}_2\text{PMe} + \text{MgBrCl}
\]

mixture was stirred an additional hour at room temperature, hydrolyzed with 100ml of 15% NH$_4$Cl, and the ether layer was separated and dried. The ether was stripped off and the residue was vacuum distilled to yield 117g (0.59 mole), 98% yield, of diphenylmethylphosphine, $\text{bp}_{1.0} 110-112^\circ$ (lit. value$^{153}$ 108-110$^\circ$ at 0.15mm).
Ph₂P(0)Me. To a rapidly stirred solution of 20.0g (0.10 mole) of Ph₂PMe in 100ml of benzene was added dropwise 13.6g (0.12 mole) of 30% H₂O₂ with occasional cooling. The reaction mixture was stirred an additional 30 minutes, the benzene layer was separated, dried, and the benzene was stripped off. The crystalline material was recrystallized once from benzene to yield 18.2g (0.084 mole), 84% yield, of fluffy, white needles of diphenylmethylphosphine oxide, mp 107-108° (lit. value 104-109°).

Ph₂PMe + H₂O₂ → Ph₂P(0)Me + H₂O

(5)

Ph₂PCH₂PPh₂·TMEDA, 4.64g (0.040 mole), was added dropwise to a solution of 25.6ml (0.040 mole) of n-butyllithium in hexane under nitrogen with stirring. After stirring the reaction mixture a few minutes, 8.0g (0.040 mole) of Ph₂PMe was then added dropwise. The reaction was mildly exothermic and a precipitate formed after stirring 15 minutes. The precipitate was dissolved in 50ml of THF and gave a deep red solution. The resulting solution was added dropwise to 10.1g (0.040 mole) of Ph₂PCl in 20ml of THF. A yellow precipitate formed immediately on mixing. After stirring 1.5 hours, the reaction mixture was poured into 500ml of water. The solid was recovered by filtration, dried under vacuum, and recrystallized once from ethanol to give 5.3g
(0.014 mole), 35% yield, of white, crystalline bis(diphenylphosphino) methane, mp 115-117° (lit. value 155 119-121°).

\[\text{[M(CH}_3\text{CN})_6\text{]}(\text{ClO}_4)_2\text{ and [Cu(CH}_3\text{CN})_4\text{]}(\text{ClO}_4)_2, M=Co or Ni.}^{156,157}\]

Approximately 5ml of acetic anhydride was added to 1.0g of the hydrated metal perchlorate. The reaction mixture was stirred until all the metal perchlorate had dissolved, cooled, and the resulting crystals were collected by filtration under nitrogen. These crystals were redissolved in acetonitrile, ether added, and crystals of \([M(CH}_3\text{CN})_6\text{]}(\text{ClO}_4)_2\) or \([Cu(CH}_3\text{CN})_4\text{]}(\text{ClO}_4)_2\) were collected. \(M=Co\), 1.3g of light pink crystals, 93% yield; \(M=Ni\), 1.1g of light purple crystals, 78% yield; \([Cu(CH}_3\text{CN})_4\text{]}(\text{ClO}_4)_2\), 0.70g of blue crystals, 52% yield.

\[\text{Cu(CH}_3\text{CN})_2\text{Cl}_2\]. To the hydrated copper chloride, 0.50g, was added approximately 5ml of acetic anhydride and stirred until the reaction mixture had cooled to room temperature. The solid was collected, washed with ether, and redissolved in acetonitrile. Ether was added to yield 0.4g of \(\text{Cu(CH}_3\text{CN})_2\text{Cl}_2\) as a light yellow precipitate.

Preparation of Ligands

\((\text{Me}_2\text{N})_3\text{PS}\).^{158} Dimethylamine was passed slowly just over the surface of a well-stirred solution of 170.0g (1.0 mole) of SPCl\(_3\) in 1000ml of CHCl\(_3\) that had been cooled to -15°. A white precipitate and fog from the amine hydrochloride formed immediately as the reagents were

\[\text{SPCl}_3 + 6\text{HNMe}_2 \rightarrow (\text{Me}_2\text{N})_3\text{PS} + 3\text{Me}_2\text{NH}_2\text{Cl} \quad (8)\]
mixed. After 3 hours, a large increase in volume was observed due to an excess of Me₂NH. After the reaction mixture had stood overnight at room temperature under nitrogen, the amine hydrochloride was removed by filtration, the CHCl₃ was stripped off, and the residue was vacuum distilled to give 143.4g (0.74 mole), 74% yield, of tris(dimethylamino)-phosphine sulfide (TDPS), bp₁.0 65-68° (lit. value¹⁵⁹,¹⁶⁰ 61° at 0.1mm and 63° at 1.2mm).

TDPS was also prepared by adding sulfur to the parent phosphine.¹⁶⁰ To a solution of 61.8g (0.38 mole) of (Me₂N)₃P in 200ml

\[(\text{Me}_2\text{N})_3\text{P} + \frac{1}{8}\text{S}_8 \rightarrow (\text{Me}_2\text{N})_3\text{PS}\]  

(9)
of benzene was added 12.2g (0.38 mole) of sulfur in 500ml of hot benzene with stirring under nitrogen. After stirring the solution an additional hour, the benzene was stripped off and the residue was vacuum distilled to yield 62.5g (0.32 mole), 84% yield, of TDPS, bp₁.0 64-66°. The infrared spectra of both samples of TDPS were identical and were comparable to the published spectrum.¹⁶¹ A proton NMR spectrum of the TDPS sample showed a sharp doublet at 7.32τ (CDCl₃ solution with TMS as an internal standard) with Jₚ-H = 11.0cps and J₁₃-C-H = 136cps (lit values 7.38τ,¹⁵⁹,¹⁶² Jₚ-H 11.3cps,¹⁵⁹ 10.8cps,¹⁶² and J₁₃-C-H 136cps¹⁶³).

A methyl iodide derivative of TDPS was prepared by refluxing TDPS with an excess of methyl iodide in nitromethane. A white precipitate was obtained by addition of ether and it was recrystallized twice
from nitromethane-THF to yield white needles of \( [(\text{Me}_2\text{N})_3\text{PSCH}_3]^+\text{I}^- \), mp 119-120°. The proton NMR spectrum of \( [(\text{Me}_2\text{N})_3\text{PSCH}_3]^+\text{I}^- \) showed two sharp doublets at 7.06\( \tau \) (N-CH\(_3\)) and 7.46\( \tau \) (S-CH\(_3\)) (CD\(_3\)NO\(_2\) solution with TMS as in internal standard) with \( J_{\text{PH}} \) of the N(CH\(_3\))\(_2\) group = 11.2cps and \( J_{\text{PH}} \) of the SCH\(_3\) group = 15.5cps. The relative area of the two doublets was approximately 6:1 as expected for alkylation of the sulfur atom.

\[ (\text{Me}_2\text{N})_3\text{PSe} \text{.}^{164} \text{Tris(dimethylamino)phosphine, } 8.15\text{g} \]  
(0.050 mole) in 50ml of acetonitrile, was added to a solution of 13.1g (0.050 mole) of KSeCN in 100ml of acetonitrile with stirring under nitrogen. The reaction mixture was stirred for an hour, the acetonitrile stripped off, and the residue was extracted with 200ml of benzene in 40ml portions. The benzene solution was evaporated to give 11.8g (0.049 mole), 98% yield, of off-white crystalline tris(dimethylamino)phosphine selenide, TDPSe.

TDPSe was extremely soluble in a variety of solvents varying in polarity from acetonitrile to hexane. Recrystallization was not attempted on the majority of the material. An analytical sample was prepared by dissolving TDPSe in ether, evaporating the solution with a
stream of nitrogen so that the temperature was very cold, and then
rapidly pipetting off the mother liquor. This was repeated three
times to yield nearly white crystals, mp 48-49°.

Anal. Calcd. for C₆H₁₆N₃PSe:
  C, 29.77; H, 7.49; Se, 32.61.

Found:    C, 30.69; H, 7.96; Se, 33.13.

Ph₂P(S)NMe₂. To a solution of 11.5g (0.050 mole) of
Ph₂PNMe₂ in 50ml of toluene was added 1.6g (0.050 mole) of sulfur in
300ml of toluene with stirring under nitrogen. The reaction

Ph₂PNMe₂ + 1/8S₈ → Ph₂P(S)NMe₂  (11)
mixture was refluxed 15 minutes, the toluene was stripped off, and the
crystalline material was recrystallized twice from ether-hexane to give
11.2g (0.043 mole), 86% yield, of clear cubes of dimethylaminodiphenyl-
phosphine sulfide, mp 91-91.5° (lit. value 165 88-90°).

Anal. Calcd. for C₁₄H₁₆NPS:
  C, 64.33; H, 6.17; S, 12.25.

Found:    C, 64.33; H, 6.27; S, 12.11.

Ph₂P(Se)NMe₂. A solution of 13.1g (0.050 mole) of KSeCN
and 11.4g (0.050 mole) of Ph₂PNMe₂ in 100ml of acetonitrile was stirred
one hour under nitrogen, the acetonitrile was stripped off, and the

Ph₂PNMe₂ + KSeCN → Ph₂P(Se)NMe₂ + KCN  (12)
solid residue was extracted with 200ml of benzene in 40ml portions. The benzene was evaporated and the solid material was recrystallized twice from ether-hexane to yield 13.9g (0.045 mole), 90% yield, of long, thick white needles of dimethylaminodiphenylphosphine selenide, mp 85-85.5°.

Anal. Calcd. for C_{14}H_{16}NPSe:
C, 54.37; H, 5.54; Se, 25.53.
Found: C, 54.65; H, 5.25; Se, 25.42.

Dimethylphosphinothioic bromide, 13.9g (0.080 mole) in 50ml of benzene, was added to a slurry of 9.3g (0.040 mole) of Ag₂O in 50ml of benzene with rapid stirring under nitrogen.

\[ 2\text{Me}_2\text{P(S)Br} + \text{Ag}_2\text{O} \rightarrow \text{Me}_2\text{P(S)OP(S)Me}_2 + 2\text{AgBr} \]  

The reaction was exothermic. The reaction mixture was refluxed two hours, filtered, and the benzene was stripped off to yield a white solid. The solid was vacuum distilled, bp 118-120°, and recrystallized once from ether-hexane to give 3.0g (0.015 mole), 38% yield, of white, flaky crystals of dimethylphosphinothioic acid anhydride (DPTA), mp 96-99°. The proton NMR of DPTA showed a sharp doublet at 7.98 ppm.

Anal. Calcd. for C₄H₁₂OP₂S₂:
C, 23.76; H, 5.98; S, 31.71.
Found: C, 23.77; H, 6.20; S, 31.40.

(CDCl₃ solution with TMS as an internal standard) with J_{P-H} = 13.0 cps.
\[
\text{Ph}_2\text{P(O)CH}_2\text{P(O)Ph}_2. \text{ To a vigorously stirred solution of 5.0g (0.013 mole) of Ph}_2\text{PCH}_2\text{PPh}_2 \text{ in 200ml of benzene was added dropwise 3.4g (0.030 mole) of 30% H}_2\text{O}_2 \text{ with occasional cooling. After stirring the}
\]
\[
\text{Ph}_2\text{PCH}_2\text{PPh}_2 + 2\text{H}_2\text{O}_2 \rightarrow \text{Ph}_2\text{P(O)CH}_2\text{P(O)Ph}_2 + 2\text{H}_2\text{O} \quad (14)
\]
the mixture for an hour, most of the benzene was stripped off and the mixture was extracted with CH\_2Cl\_2 and dried. The solvent was stripped off and the residue was recrystallized once from benzene to give 4.5g (0.011 mole), 85% yield, of white crystalline methylenebis(diphenylphosphino) dioxide, mp 177-179° (lit. value\textsuperscript{167} 178-180°).

\[
\text{Ph}_2\text{P(O)CH}_2\text{P(S)Ph}_2. \text{ Phenyllithium, 0.022 mole in 10ml of 7:3 benzene-ether solution, was added dropwise to a slurry of 4.32g (0.020 mole) of Ph}_2\text{P(O)Me in 50ml of ether under nitrogen and stirred for an additional 10 minutes. The reaction mixture turned deep reddish-brown and all the material dissolved. This solution was added}
\]
\[
\text{Ph}_2\text{P(O)Me} + \text{Ph}^-\text{Li}^+ \rightarrow \text{Ph}_2\text{P(O)CH}_2^-\text{Li}^+ + \text{PhH} \quad (15)
\]
dropwise to a solution of 4.40g (0.020 mole) of Ph\_2PCL in 20ml of ether.

\[
\text{Ph}_2\text{P(O)CH}_2^-\text{Li}^+ + \text{ClPPh}_2 \rightarrow \text{Ph}_2\text{P(O)CH}_2\text{PPh}_2 + \text{LiCl} \quad (16)
\]
The color of the dropping solution disappeared immediately and a precipitate formed. The reaction mixture was allowed to stand overnight and then treated with 0.64g (0.020 mole) of sulfur
\[ \text{Ph}_2\text{P(O)CH}_2\text{PPh}_2 + \frac{1}{8}\text{S}_8 \rightarrow \text{Ph}_2\text{P(O)CH}_2\text{P(S)Ph}_2 \]  

(17)

in 50 ml of hot benzene, refluxed 10 minutes, and the solvent was stripped off. The gummy residue was extract with chloroform, washed with water, dried, and the chloroform was stripped off to yield a light brown oil. The oil and some crystals were recrystallized from ethanol to give 3.8 g of an off-white solid, mp 203-208°. This solid was recrystallized again from ethanol to yield 3.0 g (0.007 mole), 35% yield, of white crystalline methylenebis(diphenylphosphino) oxide sulfide, mp 213-214° (lit. value 168 213-214°).

\[ \text{Ph}_2\text{P(S)CH}_2\text{P(S)Ph}_2 \]. To a well-stirred solution of 5.0 g (0.013 mole) of Ph$_2$PCH$_2$PPh$_2$ in 20 ml of benzene was added 0.90 g (0.028 mole) of sulfur in 200 ml of benzene under nitrogen.

\[ \text{Ph}_2\text{PCH}_2\text{PPh}_2 + \frac{1}{4}\text{S}_8 \rightarrow \text{Ph}_2\text{P(S)CH}_2\text{P(S)Ph}_2 \]  

(18)

The reaction mixture was refluxed 15 minutes, the benzene stripped off, and the crystalline compound recrystallized once from ethanol to yield 5.1 g (0.011 mole), 85% yield, of long, white needles of methylenebis(diphenylphosphino) disulfide (SP$_2$S), mp 174-175°. The proton NMR of SP$_2$S showed a 1:2:1 triplet at 5.97 δ (CDCl$_3$ solution with TMS as an

Anal. Calcd. for C$_{21}$H$_{22}$P$_2$S$_2$:

C, 66.95; H, 4.95; S, 14.30.

Found: C, 66.89; H, 5.08; S, 14.54.
internal standard) with a $J_{P-H} = 13.0 \text{cps}$. With acetone as a solvent, the triplet was centered at 5.69\(\tau\) with $J_{P-H} = 13.5 \text{cps}$ (lit value\textsuperscript{169} 5.48\(\tau\), $J_{P-H} = 13.5 \text{cps}$ with (CD\textsubscript{3})\textsubscript{2}SO as solvent). There also was a complex phenyl signal between 2 and 3\(\tau\) with the ratio of phenyl to methylene protons approximately 10:1 as expected.

\[
\text{Ph}_2\text{P(Se)CH}_2\text{P(Se)Ph}_2
\]

A solution of 5.0g (0.013 mole) of Ph\textsubscript{2}PCH\textsubscript{2}PPh\textsubscript{2} and 4.0g (0.028 mole) of KSeCN in 300ml of acetonitrile was refluxed 18 hours under nitrogen with stirring. The acetonitrile was stripped off and the solid residue was extracted with 250ml of benzene.

\[
\text{Ph}_2\text{PCH}_2\text{PPPh}_2 + 2\text{KSeCN} \rightarrow \text{Ph}_2\text{P(Se)CH}_2\text{P(Se)Ph}_2 + 2\text{KCN} \quad (19)
\]

The benzene fraction was evaporated to yield an off-white solid which was recrystallized once from ethanol to give 3.76g (0.007 mole), 55% yield, of white crystalline methylenebis(diphenylphosphino) diselenide (SeP\textsubscript{2}Se), mp 183-184\degree. A proton NMR of SeP\textsubscript{2}Se showed a 1:2:1 triplet at 5.63\(\tau\) (CDCl\textsubscript{3} solution with TMS as an internal standard) with $J_{P-H} = 13.0 \text{cps}$ (lit. value\textsuperscript{169} 5.17\(\tau\), $J_{P-H} = 13.4 \text{cps}$ with (CD\textsubscript{3})\textsubscript{2}SO as solvent). There also was a complex phenyl signal between 2 and 3\(\tau\) with the ratio of phenyl to methylene protons approximately 10:1.

Anal. Calcd. for C\textsubscript{21}H\textsubscript{22}P\textsubscript{2}Se\textsubscript{2}:

- C, 55.37; H, 4.09; Se, 29.12.
- Found: C, 55.53; H, 4.08; Se, 29.31.
Reactions and Complexes of $(\text{Me}_2\text{N})_3\text{PS}$ (TDPS)

In general, preparations and filtrations of TDPS compounds as well as all other ligands and their complexes were done under an atmosphere of dry nitrogen.

$[\text{Co(TDPS)}_4](\text{ClO}_4)_2$. To 0.50g (1.0 mmole) of the pink acetonitrile complex $[\text{Co(\text{CH}_3\text{CN})}_6](\text{ClO}_4)_2$ was added 5.0g (25 mmoles) of TDPS. There was an instantaneous color change from pink to bluish-green. The reaction mixture was stirred overnight and then a few ml of ether added to complete precipitation. The green precipitate was collected by filtration and washed with ether, yield 50%.

Anal. Calcd. for $\text{C}_{24}\text{H}_{72}\text{N}_{12}\text{Cl}_2\text{CoO}_8\text{P}_4\text{S}_4$:

$\text{C}$, 27.74; $\text{H}$, 6.98; $\text{Cl}$, 6.82.

Found: $\text{C}$, 27.57; $\text{H}$, 6.91; $\text{Cl}$, 6.86.

$\text{Co(TDPS)}_2\text{Cl}_2$. Cobalt chloride, 0.76g (0.006 mole), was dissolved in 8.0g (0.041 mole) of TDPS. The solution was filtered, ether added just to the point of initiating precipitation, and the reaction mixture allowed to stand for several minutes. The resulting deep blue crystals were collected and washed with hexane, yield 45%.

Anal. Calcd. for $\text{C}_{12}\text{H}_{36}\text{N}_6\text{Cl}_2\text{CoP}_2\text{S}_2$:

$\text{C}$, 27.69; $\text{H}$, 6.98; $\text{Cl}$, 13.63.

Found: $\text{C}$, 27.49; $\text{H}$, 7.18; $\text{Cl}$, 13.96.
The following complexes were prepared in the same manner as the cobalt chloride complex:

**Co(TDPS)_2Br_2.** Turquoise crystals, yield 70%.

Anal. Calcd. for C_{12}H_{36}N_6Br_2CoP_2S_2:
- C, 23.65; H, 5.94; Br, 26.23.
- Found: C, 23.50; H, 5.90; Br, 26.45.

**Co(TDPS)_2I_2.** Dark green crystals, hexane was used to initiate precipitation, yield 93%.

Anal. Calcd. for C_{12}H_{36}N_6CoI_2P_2S_2:
- C, 20.49; H, 5.16; I, 36.09.
- Found: C, 20.46; H, 4.97; I, 35.91.

**[Ni(TDPS)]_4(ClO_4)_2.** The reddish-brown nickel perchlorate complex was prepared in the same manner as the cobalt perchlorate complex, yield 94%. However, in this case, the color change was from light purple to reddish-brown.

Anal. Calcd. for C_{24}H_{72}N_{12}Cl_2NiO_8P_4S_4:
- C, 27.74; H, 6.98; Cl, 6.82.
- Found: C, 27.55; H, 7.13; Cl, 6.73.

**[Cu(TDPS)]_4ClO_4.** TDPS, 5.0g (0.025 mole), was added to 0.48g (0.001 mole) of the blue Cu(II)-acetonitrile complex, [Cu(CH_3CN)_4](ClO_4)_2. The solution became colorless immediately after addition of the ligand. After stirring the reaction mixture for an
hour, the resulting precipitate was collected. Addition of a small amount of ether to the clear filtrate gave white crystalline flakes of the Cu(I) complex, yield 44%.

Anal. Calcd. for $C_{24}H_{72}N_{12}ClCuO_4P_4S_4$:

\[
\begin{align*}
C, & \text{ 30.50; } \text{H, 7.62; } \text{Cl, 3.81.} \\
\text{Found: } & \text{ C, 30.29; H, 7.65; Cl, 3.96.}
\end{align*}
\]

The initial precipitate was washed with THF to remove any traces of $[\text{Cu(TDPS)_4}]\text{ClO}_4$ and recrystallized once from nitromethane-ether to yield white crystals. This material will be shown later to be the perchlorate salt of the oxidized ligand, $[(\text{Me}_2\text{N})_3\text{PS}_2\text{P(NMe}_2\text{)}_3]\text{CuCl}_2$.

Anal. Calcd. for $C_{12}H_{36}N_6\text{Cl}_{12.08}P_2S_2$:

\[
\begin{align*}
C, & \text{ 24.42; } \text{H, 6.16; } \text{Cl, 12.05; S, 10.88.} \\
\text{Found: } & \text{ C, 24.41; H, 6.16; Cl, 12.09; S, 11.12.} \\
\text{Found: } & \text{ 24.56 6.21 12.20 11.03.}
\end{align*}
\]

**Copper(II) Chloride Reaction.** A copper-containing complex was prepared by stirring cupric chloride in approximately a tenfold excess of TDPS for four hours. The mixture was then filtered to yield an orange precipitate and a brown solution. All attempts to obtain solid material from the brown filtrate were unsuccessful. The orange precipitate was washed with nitromethane to give a brown residue and a deep red solution. Addition of ether to the red solution yielded red crystals of $[(\text{Me}_2\text{N})_3\text{PS}_2\text{P(NMe}_2\text{)}_3]\text{Cu}_2\text{Cl}_6$. 
Anal. Calcd. for C_{12}H_{36}N_{6}Cl_{6}Cu_{2}P_{2}S_{2}:

C, 19.74; H, 4.97; Cl, 29.13.

Found: C, 19.67; H, 5.04; Cl, 29.03.

Identical red crystals were also obtained in much better yield from the reaction of Cu(CH_{3}CN)_{2}Cl_{2} in acetonitrile with an excess of TDPS. The color changed from brownish-yellow to deep red when TDPS was added and all the material dissolved. Addition of ether initiated precipitation of red crystals of [(Me_{2}N)_{3}PS_{2}P(NMe_{2})_{3}][Cu_{2}Cl_{6}].

Anal. Found: C, 20.27; H, 5.22; Cl, 29.81.

These red crystals were also prepared by adding 0.24g (0.4 mmole) of [(Me_{2}N)_{3}PS_{2}P(NMe_{2})_{3}](ClO_{4})_{2} dissolved in 10ml of acetonitrile to a solution of 0.11g (0.8 mmole) of CuCl_{2} and 0.034g (0.8 mmole) of LiCl in 50ml of acetonitrile. The deep red solution was concentrated to 20ml, 5ml of ether added, and the solution allowed to stand. The bright red crystals of [(Me_{2}N)_{3}PS_{2}P(NMe_{2})_{3}][Cu_{2}Cl_{6}] were collected, yield 50%.

Anal. Found: C, 19.86; H, 5.10; Cl, 29.33.

Bromine Reaction. Bromine, 1.0g (0.013 mole) in 20ml of acetonitrile, was added dropwise to a solution of 1.65g (0.0085 mole) of TDPS in 20ml of acetonitrile. The reaction was exothermic and the color changed from deep red to orangish-yellow. A small amount of ether was added and the solution was allowed to stand overnight in the
refrigerator. The resulting orange crystals of 
\[ (\text{Me}_2\text{N})_3\text{PS}_2\text{P(NMe}_2)_3][\text{Br}_3]_2 \] were collected, 2.40g (0.0028 mole), 67% yield.

Anal. Calcd. for \( \text{C}_{12}\text{H}_{36}\text{N}_6\text{Br}_6\text{P}_2\text{S}_2 \):

\[ \begin{align*}
\text{C}, & \quad 16.44; \\
\text{H}, & \quad 4.17; \\
\text{Br}, & \quad 55.11.
\end{align*} \]

Found: \( \begin{align*}
\text{C}, & \quad 16.18; \\
\text{H}, & \quad 4.26; \\
\text{Br}, & \quad 53.35.
\end{align*} \)

\( \text{Pd(TDPS)}_2\text{Cl}_2 \). To a solution of 0.56g (0.002 mole) of \( \text{Na}_2\text{PdCl}_4 \) in 200ml of THF was added 2.0g (0.010 mole) of TDPS. The solution was concentrated and addition of a small amount of ether caused precipitation of red crystals. The complex was recrystallized once from THF-ether in the presence of excess ligand, yield 55%. Recrystallizing this compound in the absence of excess ligand resulted in the formation of the dimer, \( [\text{Pd(TDPS)}\text{Cl}_2]_2 \).

Anal. Calcd. for \( \text{C}_{12}\text{H}_{36}\text{N}_6\text{Cl}_2\text{Pd}_2\text{S}_2 \):

\[ \begin{align*}
\text{C}, & \quad 25.38; \\
\text{H}, & \quad 6.39; \\
\text{Cl}, & \quad 12.49.
\end{align*} \]

Found: \( \begin{align*}
\text{C}, & \quad 25.41; \\
\text{H}, & \quad 6.54; \\
\text{Cl}, & \quad 12.48.
\end{align*} \)

\( \text{Ag(TDPS)}\text{NO}_3 \). A suspension of 0.34g (0.002 mole) of \( \text{AgNO}_3 \) and 1.6g (0.008 mole) of TDPS in THF was stirred overnight. White needles were obtained from the THF solution by concentrating the solution and adding a small amount of ether, yield 90%.

Anal. Calcd. for \( \text{C}_6\text{H}_{18}\text{N}_4\text{Ag}_3\text{PS} \):

\[ \begin{align*}
\text{C}, & \quad 19.74; \\
\text{H}, & \quad 4.97; \\
\text{N}, & \quad 15.31.
\end{align*} \]

Found: \( \begin{align*}
\text{C}, & \quad 19.70; \\
\text{H}, & \quad 5.01; \\
\text{N}, & \quad 15.14.
\end{align*} \)
[Ag(TDPS)\(_2\)]\(\text{ClO}_4\). Silver perchlorate, 0.42 g (0.001 mole) in 20 ml of THF, was added to a solution of 2.0 g (0.010 mole) of TDPS in 50 ml of ether. A white precipitate formed immediately; this was collected and recrystallized three times from THF-ether in the presence of excess ligand to yield long, white needles, yield 64%.

Anal. Calcd. for \(\text{C}_{12}\text{H}_{36}\text{N}_6\text{AgClO}_4\text{P}_2\text{S}_2\):
C, 24.11; H, 6.08; Cl, 5.95.

Found: C, 23.58; H, 6.06; Cl, 5.50.

[Hg(TDPS)Br\(_2\)]\(_2\). This complex was prepared in the same manner as the palladium chloride complex, yield 60%.

Anal. Calcd. for \(\text{C}_{12}\text{H}_{36}\text{N}_6\text{Br}_4\text{Hg}_2\text{P}_2\text{S}_2\):
C, 12.97; H, 3.26; Br, 28.76.

Found: C, 12.95; H, 3.36; Br, 28.10.

Preparation of a \(\text{Ph}_3\text{PS}\) Complex

[Cd(\(\text{Ph}_3\text{PS}\)\)_2]. Cadmium iodide, 0.36 g (1.0 mmole) in 20 ml of THF, was added to a solution of 0.59 g (2.0 mmole) of \(\text{Ph}_3\text{PS}\) in 20 ml of dichloromethane. Hexane was added until the solution just turned cloudy and then it was allowed to stand. The resulting white crystals were collected by filtration, yield 89%. Recrystallization

Anal. Calcd. for \(\text{C}_{36}\text{H}_{30}\text{Cd}_2\text{I}_4\text{P}_2\text{S}_2\):
C, 32.73; H, 2.29; I, 38.42.

Found: C, 32.41; H, 2.28; I, 38.56.

of this complex yielded a mixture of the free ligand and the complex.
Preparation of $\text{Me}_2\text{P(S)P(S)Me}_2$ (TMD) and $\text{Me}_2\text{P(S)OP(S)Me}_2$ (DPTA) Complexes

$\text{Co(TMD)Cl}_2$. To a solution of 0.13 g (1.0 mmole) of $\text{CoCl}_2$ in 50 ml of THF was added 0.18 g (1.0 mmole) of TMD in 50 ml of $\text{CH}_2\text{Cl}_2$. The solution was concentrated, a few ml of ether added, and the resulting deep blue crystals were collected on a filter, yield 73%.

Anal. Calcd. for $\text{C}_4\text{H}_{12}\text{Cl}_2\text{CoP}_2\text{S}_2$:  
C, 15.20; H, 3.83; Cl, 22.44.  
Found: C, 15.47; H, 3.94; Cl, 22.65.

The following complexes were prepared in the same manner:

$\text{Co(TMD)Br}_2$. Bright blue crystals, yield 45%.

Anal. Calcd. for $\text{C}_4\text{H}_{12}\text{Br}_2\text{CoP}_2\text{S}_2$:  
C, 11.86; H, 2.99; Br, 39.22.  
Found: C, 12.31; H, 3.20; Br, 39.33.

$\text{Co(TMD)I}_2$. Olive-green crystals, yield 45%.

Anal. Calcd. for $\text{C}_4\text{H}_{12}\text{I}_2\text{CoP}_2\text{S}_2$:  
C, 9.61; H, 2.43; I, 50.87.  
Found: C, 9.82; H, 2.49; I, 50.30.

$\text{Co(DPTA)Br}_2$. Dark blue crystals, yield 60%.

Anal. Calcd. for $\text{C}_4\text{H}_{12}\text{Br}_2\text{CoOP}_2\text{S}_2$:  
C, 11.41; H, 2.88; Br, 37.99.  
Found: C, 11.63; H, 3.10; Br, 37.83.
Co(DPTA)I$_2$. Dark green crystals, yield 73%.

Anal. Calcd. for C$_{4}$H$_{12}$CoI$_2$OP$_2$S$_2$:

C, 9.33; H, 2.35; I, 49.29.

Found: C, 9.32; H, 2.38; I, 50.17.

Preparation of Ph$_2$P(O)CH$_2$P(O)Ph$_2$ (OP$_2$O) Complexes

[Co(OP$_2$O)$_3$](ClO$_4$)$_2$. To a solution of 0.25g (0.50 mmole) of [Co(CH$_3$CN)$_6$](ClO$_4$)$_2$ in 20ml of nitromethane was added 0.42g (1.0 mmole) of OP$_2$O dissolved in 20ml of dichloromethane. The solution remained pink in color. About 10ml of ether was added and the pink crystals were collected, yield 75%.

Anal. Calcd. for C$_{75}$H$_{66}$Cl$_2$CoO$_{14}$P$_6$:

C, 59.69; H, 4.42; Cl, 4.70.

Found: C, 59.52; H, 4.15; Cl, 4.96.

[Co(OP$_2$O)$_3$][CoBr$_4$]. Methylenebis(diphenylphosphino) dioxido, 0.42g (1.0 mmole) in 20ml of dichloromethane was added to a solution of 0.22g (1.0 mmole) of CoBr$_2$ in 50ml of THF. Light blue crystals began to form after a few minutes and after the reaction mixture had stood one hour, these crystals were collected, yield 98%.

Anal. Calcd. for C$_{75}$H$_{66}$Br$_4$CoO$_{2}$6P$_6$:

C, 53.68; H, 3.97; Br, 19.07.

Found: C, 54.27; H, 4.23; Br, 19.35.
[Co(OP$_2$O)$_3$][CoI$_4$]. This light green complex was prepared in the same manner as the cobalt bromide containing complex, yield 91%.

Anal. Calcd. for C$_{75}$H$_{66}$Co$_2$I$_4$O$_6$P$_6$:
C, 48.06; H, 3.55; I, 27.08.

Found: C, 47.50; H, 3.63; I, 27.44.

[Ni(OP$_2$O)$_3$][NiBr$_4$]. To a solution of 0.22g (1.0 mmole) of NiBr$_2$ in 200ml of ethanol was added 0.42g (1.0 mmole) of OP$_2$O in 20ml of dichloromethane. The solution was concentrated to 30ml and allowed to stand in the refrigerator, however, no crystals formed. Ether, approximately 50ml, was added slowly to the solution and the resulting light blue-green crystals were collected, yield 73%.

Anal. Calcd. for C$_{75}$H$_{66}$Br$_4$Ni$_2$O$_6$P$_6$:
C, 53.68; H, 3.97; Br, 19.07.

Found: C, 52.79; H, 4.18; Br, 18.63.

[Pd(OP$_2$O)$_3$][PdCl$_4$]. To a solution of 0.29g (1.0 mmole) of Na$_2$PdCl$_4$ in 200ml of THF was added 0.42g (1.0 mmole) of OP$_2$O in 20ml of dichloromethane. A precipitate formed immediately. After stirring the reaction mixture one hour, the orange crystals were collected, yield 94%.

Anal. Calcd. for C$_{75}$H$_{66}$Cl$_4$Pd$_2$O$_6$P$_6$:
C, 56.14; H, 4.15; Cl, 8.85.

Found: C, 55.87; H, 3.97; Cl, 9.34.
Preparation of $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{S})\text{Ph}_2\text{ (OP}_2\text{S)}$ Complexes

$\text{Zn(OP}_2\text{S)}\text{I}_2$. Methylenesixdiphosphino) oxide sulfide, 0.22g (0.50 mmole) in 20ml of dichloromethane was added to a solution of 0.16g (0.50 mmole) of $\text{ZnI}_2$ in 20ml of THF. Hexane was added until the solution just turned cloudy and then it was allowed to stand. The resulting white crystals were collected, yield 95%.

Anal. Calcd. for $\text{C}_{25}\text{H}_{22}\text{I}_2\text{OP}_2\text{S}\text{Zn}$:

\[
\text{C}, 39.93; \text{H}, 2.95; \text{I}, 33.77.
\]

Found: \[
\text{C}, 39.25; \text{H}, 3.07; \text{I}, 34.52.
\]

The following compounds were prepared in the same manner:

$\text{Cd(OP}_2\text{S)}\text{I}_2$. White crystals, yield 38%.

Anal. Calcd. for $\text{C}_{25}\text{H}_{22}\text{CdI}_2\text{OP}_2\text{S}$:

\[
\text{C}, 37.54; \text{H}, 2.77; \text{I}, 31.74.
\]

Found: \[
\text{C}, 37.75; \text{H}, 2.92; \text{I}, 32.12.
\]

$\text{Hg(OP}_2\text{S)}\text{I}_2$. White crystals, yield 77%.

Anal Calcd. for $\text{C}_{25}\text{H}_{22}\text{HgI}_2\text{OP}_2\text{S}$:

\[
\text{C}, 33.86; \text{H}, 2.51; \text{I}, 28.62.
\]

Found: \[
\text{C}, 33.75; \text{H}, 2.43; \text{I}, 28.19.
\]

$[\text{Ag(OP}_2\text{S)}\text{ClO}_4]$. White powder, with the ratio of ligand to $\text{AgClO}_4$ used 2:1, yield 56%.

Anal. Calcd. for $\text{C}_{50}\text{H}_{44}\text{AgClO}_6\text{P}_4\text{S}_2$:

\[
\text{C}, 55.91; \text{H}, 4.14; \text{Cl}, 3.21.
\]

Found: \[
\text{C}, 54.25; \text{H}, 4.02; \text{Cl}, 3.76.
\]
Preparation of Ph$_2$P(S)CH$_2$P(S)Ph$_2$ (SP$_2$S) Complexes

[Co(SP$_2$S)$_2$](ClO$_4$)$_2$. This complex was prepared in the same manner as [Co(OP$_2$O)$_3$](ClO$_4$)$_2$, however the solution changed color from pink to blue-green immediately as the ligand was being added. Green crystals, yield 83%.

Anal. Calcd. for C$_{50}$H$_{44}$Cl$_2$CoO$_8$P$_4$S$_4$:
C, 51.98; H, 3.84; Cl, 6.14.

Found: C, 51.79; H, 3.78; Cl, 6.19.

The following complexes were prepared in the same manner as Co(TMD)Cl$_2$:

Co(SP$_2$S)Br$_2$. Blue crystals, yield 76%.

Anal. Calcd. for C$_{27}$H$_{22}$Br$_2$CoP$_2$S$_2$:
C, 45.01; H, 3.32; Br, 23.95.

Found: C, 44.29; H, 3.36; Br, 24.66.

Co(SP$_2$S)I$_2$·1/2THF. Dark green crystals, yield 60%.

Anal. Calcd. for C$_{27}$H$_{26}$CoI$_2$O$_{0.5}$P$_2$S$_2$:
C, 40.67; H, 3.04; I, 31.84.

Found: C, 40.29; H, 3.64; I, 32.37.

[Ni(SP$_2$S)$_2$](ClO$_4$)$_2$. This complex was prepared in the same manner as [Co(OP$_2$O)$_3$](ClO$_4$)$_2$. The color of the solution changed from blue to yellow immediately as the ligand was being added. Yellow powder, yield 62%.
Anal. Calcd. for $C_{50}H_{44}Cl_{2}NiO_{8}P_{4}S_{4}$:

C, 52.03; H, 3.84; Cl, 6.14.

Found: C, 52.46; H, 4.19; Cl, 6.10.

Ni(SP$_2$S)Br$_2$ · 1/2THF. A suspension of 0.23g (0.50 mmole) of SP$_2$S and 0.11g (0.50 mmole) of NiBr$_2$ were refluxed overnight in 300ml of THF. The pink solution was filtered, concentrated to 30ml of a new green solution, and the resulting green crystals collected, yield 41%.

Anal. Calcd. for $C_{27}H_{26}Br_{2}NiO_{0.5}P_{2}S_{2}$:

C, 46.12; H, 4.01; Br, 22.73.

Found: C, 46.31; H, 4.19; Br, 22.60.

Ni(SP$_2$S)I$_2$ · 1/2CH$_2$Cl$_2$. To a solution of 0.45g (1.0 mmole) of SP$_2$S in 20ml of dichloromethane was added 1.0 mmole of NiI$_2$ (prepared by dissolving [Ni(H$_2$O)$_6$](NO$_3$)$_2$ and NaI in THF, filtering off the resulting NaNO$_3$, and dehydrating the solution with 2,2'-dimethoxypropane$^{170}$). The solution was concentrated, a few ml of hexane added, and the resulting deep red crystals were collected, yield 38%.

Anal. Calcd. for $C_{25.5}H_{23}Cl_{1.5}NiP_{2}S_{2}$:

C, 38.11; H, 2.89; Cl, 4.42; I, 31.59.

Found: C, 38.30; H, 3.18; Cl, 4.47; I, 31.13.

Pd(SP$_2$S)Cl$_2$. To a solution of 0.45g (1.0 mmole) of SP$_2$S in 50ml of hot acetonitrile was added 0.18g (1.0 mmole) of PdCl$_2$ and 0.084g (2.0 mmole) of LiCl dissolved in 100ml of hot acetonitrile and allowed
to cool. The resulting orange crystals were recrystallized once from DMF-ethanol to give yellow, needle-like crystals, yield 65%.

Anal. Calcd. for C₂₅H₂₂Cl₂P₂PdS₂:
C, 47.98; H, 3.54; Cl, 11.33.

Found: C, 47.82; H, 3.77; Cl, 10.87.

Pd(SP₂S)Br₂. To a solution of 0.45g (1.0 mmole) of SP₂S in 20ml of dichloromethane was added 0.29g (1.0 mmole) of Na₂PdCl₄ and 0.87g (10 mmoles) of LiBr in 100ml of THF. The solution was concentrated and the resulting red crystals recrystallized once from DMF-ethanol to yield long, orange needles, yield 72%.

Anal. Calcd. for C₂₅H₂₂Br₂P₂PdS₂:
C, 42.01; H, 3.10; Br, 22.36.

Found: C, 41.79; H, 3.14; Br, 22.47.

Pd(SP₂S)I₂. A solution of 0.36g (1.0 mmole) of PdI₂ and 0.27g (2.0 mmole) of LiI in 50ml of THF was added to a solution of 0.45g (1.0 mmole) of SP₂S in 20ml of dichloromethane. The solution was concentrated, a few ml of dichloromethane added, and the resulting purple crystals were recrystallized once from DMF-ethanol to give deep purple crystals, yield 79%.

Anal. Calcd. for C₂₅H₂₂I₂P₂PdS₂:
C, 37.12; H, 2.74; I, 31.39.

Found: C, 37.03; H, 2.89; I, 30.98.
[Ag(SP₂S)₂]ClO₄. To a solution of 0.45g (1.0 mmole) of SP₂S in 20ml of dichloromethane was added 0.10g (0.50 mmole) of AgClO₄ in 20ml of THF. Ether was added until the solution just turned cloudy and then it was allowed to stand. The resulting white crystals were collected and recrystallized once from dichloromethane-ether to give long, white fibrous needles, yield 82%.

Anal. Calcd. for C₅₀H₄₄AgClO₄P₄S₄:
C, 54.38; H, 4.02; Cl, 3.21.

Found: C, 54.67; H, 3.98; Cl, 3.16.

The following compounds were prepared in the same manner:

[Zn(SP₂S)₂](ClO₄)₂. White crystals, not recrystallized, yield 93%.

Anal. Calcd. for C₅₀H₄₄Cl₂O₈P₄S₄Zn:
C, 51.80; H, 3.83; Cl, 6.11.

Found: C, 52.04; H, 3.78; Cl, 5.97.

[Cd(SP₂S)₂](ClO₄)₂. White crystals, yield 83%.

Anal. Calcd. for C₅₀H₄₄CdCl₂O₈P₄S₄:
C, 49.62; H, 3.68; Cl, 5.87.

Found: C, 49.55; H, 3.56; Cl, 5.85.

[Hg(SP₂S)₂](ClO₄)₂. White crystals, not recrystallized, yield 97%.

Anal. Calcd. for C₅₀H₄₄Cl₂HgO₈P₄S₄:
C, 46.33; H, 3.44; Cl, 5.47.

Found: C, 45.54; H, 3.54; Cl, 5.69.
The following compounds were prepared in the same manner as

\[ \text{Zn(\text{OP}_2\text{S})I}_2 : \]

\[ \text{Zn(SP}_2\text{S})I_2. \] White crystals, recrystallized once from dichloromethane-hexane, yield 90%.

Anal. Calcd. for \( C_{25}H_{22}I_2P_2S_2Zn: \)
\[ \text{C, 39.10; H, 2.89; I, 33.06.} \]
Found: \[ \text{C, 39.45; H, 3.07; I, 32.88.} \]

\[ \text{Cd(SP}_2\text{S})I_2. \] White crystals, yield 98%.

Anal. Calcd. for \( C_{25}H_{22}CdI_2P_2S_2: \)
\[ \text{C, 36.85; H, 2.77; I, 31.15.} \]
Found: \[ \text{C, 36.80; H, 2.66; I, 31.34.} \]

\[ \text{Hg(SP}_2\text{S})I_2. \] Off-white crystals, recrystallized once from dichloromethane-ether, yield 95%.

Anal. Calcd. for \( C_{25}H_{22}HgI_2P_2S_2: \)
\[ \text{C, 33.25; H, 2.46; I, 28.18.} \]
Found: \[ \text{C, 33.14; H, 2.53; I, 28.20.} \]

Preparation of \( \text{Ph}_2\text{P(Se)CH}_2\text{P(Se)Ph}_2(\text{SeP}_2\text{Se}) \) Complexes

The following complexes were prepared in the same manner as \( \text{Co(TMD)Cl}_2 \) except the complexes were also dried at 56° in \text{vacuo} overnight:
Co\(\text{SeP}_2\text{S})\text{Cl}_2 \cdot 1/2\text{THF}\) (before drying). Blue crystals.

Anal. Calcd. for \(\text{C}_{27}\text{H}_{26}\text{Cl}_2\text{Co}^0.5\text{P}_2\text{S}_2\):

\[
\begin{align*}
\text{C}, & \quad 45.76; \text{H}, 3.70; \text{Cl}, 10.17. \\
\text{Found:} & \quad \text{C}, 46.34; \text{H}, 4.27; \text{Cl}, 10.39.
\end{align*}
\]

Co\(\text{SeP}_2\text{Se})\text{Cl}_2\) (after drying). Blue powder, yield 89%.

Anal. Calcd. for \(\text{C}_{25}\text{H}_{22}\text{Cl}_2\text{CoP}_2\text{Se}_2\):

\[
\begin{align*}
\text{C}, & \quad 44.67; \text{H}, 3.30; \text{Cl}, 10.56. \\
\text{Found:} & \quad \text{C}, 44.52; \text{H}, 3.17; \text{Cl}, 10.78.
\end{align*}
\]

Co\(\text{SeP}_2\text{Se})\text{Br}_2 \cdot 1/2\text{THF}\). Bright green crystals, yield 81%.

Anal. Calcd. for \(\text{C}_{27}\text{H}_{26}\text{Br}_2\text{Co}^0.5\text{P}_2\text{Se}_2\):

\[
\begin{align*}
\text{C}, & \quad 40.93; \text{H}, 3.29; \text{Br}, 19.93. \\
\text{Found:} & \quad \text{C}, 40.98; \text{H}, 3.57; \text{Br}, 19.66.
\end{align*}
\]

Co\(\text{SeP}_2\text{Se})\text{I}_2 \cdot 3/4\text{THF}\). Dark green crystals, yield 67%.

 Anal. Calcd. for \(\text{C}_{28}\text{H}_{28}\text{CoI}_2^0.75\text{P}_2\text{Se}_2\):

\[
\begin{align*}
\text{C}, & \quad 36.99; \text{H}, 3.10; \text{I}, 27.92. \\
\text{Found:} & \quad \text{C}, 37.04; \text{H}, 3.21; \text{I}, 28.29.
\end{align*}
\]

\(\text{Pd(SeP}_2\text{Se})\text{Cl}_2\). To a solution of 0.20g (0.70 mmole) of \(\text{Na}_2\text{PdCl}_4\) in 40ml DMF was added 0.38g (0.70 mmole) of Se\(\text{P}_2\text{Se}\) in 10ml of dichloromethane. The solution was diluted to 250ml with ethanol and allowed to stand. The resulting orange crystals were collected on a filter, yield 72%.
Anal. Calcd. for $C_{25}H_{22}Cl_2P_2PdSe_2$:

\begin{align*}
\text{C, 41.72; H, 3.08; Cl, 9.87.} \\
\text{Found: C, 41.69; H, 2.96; Cl, 9.67.}
\end{align*}

$\text{Pd(SeP_2Se)Br}_2$. This complex was prepared in the same manner as $\text{Pd(SP_2S)Br}_2$ except that these red crystals were not recrystallized.

Anal. Calcd. for $C_{25}H_{22}Br_2P_2PdSe_2$:

\begin{align*}
\text{C, 37.14; H, 2.74; Br, 19.77; Se, 19.53.} \\
\text{Found: C, 37.16; H, 2.80; Br, 19.84; Se, 19.76.}
\end{align*}

**Attempted Complexes**

**TDPS.** Complexes were attempted with $\text{NiCl}_2$, $\text{NiBr}_2$, and $\text{FeCl}_3$ following the same procedure as that used for the cobalt halides. Although they did give bright blue, green, and black solutions, respectively, no solid complexes could be isolated from the intractable oils.

\begin{align*}
\text{(Me}_2\text{N)}_3\text{PSe, Ph}_2\text{P(S)NMe}_2, \text{and Ph}_2\text{P(Se)NMe}_2. \text{ Attempts to prepare complexes of these ligands with CoI}_2 \text{ following the same procedure as that used to prepare Co(TMD)}\text{I}_2 \text{ were unsuccessful.}
\end{align*}

**Ph}_3\text{PS.** There was no indication that any complexation occurred between this ligand and CoI}_2 \text{ or ZnI}_2 \text{ following the Co(TMD)}\text{I}_2 \text{ procedure or the method used to obtain the CdI}_2 \text{ complex.}

**TMD and DPTA.** TMD does yield well-formed green crystals with $[\text{Co(CH}_3\text{CN})_6]\text{(ClO}_4)_2$, however, this complex detonated with considerable
force as it was being collected from a sintered glass funnel. No further attempt was made to prepare this complex. A complex of DPTA was attempted with CoCl₂ and a solid was isolated; however, the infrared spectrum showed that little or no DPTA was present.

\[
\text{OP}_2\text{S}. \quad \text{Attempts to complex } \text{OP}_2\text{S with } \text{Na}_2\text{PdCl}_4 \text{ and } \text{CoI}_2 \text{ yielded impure solids which turned to oils when recrystallization from dichloromethane or THF was attempted.}
\]

\[
\text{SeP}_2\text{Se}. \quad \text{An attempt to obtain a complex of NiI}_2 \text{ was made by the same procedure as that used for SP}_2\text{S; however, no solid material was isolated.}
\]

**Instrumental Analysis**

**Spectra.** Infrared spectra were obtained with a Perkin-Elmer Model 337 grating spectrophotometer using Nujol mulls between potassium bromide plates and calibrated with a thin film of polystyrene. Electronic spectra of the complexes in solution using a matched set of 5.0, 1.0, or 0.10cm quartz cells and in the solid state using Nujol mulls supported on filter paper 171 were obtained with a Cary Model 14 recording spectrophotometer. NMR spectra were obtained on a Varian A-60 spectrometer at 37° and occasionally at lower temperatures with the Variable Temperature Probe.

**Conductance Measurements.** The measurements were performed at 23±1° with an Industrial Instruments Model RC-16B conductivity bridge
calibrated with an aqueous solution of potassium chloride of known concentration (0.010M). The solutions studied were approximately $10^{-3}$ molar in nitromethane or DMF solutions. Expected molar conductance values for a 1:1 electrolyte are: in nitromethane $70-100\text{cm}^2/\text{ohm-mole}^{172}$ and in DMF, 70-90; whereas a 2:1 electrolyte in DMF is 150-180.$^{173}$

**Magnetic Measurements.** Magnetic moments were determined using a Faraday susceptibility balance at 23±1° and calibrated with Hg[Co(NCS)$_4$]. The magnetic measurements were determined at two different field strengths to check for ferromagnetic impurities. The observed susceptibility values were corrected for diamagnetism of the ligands using Pascal’s constants$^{174}$ and temperature independent paramagnetism $(2.09/\Delta)^{175}$ for the tetrahedral cobalt(II) complexes. The diamagnetic contributions of OP$_2$O, SP$_2$S, and SeP$_2$Se were determined experimentally and found to be -247, -179, and $-361 \times 10^{-6}$ cgs units, respectively. The diamagnetic contribution of TDPS was determined from the experimental molar susceptibility of the methyl iodide derivative after subtracting Pascal’s constants for CH$_3$ and I$^-$. The experimental diamagnetic correction for TDPS was $-106 \times 10^{-6}$ cgs units. Due to the high vapor pressure of TMD and DPTA, the diamagnetic contributions of these ligands could not be determined conveniently on the available balance.

**Melting Point Determinations.** Melting points were determined on a Nalge–Axelrod Apparatus, except for DPTA, and are all uncorrected. The melting point of DPTA was determined in a well–stirred mineral oil bath in a sealed capillary.
RESULTS AND DISCUSSION

Ligands

In this investigation the ligands were carefully chosen for the expressed purpose of preparing phosphine sulfide and selenide complexes of cobalt(II) and nickel(II), which were unknown at the time this research was begun. These ligands illustrate three approaches that are generally applicable when one attempts to prepare a metal complex with a new type of ligand. One may attempt to increase the basicity of the donor group, or to utilize the added stability of a chelate ring, or to incorporate a combination of these two effects.

No triphenyl- or trimethylphosphine sulfide complexes of cobalt or nickel had been reported before this study was begun.127,138,143 In an attempt to increase the basicity of the phosphine sulfide and selenide groups, the following ligands were prepared: (Me₂N)₃PS, (Me₂N)₃PSe, Ph₂P(S)NMe₂, and Ph₂P(Se)NMe₂. These molecules incorporate the potentially greater inductive effect of the dimethylamino group over the methyl or phenyl group. That is, based on basicity studies with dimethylamino groups on phosphorous, resonance form II should make a significant contribution to the

\[
\text{Me}_2\text{N}^- \equiv \text{P}=\text{X} \leftrightarrow \text{Me}_2\text{N}^+ = \text{P}^- \equiv \text{X}^- \]

I                   II

51
The increased basicity of (Me₂N)₃PO over Me₃PO toward trimethylsilane as an acid has been ascribed to the added inductive effect of the dimethylamino group. ⁷⁵

Bidentate diphosphine dioxides of the general formula \( Y_2P(0)CH_2P(0)Y_2 \), exhibit⁶⁰,⁶⁸ a very strong coordinating ability with metal ions, displacing all the halide atoms from the metal ion, but do not exert a very strong ligand field (approximate \( D_q \) value of 720cm⁻¹ toward nickel). Moreover, this type of ligand shows a much greater ability to extract metal ions from solution, often several orders of magnitude greater, than the analogous monodentate phosphine oxides. ⁷³,⁷⁶,⁷⁷ Since similar properties might be expected to prevail with other analogous diphosphine dichalcogenides, the potential chelating ligands Ph₂P(O)CH₂P(S)Ph₂, Ph₂P(S)CH₂P(S)Ph₂, and Ph₂P(Se)CH₂P(Se)Ph₂ were synthesized for this study. In addition to date, no complexes of Me₂P(S)P(S)Me₂ with cobalt or nickel had been reported even though attempts had been made previously. ¹³⁸,¹⁴⁵ Thus this related chelating ligand was reinvestigated.

Joesten and co-workers⁶²,⁶⁷,⁶⁸ have shown that the ligands \( (\text{Me}_2\text{N})_2P(0)XP(0)(\text{NMe}_2)_2 \), when \( X = 0, \text{NMe} \), exert a stronger ligand field (\( D_q = 727 \) and 726cm⁻¹ respectively) than when \( X = \text{CH}_2 \) (\( D_q = 707\text{cm}^{-1} \)) with nickel(II). In an effort to determine if chelating phosphine sulfides containing a hetero atom between the two phosphorous atoms also exhibited an increased ligand field strength, the ligand Me₂P(S)OP(S)Me₂ was prepared for this study. Moreover, the coordination properties and increased inductive effect of the bridging oxygen
in $\text{Me}_2\text{P(S)}\text{OP(S)}\text{Me}_2$ could be compared directly with those of $\text{Me}_2\text{P(S)}\text{P(S)}\text{Me}_2$ which contains a phosphorous-phosphorous bond.

Although the coordination properties of monodentate phosphine oxides have been well established, the particular diphosphine dioxide needed for a direct comparison with the other diphosphine dichalco- genides, $\text{Ph}_2\text{P(O)}\text{CH}_2\text{P(O)}\text{Ph}_2$, had not been investigated previously. Thus the complexes of this ligand were also investigated in order to provide a complete series of phosphine derivatives with oxygen, sulfur, and selenium as the donor atoms.

The phosphine sulfide ligands, except for $\text{Me}_2\text{P(S)}\text{OP(S)}\text{Me}_2$, were prepared in nearly quantitative yield by adding elemental sulfur to the parent phosphine. There are a variety of reagents by which the

$$ R_3\text{P} + \frac{1}{8}\text{S}_8 \rightarrow R_3\text{PS} \quad (20) $$

phosphine is converted to phosphine sulfide;\(^{176}\) some of these reagents are $\text{HgS}$, $\text{CS}_2$, and $\text{S}_2\text{O}_3^{2-}$. However, none of the reactions are as easy nor as free from side reactions and give as high a yield as with elemental sulfur. Tris(dimethylamino)phosphine sulfide was prepared in this manner with elemental sulfur, although it is possible to

$$ \text{PCl}_3 + 6\text{HNMe}_2 \rightarrow (\text{Me}_2\text{N})_3\text{P} + 3\text{Me}_2\text{NH}_2\text{Cl} \quad (21) $$

$$ (\text{Me}_2\text{N})_3\text{P} + \frac{1}{8}\text{S}_8 \rightarrow (\text{Me}_2\text{N})_3\text{PS} \quad (22) $$

prepare it from $\text{SPCl}_3$ and dimethylamine. However, the latter reaction

$$ \text{SPCl}_3 + 6\text{HNMe}_2 \rightarrow (\text{Me}_2\text{N})_3\text{PS} + 3\text{Me}_2\text{NH}_2\text{Cl} \quad (23) $$
often yielded a mixture of \((\text{Me}_2\text{N})_3\text{PS}\) and \((\text{Me}_2\text{N})_2\text{P(S)Cl}\). This mixture was nearly impossible to separate by distillation, because both components have very similar boiling points. Moreover, \((\text{Me}_2\text{N})_2\text{P(S)Cl}\) was very resistant to further aminolysis. Better yields of \((\text{Me}_2\text{N})_3\text{PS}\) in a shorter period of time could be obtained by first preparing \((\text{Me}_2\text{N})_2\text{P}\) followed by addition of sulfur.

There are few reported preparations\(^{166}\) of compounds of the type, \(\text{R}_2\text{P(S)OP(S)R}_2\), although it may be possible to use procedures that have been used to prepare \((\text{RO})_2\text{P(S)OP(S)(OR)}_2\),\(^{177}\) \(\text{R}_2\text{P(S)SP(S)R}_2\),\(^{176}\) or \(\text{R}_2\text{P(S)OP(O)R}_2\).\(^{177-179}\) However, since \(\text{Me}_2\text{P(S)OP(S)Me}_2\) was prepared in two simple steps with an overall yield of 35%, there was no necessity to experiment with alternate procedures.

The phosphine selenides were prepared cleanly and in good yield from the parent phosphine and KSeCN.\(^{164}\) An alternate preparation would have necessitated using elemental selenium, either by direct fusion of the reagents or by refluxing the parent phosphine with selenium in a suitable solvent.\(^{180}\) The latter procedure, however, usually does not give as high a yield and the resulting phosphine selenides are often difficult to purify.

The phosphines containing dimethylamino substituents were prepared in good yield from the reaction of the phosphorous chloride derivative and dimethylamine. Either liquid or gaseous dimethylamine may be used with little affect on the amount of product obtained. By isolating the reaction mixture from both oxygen and moisture with a dry
nitrogen atmosphere the yields were improved by approximately 10%, as compared to the procedure using only a drying tube.

Methylenebis(diphenylphosphino) oxide sulfide was prepared by the only convenient method available. It is generally impossible to oxidize selectively just one phosphorous in a diphosphine so that the mono-phosphoryl group must be "built-in". That is, the diphosphine monoxide, \( \text{Ph}_2\text{P(0)}\text{CH}_2\text{PPPh}_2 \) must be prepared first and then sulfur may be added to form \( \text{Ph}_2\text{P(0)}\text{CH}_2\text{P(S)}\text{Ph}_2 \).

\[
\text{Ph}_2\text{P(0)}\text{CH}_2\text{Li}^+ + \text{ClPPPh}_2 \rightarrow \text{Ph}_2\text{P(0)}\text{CH}_2\text{PPPh}_2 + \text{LiCl} \tag{24}
\]

\[
\text{Ph}_2\text{P(0)}\text{CH}_2\text{PPPh}_2 + \frac{1}{8}\text{S}_8 \rightarrow \text{Ph}_2\text{P(0)}\text{CH}_2\text{P(S)}\text{Ph}_2 \tag{25}
\]

**Infrared Spectra of the Ligands and the Metal Complexes**

\( \text{Ph}_2\text{P(0)}\text{CH}_2\text{P(0)}\text{Ph}_2 \). The infrared spectrum of methylenebis-(diphenylphosphino) dioxido* (Fig. 1), \( \text{OP}_2\text{O} \), contains two strong peaks at 1205 and 1192 cm\(^{-1}\) which are absent in the parent phosphine (Fig. 1) or other dichalcogenides; they are assigned to the \( \text{P}=\text{O} \) stretching frequency (previous literature assignments are at 1204 cm\(^{-1}\) and 1190 cm\(^{-1}\) ). The infrared spectra of the \( \text{OP}_2\text{O} \)-metal complexes (Fig. 2) are all very similar to that of the free ligand and almost identical to each other except for the position of the \( \text{P}=\text{O} \) stretching frequency (Table II). In the cobalt and nickel complexes the \( \text{P}=\text{O} \)

*Named according to preferred Chemical Abstracts nomenclature; these types of compounds may also be named bis(diphenylphosphoryl)-methane.
FIGURE 1. INFRARED SPECTRA OF \( \text{Ph}_2\text{PCH}_2\text{PPh}_2(\neg\neg) \) and \( \text{Ph}_2\text{P(0)CH}_2\text{P(0)Ph}_2(\neg\neg\neg) \)
FIGURE 2. INFRARED SPECTRA OF [Co(OP₂O)₃][CoI₄] (---) and [Pd(OP₂O)₃][PdCl₄] (−)
absorption is shifted to lower energy by approximately $40 \text{cm}^{-1}$ and appears as a rounded band centered at $1160 \text{cm}^{-1}$. The P=O frequency in the palladium complex, however, occurs at $1200 \text{cm}^{-1}$.

### TABLE 11

**THE P=O STRETCHING FREQUENCY IN METAL COMPLEXES OF METHYLENEBIS(DIPHENYLPHOSPHINO) DIOXIDE**

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v_{\text{P}=\text{O}}(\text{cm}^{-1}))^a</th>
<th>Compound</th>
<th>(v_{\text{P}=\text{O}}(\text{cm}^{-1}))^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{OP}_2\text{O})</td>
<td>1192, 1205</td>
<td>([\text{Co(\text{OP}_2\text{O})}_3][\text{CoI}_4])</td>
<td>1160</td>
</tr>
<tr>
<td>([\text{Co(\text{OP}_2\text{O})}_3]\text{ClO}_4\text{O}_2)</td>
<td>1160</td>
<td>([\text{Ni(\text{OP}_2\text{O})}_3][\text{NiBr}_4])</td>
<td>1165</td>
</tr>
<tr>
<td>([\text{Co(\text{OP}_2\text{O})}_3][\text{CoBr}_4])</td>
<td>1165</td>
<td>([\text{Pd(\text{OP}_2\text{O})}_3][\text{PdCl}_4])</td>
<td>1200</td>
</tr>
</tbody>
</table>

^aValues are \(\pm 2 \text{cm}^{-1}\).

Cotton et al.\(^{182}\) have listed three possibilities that may affect the P=O bond order on coordination (these same considerations also may be applied to the other phosphorous chalcogenide bond orders). 1. The formation of the oxygen-metal bond would enhance the \(\dfrac{\uparrow}{\downarrow} + \dfrac{\sigma}{\sigma}\) \(\sigma\)-bond and should tend to increase the bond order. 2. Simultaneously, the \(\pi\)-\(\pi\) back-bonding, \(\dfrac{\uparrow}{\downarrow} + \dfrac{\sigma}{\sigma}\), will tend to decrease, thus decreasing the bond order. 3. For transition metals with low energy filled d-orbitals, there may be a drift of metal \(\pi\)-electrons toward the oxygen \(p\sigma\)-orbitals, thus displacing the oxygen \(p\pi\)-electrons toward empty \(d\sigma\)-orbitals of phosphorous. This would also tend to increase the bond order.

In most phosphine oxide complexes, the second effect must be dominant since the P=O stretching frequency decreases. However, not
all phosphine oxide complexes exhibit this decrease in the P=O frequency. If the bond order of the P=O group remains the same in the complex as in the free ligand, the P=O frequency should increase 50-150cm⁻¹ as a result of a kinematic effect. Thus no shift in the P=O frequency of a coordinated phosphine oxide would represent an actual decrease in the bond order. For example, the infrared spectrum of \( \mu_4 \)-oxo-hexa-μ-chloro-tetrakis [(triphenylphosphine oxide) copper (II)], \( \text{Cu}_4\text{OC}\_6\text{(Ph}_3\text{PO)}\_4 \), shows the P=O band at 1194cm⁻¹ which is the same as the P=O frequency in the free phosphine oxide. However, the X-ray crystallographic study of the structure showed¹⁹ that all the phosphine oxides were, indeed, coordinated. There is a linear arrangement of the phosphorous-oxygen-copper atoms, suggesting considerable π-bonding between phosphorous, oxygen, and copper. Thus the shift of

![Perspective Drawing of the Structure of \( \mu_4 \)-Oxo-Hexa-μ-Chloro-Tetrakis[(Triphenylphosphine Oxide) Copper(II)]. The Phenyl Groups Are Omitted. (Reproduced from Inorg. Chem., 6, 496 (1967)).](image-url)
the $P=0$ frequency to lower energy in the cobalt and nickel complexes of $OP_2O$ indicates coordination through the oxygen atoms. The lack of a shift in the palladium complex does not exclude oxygen coordination; it may be explained on the basis of a relative decrease in the oxygen-metal interaction and/or an increase in the $\pi$-bonding between palladium and oxygen. Both effects may operate simultaneously since palladium(II), a "soft" metal, may not bond as strongly with the "hard" phosphine oxide as a borderline metal such as cobalt(II) or nickel(II). In addition, $\pi$-bonding would be expected to be more important for palladium than for cobalt or nickel.

$$\text{Ph}_2\text{P(S)CH}_2\text{P(S)}\text{Ph}_2.$$ The $P=S$ stretching frequency in methylenebis(diphenylphosphino) disulfide, $SP_2S$, cannot be assigned unambiguously since the spectrum is complicated by the appearance of three additional bands at 628, 614, and $596\text{cm}^{-1}$ when the infrared spectrum of $SP_2S$ (Fig. 4) is compared with that of the parent phosphine and the other two dichalcogenides. Both triphenyl- and diphenylmethylphosphine sulfide have two similar bands at 635 and $615\text{cm}^{-1}$ and at 622 and $613\text{cm}^{-1}$ respectively, where the band at $635\text{cm}^{-1}$ was previously assigned$^{138,143}$ as the $P=S$ frequency in triphenylphosphine sulfide. The bands at 615 and $613\text{cm}^{-1}$ do not appear to be part of the $P=S$ frequency, but are probably a combination of the $P=S$ fundamental with some other vibration. This has been suggested for the naphthyl-substituted phosphine sulfides.$^{135}$ It is reasonable to assign the band at $628\text{cm}^{-1}$ in $SP_2S$ as the $P=S$ stretching frequency on the basis of a comparison with similar phosphine sulfides.
FIGURE 4. INFRARED SPECTRA OF $\text{Ph}_2\text{P(S)CH}_2\text{P(S)Ph}_2$ (---) and $\text{Co(SP}_2\text{S)}\text{Br}_2$ (-)
The infrared spectra of all the SP₂S-metal complexes (Fig. 4) are very similar and are essentially unchanged from that of the free ligand except for the bands at 628, 614, and 596 cm⁻¹. The band at 628 cm⁻¹ is shifted approximately 50 cm⁻¹ to lower energy (Table 12) and the band at 614 cm⁻¹ is reduced from a medium intensity to a very weak or non-existent band for the metal halides. This band, however, is still of weak to medium intensity for the perchlorate complexes. The

TABLE 12

THE P=S STRETCHING FREQUENCIES IN METAL COMPLEXES OF METHYLENEBIS(DIPHENYLPHOSPHINO) DISULFIDE

<table>
<thead>
<tr>
<th>Compound</th>
<th>νP=S(cm⁻¹)ᵃ</th>
<th>Compound</th>
<th>νP=S(cm⁻¹)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP₂S</td>
<td>628</td>
<td>Pd(SP₂S)I₂</td>
<td>570</td>
</tr>
<tr>
<td>[Co(SP₂S)₂] (ClO₄)₂</td>
<td>568</td>
<td>[Ag(SP₂S)₂] ClO₄</td>
<td>580</td>
</tr>
<tr>
<td>Co(SP₂S)Br₂</td>
<td>568</td>
<td>[Zn(SP₂S)₂] (ClO₄)₂</td>
<td>568</td>
</tr>
<tr>
<td>Co(SP₂S)I₂·1/2THF</td>
<td>570</td>
<td>Zn(SP₂S)I₂</td>
<td>572</td>
</tr>
<tr>
<td>[Ni(SP₂S)₂] (ClO₄)₂</td>
<td>570</td>
<td>[Cd(SP₂S)₂] (ClO₄)₂</td>
<td>568</td>
</tr>
<tr>
<td>Ni(SP₂S)Br₂·1/2THF</td>
<td>572</td>
<td>Cd(SP₂S)I₂</td>
<td>573</td>
</tr>
<tr>
<td>Ni(SP₂S)I₂·1/2CH₂Cl₂</td>
<td>570</td>
<td>[Hg(SP₂S)₂] (ClO₄)₂</td>
<td>565</td>
</tr>
<tr>
<td>Pd(SP₂S)Cl₂</td>
<td>568</td>
<td>Hg(SP₂S)I₂</td>
<td>570</td>
</tr>
<tr>
<td>Pd(SP₂S)Br₂</td>
<td>570</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ᵃValues are ±2 cm⁻¹.

The similarity of the infrared spectra of the SP₂S-metal complexes to that of the free ligand indicates that the ligand coordinates
as a discrete moiety. Moreover, the reduction of the P=S stretching frequency on coordination indicates that the bonding of the ligand is, indeed, through the sulfur atoms.

\[ \text{Ph}_2\text{P(O)CH}_2\text{P(S)Ph}_2 \]  

The infrared spectrum of methylene-bis(diphenylphosphino) oxide sulfide, \( \text{OP}_2\text{S} \), (Fig. 5) exhibits a strong band at 1192 cm\(^{-1}\) which is absent in the infrared spectra of the parent phosphine and methylenebis(diphenylphosphino) disulfide and is assigned to the P=O stretching frequency. There is also a strong band at 609 cm\(^{-1}\) which is absent in the parent phosphine and methylenebis(diphenylphosphino) dioxide and is assigned to the P=S stretching frequency.

Except for the bands at 1192 and 609 cm\(^{-1}\), the infrared spectra of all the metal complexes of \( \text{OP}_2\text{S} \) (Fig. 5) are very similar and essentially unchanged from that of the free ligand. In the metal complexes the bands at 1192 and 609 cm\(^{-1}\) are shifted to lower energy by approximately 40-50 and 25-35 cm\(^{-1}\), respectively. Since these shifts in the P=O and P=S frequencies are comparable to those observed in other phosphine oxide and sulfide complexes, this is interpreted as indicating that the metal binds through both the oxygen and sulfur atoms (Table 13).

\[ \text{Ph}_2\text{P(Se)CH}_2\text{P(Se)Ph}_2 \]  

Unambiguous assignment of the P=Se stretching frequency in the infrared spectrum of methylenebis(diphenyl-phosphino) diselenide (Fig. 6), \( \text{SeP}_2\text{Se} \), is impossible owing to the presence of a number of medium-to-strong absorptions in both the parent phosphine and the two other dichalcogenides between 450 and 550 cm\(^{-1}\), where the P=Se stretching frequency is expected.\(^{137,164}\) The infrared spectra
FIGURE 5. INFRARED SPECTRA OF \( \text{Ph}_2\text{P}(0)\text{CH}_2\text{P}(\text{S})\text{Ph}_2 \) (—) and \( \text{Zn}(\text{OP}_2\text{S})\text{I}_2 \) (—)
FIGURE 6. INFRARED SPECTRUM OF \( \text{Ph}_2\text{P(Se)CH}_2\text{P(Se)Ph}_2 \)
of the SeP$_2$Se-metal complexes (Fig. 7) are essentially the same as that of the free ligand and indicate that the ligand has remained intact on coordination. Even though definitive evidence for coordination through the selenium atoms is lacking, there are no other sites for coordination in the ligand without altering the structure of the free ligand. The infrared spectra seem to preclude this latter possibility. Moreover, the elemental analysis of the free ligand and of the palladium bromide complex contained the theoretical amount of selenium.

TABLE 13

<table>
<thead>
<tr>
<th>Compound</th>
<th>νP=O (cm$^{-1}$)$^a$</th>
<th>νP=S (cm$^{-1}$)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OP$_2$S</td>
<td>1192</td>
<td>609</td>
</tr>
<tr>
<td>Zn(OP$_2$S)I$_2$</td>
<td>1150</td>
<td>584</td>
</tr>
<tr>
<td>Cd(OP$_2$S)I$_2$</td>
<td>1160</td>
<td>585</td>
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<tr>
<td>Hg(OP$_2$S)I$_2$</td>
<td>1160</td>
<td>586</td>
</tr>
<tr>
<td>[Ag(OP$_2$S)$_2$]ClO$_4$</td>
<td>1170</td>
<td>585</td>
</tr>
</tbody>
</table>

$^a$Values are ±2 cm$^{-1}$.

Me$_2$P(S)P(S)Me$_2$. Tetramethyldiphosphine disulfide (TMD) has been assigned a trans configuration based on the infrared and Raman spectra which show no coincidental bands.$^{183,184}$ An X-ray crystallography study has confirmed that the molecule has the trans configuration and a center of symmetry in the crystal.$^{185}$ The Raman active band at
FIGURE 7. INFRARED SPECTRA OF \( \text{Co(Se}_2\text{Se)}\text{Cl}_2 \) (−) and \( \text{Co(Se}_2\text{Se)}\text{Cl}_2 \cdot 1/2\text{THF} \) (−)
610 cm\(^{-1}\) has been assigned as the symmetrical P=S stretching frequency (\(v_2\)), whereas the infrared active band at 570 cm\(^{-1}\) was assigned as the asymmetric P=S stretching frequency (\(v_1\)). The increased complexity of the infrared spectra in the TMD complexes, compared with the spectrum of the free ligand, has been interpreted\(^{136,138}\) as indicating that the ligand undergoes a rearrangement from the trans structure to a cis form on coordination (Fig. 8). Both P=S stretching frequencies appear in the infrared spectra of the complexes at 585 and 542 cm\(^{-1}\) (Table 14); the shift to lower energy is due to the reduction in the P=S bond order as a result of forming the metal-sulfur bond. The infrared spectra strongly indicate that TMD coordinates as a chelating bidentate ligand.

**TABLE 14**

THE P=S STRETCHING FREQUENCIES FOR THE METAL COMPLEXES OF TETRAMETHYLDIPHOSPHINE DISULFIDE AND DIMETHYLPHOSPHINOTHIOIC ACID ANHYDRIDE

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v_2) (610)(^b),570</th>
<th>(v_1)</th>
<th>Compound</th>
<th>(v_2)(595)</th>
<th>(v_1)</th>
<th>DPTA</th>
<th>Co(DPTA)Br(_2)</th>
<th>558, (520)(^c)</th>
<th>Co(DPTA)I(_2)</th>
<th>555, (515)(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMD</td>
<td></td>
<td></td>
<td></td>
<td>DPTA</td>
<td>595</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(TMD)Cl(_2)</td>
<td>590, 547</td>
<td></td>
<td></td>
<td>Co(DPTA)Br(_2)</td>
<td>558, (520)(^c)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(TMD)Br(_2)</td>
<td>585, 542</td>
<td></td>
<td></td>
<td>Co(DPTA)I(_2)</td>
<td>555, (515)(^c)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(TMD)I(_2)</td>
<td>585, 542</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

\(^a\) Values are ±2 cm\(^{-1}\).

\(^b\) Raman active only.

\(^c\) Possibly a P=S stretching frequency.
Figure 8. Infrared spectra of $\text{Me}_2\text{P(S)P(S)Me}_2$ (---) and $\text{Co(TMD)Br}_2$ (--)
Spectral work comparable to that of TMD has not been reported for dimethylphosphinothioic acid anhydride, DPTA, or related compounds; however, only one band (at 595 cm\(^{-1}\)) appears in the 500–650 cm\(^{-1}\) region of the infrared spectrum (Fig. 9) and it is assigned to the P=S stretching frequency. As in the case of TMD, the infrared spectrum of DPTA becomes more complicated on coordination. The two bands at approximately 560 and 520 cm\(^{-1}\) (Fig. 9) are assigned to the P=S frequency (Table 14). Although the spectral evidence is not as definite as in the TMD case, it appears that DPTA also coordinates as a chelating bidentate ligand.

The infrared spectra of all the metal complexes of tris(dimethylamino)phosphine sulfide, TDPS, are very similar and are essentially unchanged from that of the uncoordinated ligand except for three absorptions at 740, 720, and 565 cm\(^{-1}\) (Fig. 10). The two peaks at 720 and 740 cm\(^{-1}\) split further apart (up to 60 cm\(^{-1}\)) in the complexes and the P=S stretching frequency (565 cm\(^{-1}\) in the free ligand) is shifted to lower energy by approximately 15 to 20 cm\(^{-1}\) (Table 15). The shift of the P=S frequency to lower energy indicates that coordination has occurred through the sulfur atom in the ligand, since coordination through the nitrogen should raise the P=S frequency. Moreover, by refluxing the free ligand with excess methyl iodide one obtains only the monomethylated derivative in which the methyl group is attached to sulfur. The entire infrared spectrum of [(Me\(_2\)N)\(_3\)P-S-CH\(_3\)]\(^+\)I\(^-\) is very similar to those of the metal complexes with the P=S frequency reduced 20 cm\(^{-1}\). The NMR of [(Me\(_2\)N)\(_3\)PSCH\(_3\)]\(^+\)I\(^-\) showed two sharp doublets.
FIGURE 9. INFRARED SPECTRA OF $\text{Me}_2\text{P(S)}\text{OP(S)}\text{Me}_2$ (---) and $\text{Co(DPTA)}\text{I}_2$ (—)

ABSORBANCE

FREQUENCY (CM$^{-1}$)

1200 1000 700 500

P=S
FIGURE 10. INFRARED SPECTRA OF (Me$_2$N)$_3$PS(—) and Co(TDPS)$_2$Cl$_2$(—)
at 7.06τ (N-CH₃) and 7.46τ (S-CH₃) with Jₚ₋Η of the N(CH₃)₂ group = 11.2cps and Jₚ₋Η of the SCH₃ group = 15.5cps (Fig. 11). The relative area of the two doublets was approximately 6:1 as expected for alkylation of the sulfur atom. The methyl iodide reaction seems to indicate that the lone pair of electrons on nitrogen is not available for bonding and that the nitrogen atoms do not possess appreciable nucleophilic character. This behavior is consistent with previous observations that the nitrogen atom of a phosphoramidate group is not very basic.¹⁸⁶ In any case, the coordination of TDPS undoubtedly occurs via the thiophosphoryl group.

**TABLE 15**

| THE P=S STRETCHING FREQUENCY IN THE METAL COMPLEXES OF TRIS(DIMETHYLAMINO)PHOSPHINE SULFIDE |

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν_P=S(cm⁻¹)ᵃ</th>
<th>Compound</th>
<th>ν_P=S(cm⁻¹)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDPS</td>
<td>565</td>
<td>[Cu(TDPS)₄]ClO₄</td>
<td>552</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Co(TDPS)₄</a>₂</td>
<td>543</td>
<td>Pd(TDPS)₂Cl₂</td>
<td>548</td>
</tr>
<tr>
<td>Co(TDPS)₂Cl₂</td>
<td>550</td>
<td>[Ag(TDPS)₂]ClO₄</td>
<td>550</td>
</tr>
<tr>
<td>Co(TDPS)₂Br₂</td>
<td>550</td>
<td>Ag(TDPS)NO₃</td>
<td>545</td>
</tr>
<tr>
<td>Co(TDPS)₂I₂</td>
<td>548</td>
<td>[Hg(TDPS)Br₂]₂</td>
<td>543</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Ni(TDPS)₄</a>₂</td>
<td>543</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ᵃValues are ±2cm⁻¹.

To rationalize the reduced basicity of the P-NR₂ group, one might consider that the nitrogen lone pair was involved in π*-dπ bonding.
FIGURE 11. NMR SPECTRUM OF [(Me₂N)₃P=S-CH₃]+I⁻, CD₃NO₂ SOLUTION
with empty d-orbitals of phosphorous or that it was located in a sterically unfavorable situation. The importance of pπ-dπ bonding between phosphorous and nitrogen is indicated by recent x-ray structural results on \([\text{PN(NMe}_2\text{)}_2]_4\)\(^{187}\) and \([\text{PN(NMe}_2\text{)}_2]_6\)\(^{188}\). The exocyclic P-N bond distance in the two compounds are 1.67Å, significantly shorter than the P-N single bond value of 1.77Å. A short exocyclic P-N bond (1.614 ± 0.002Å) was also observed in the octamethylpyrophosphoramide ligand when it was coordinated to copper(II).\(^{189}\) Moreover, in all three examples cited, the nearly planar nature of the exocyclic dimethylamino group is consistent with sp\(^2\) hybridization around nitrogen and significant P-N double bonding. However, the degree to which pπ-dπ bonding restricts rotation of the dimethylamino group around the P-N bond is questionable on the basis of limited NMR data. The low temperature (-60°) NMR spectra of \(\text{Ph}_2\text{PNMe}_2\) and \(\text{Ph}_2\text{P(S)NMe}_2\) showed no tendency of the N-methyl doublet (due to P-H coupling) to undergo further splitting. Any P-N double bonding would present a rotational barrier for the \(-\text{NMe}_2\) group and the two methyl groups would be magnetically non-equivalent. This experiment does not totally exclude P-N π-interaction, but its importance in a barrier to the free rotation of the \(-\text{NMe}_2\) group at room temperature must be small.

Ph\(_3\)PS. The infrared spectrum of the cadmium iodide complex of triphenylphosphine sulfide is very similar to the previously reported spectra of \(\text{Ph}_3\text{PS}\) complexes;\(^{138}\) the P=S stretching frequency is reduced in energy from 635 to 595cm\(^{-1}\).
Perchlorate and Nitrate Anions. The perchlorate and nitrate containing complexes also exhibit infrared bands characteristic of these anions. The strong perchlorate bands at approximately 1090 and 625 cm\(^{-1}\) show no signs of splitting; thus, the Cl\(_{10}\) ions retain their Td symmetry and are assumed to be uncoordinated. The silver nitrate complex of TDPS is one case of nitrate coordination and it will be discussed later under silver(I) compounds.

\[ \text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2 \] Complexes

Even though the ligand, methylenebis(diphenylphosphino)dioxide, OP\(_2\)O, and the various metal halides were mixed in a 1:1 molar ratio in attempts to obtain complexes with the same stoichiometry and structure as the SP\(_2\)S and SeP\(_2\)Se complexes, the elemental analysis and conductivity (Table 15) indicate that OP\(_2\)O displaces all the halide atoms from one metal ion to form an octahedral cation which was isolated as the complex, \([\text{M(OP}_2\text{O})_3][\text{NX}_4]\). This strong tendency of OP\(_2\)O to form a complex of the metal with a maximum coordination number is demonstrated by the cobalt perchlorate complex. The six-coordinate, bi-univalent electrolyte, \([\text{Co(OP}_2\text{O})_3]\text{ClO}_4\), was isolated during attempts to obtain the four-coordinate complex, \([\text{Co(OP}_2\text{O})_2]^{2+}\), where the molar ratio of ligand to metal was held at 2:1. Other related dioxides also tend to form complexes with a maximum coordination number; however, in these cases the ligand was always present in excess. 60,68
TABLE 15

CONDUCTANCE AND MAGNETIC DATA FOR THE METAL COMPLEXES OF METHYLENEBIS(DIPHENYLPHOSPHINO) DIOXIDE

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Lambda_M^a )</th>
<th>( M_{\text{corr.}}^a \times 10^6 \text{ (cgsu)} )</th>
<th>Diamagnetic ( x_{\text{corr.}}^a \times 10^6 \text{ (cgsu)} )</th>
<th>TIP ( x_{\text{corr.}}^a \times 10^6 \text{ (cgsu)} )</th>
<th>( \mu_{\text{eff.}} \text{ (BM)}^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(OP}_2\text{O)}_3]\text{ClO}_4)_2)</td>
<td>146</td>
<td>10,440</td>
<td>-820</td>
<td>-</td>
<td>5.00</td>
</tr>
<tr>
<td>([\text{Co(OP}_2\text{O)}_3\text{]}\text{CoBr}_4)</td>
<td>102</td>
<td>19,410</td>
<td>-754</td>
<td>750</td>
<td>9,144</td>
</tr>
<tr>
<td>([\text{Co(OP}_2\text{O)}_3\text{]}\text{CoI}_4)</td>
<td>b</td>
<td>20,260</td>
<td>-970</td>
<td>800</td>
<td>9,910</td>
</tr>
<tr>
<td>([\text{Ni(OP}_2\text{O)}_3\text{]}\text{NiBr}_4)</td>
<td>117</td>
<td>9,940</td>
<td>-754</td>
<td>-</td>
<td>5,580</td>
</tr>
<tr>
<td>([\text{Pd(OP}_2\text{O)}_3\text{]}\text{PdCl}_4)</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(a\) Solutions were \(-10^{-3}\) in nitromethane except the palladium complex which was \(-10^{-3}\)M in DMF.

\(b\) Insoluble.

\(c\) The magnetic moments for the octahedral metal complexes of \(\text{OP}_2\text{O}\) containing tetrahalo metal anions were determined by subtracting the molar susceptibility of \([(\text{n-C}_4\text{H}_9)_4\text{N}]_2\text{CoBr}_4,_{191} [(\text{n-C}_4\text{H}_9)_4\text{N}]_2\text{CoI}_4,_{191} \) and \([(\text{C}_2\text{H}_5)_4\text{N}]_2\text{NiBr}_4,_{192} \) which had been corrected for diamagnetism and for temperature independent magnetism of the cobalt anions, from the overall molar susceptibility of the complexes corrected only for the diamagnetism of \([\text{M(OP}_2\text{O)}_3]^2+\).

Values are \(\pm 0.05\text{BM}\) except for the complexes containing \(\text{MX}_4^{2-}\) anions, which are \(\pm 0.10\text{BM}\).

The electronic spectrum of \([\text{Co(OP}_2\text{O)}_3]\text{ClO}_4)_2\) exhibits the band maxima and extinction coefficients typical of octahedral cobalt(II) complexes (Fig. 12, Table 16). The weak band at \(18,380\text{cm}^{-1}\) and the shoulder at \(20,510\text{cm}^{-1}\) are assigned the \(4\text{T}_{1g} \rightarrow 4\text{A}_{2g}\) (P) and \(4\text{T}_{1g} \rightarrow 4\text{T}_{2g}\) (P) transitions, respectively. Moreover, in the electronic
FIGURE 12. ELECTRONIC SPECTRA OF $[\text{Co}(\text{OP}_2\text{O})_3\text{]}\text{(ClO}_4\text{)}_2$ (--), $\text{CH}_3\text{NO}_2$ SOLUTION, AND $[\text{Co}(\text{OP}_2\text{O})_3]\text{[CoBr}_4\text{]}$ (-), NUJOL MULL
spectra of the \([\text{Co(O}_2\text{P})_3\text{CoX}_4]\) complexes, one can observe characteristic absorption bands for both the tetrahedral and octahedral cobalt(II) ions (Fig. 12). The bands of high intensity between 14,000-16,000 cm\(^{-1}\) and around 5,000 cm\(^{-1}\) correspond fairly well with the reported\(^1\) spectra of the \(\text{CoBr}_4^{2-}\) and \(\text{CoI}_4^{2-}\) anions. The band of low intensity common to both the cobalt bromide and iodide complexes around 18,300 cm\(^{-1}\) corresponds to the 18,380 cm\(^{-1}\) band of the octahedral complex \([\text{Co(O}_2\text{P})_3\text{ClO}_4]_2\).

The magnetic data (Table 15) for the \([\text{Co(O}_2\text{P})_3\text{CoX}_4]\) complexes also provide further support for this proposed formulation. After subtracting the contribution of the tetrahalo cobalt anions, the magnetic moment of the cation was found to be 4.94 and 4.97 BM, in good agreement with the experimental magnetic moment of 5.00 BM for the octahedral \([\text{Co(O}_2\text{P})_3]^{2+}\) cation.

As in the case of the cobalt halides, \(\text{O}_2\text{P}\) forms the mixed octahedral-tetrahedral nickel complex \([\text{Ni(O}_2\text{P})_3\text{NiBr}_4]\). The electronic spectrum of \([\text{Ni(O}_2\text{P})_3\text{NiBr}_4]\) is comparable with that of the reported spectra\(^2\) of the tetrahedral \(\text{NiBr}_4^{2-}\) anion. The high intensity and complexity of the \(\text{NiBr}_4^{2-}\) spectrum obscures the low intensity bands of the octahedral \([\text{Ni(O}_2\text{P})_3]^{2+}\) cation. However, the magnetic moment of the complex after subtracting the contribution due to the tetrahedral \(\text{NiBr}_4^{2-}\) anion is 3.22 BM, in good agreement with other octahedral nickel(II) complexes.
TABLE 16

ELECTRONIC SPECTRAL DATA FOR THE METAL COMPLEXES OF
METHYLENEBIS(DIPHENYLPHOSPHINO) DIOXIDE

| Compound | Medium | $E_{\text{max.}} (\text{cm}^{-1})^a$ | $\lambda_{\text{max.}} (\mu\text{m})$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Co(OP}_2\text{O)}_3]^{2-}(\text{ClO}_4)^{-}_2$</td>
<td>1.72x10^{-2} M in CH$_3$NO$_2$</td>
<td>20,510 sh</td>
<td>488</td>
</tr>
<tr>
<td></td>
<td>Nujol mull</td>
<td>18,380 (16)</td>
<td>544</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20,510 sh</td>
<td>488</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18,380</td>
<td>544</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8,330</td>
<td>1,200</td>
</tr>
<tr>
<td>$[\text{Co(OP}_2\text{O)}_3][\text{CoBr}_4]^{-}$</td>
<td>3.6x10^{-3} M in CH$_3$NO$_2$</td>
<td>18,180 (28) 14,370 (566)</td>
<td>550 696</td>
</tr>
<tr>
<td></td>
<td>Nujol mull</td>
<td>16,100 (347) 7,020 (47)</td>
<td>621 1,425</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,900 (431) 4,820 (33)</td>
<td>671 2,075</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18,180 13,830</td>
<td>550 700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15,600 5,560</td>
<td>641 723</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15,040</td>
<td>665 1,800</td>
</tr>
<tr>
<td>$[\text{Co(OP}_2\text{O)}_3][\text{CoI}_4]^{-}$</td>
<td>Nujol mull</td>
<td>18,320 12,740</td>
<td>546 785</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,350 4,940</td>
<td>697 2,025</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13,810</td>
<td>724</td>
</tr>
<tr>
<td>$[\text{NI(OP}_2\text{O)}_3][\text{NIBr}_4]$</td>
<td>5.0x10^{-3} M in CH$_3$NO$_2$</td>
<td>16,000 (200)</td>
<td>625</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,290 sh</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8,550 (56)</td>
<td>1,170</td>
</tr>
<tr>
<td></td>
<td>Nujol mull</td>
<td>28,250 14,290</td>
<td>354 700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18,180 sh 13,700</td>
<td>550 730</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,810 sh 6,210</td>
<td>675 1,450</td>
</tr>
</tbody>
</table>
TABLE 16 — Continued

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>E max. (cm(^{-1}))(^a)</th>
<th>λ max. (µ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pd(OP(_2)O(_3)]([PdCl(_4)])</td>
<td>1.0x10(^{-2})M in DMF</td>
<td>29,630(2,100)</td>
<td>338</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25,110(400)</td>
<td>438</td>
</tr>
<tr>
<td></td>
<td>Nujol mull</td>
<td>21,050</td>
<td>475</td>
</tr>
</tbody>
</table>

\(^a\)Molar extinction coefficients are in parenthesis. sh = shoulder.

The elemental analysis and conductivity values of [Pd(OP\(_2\)O\(_3\)]\([PdCl\(_4\)]\) are consistent with the intriguing possibility that this complex also contains six-coordinate palladium(II). Moreover, it is the first reported complex of palladium with a phosphine oxide. Although the complexes of OP\(_2\)O with cobalt and nickel halides indicate that the ligand can readily displace all the halide atoms to form the octahedral metal complex, a similar behavior with palladium is quite remarkable for two reasons. First, few octahedral complexes of palladium have been reported\(^{194,195}\) and secondly, oxygen donors are generally poor ligands for palladium(II). The electronic spectrum of [Pd(OP\(_2\)O\(_3\)]\([PdCl\(_4\)]\) (Fig. 13) compares favorably to the reported\(^{196}\) spectrum of PdCl\(_4\)\(^{2-}\). The shift of the band maxima to higher energy in solution is typical of PdCl\(_4\)\(^{2-}\) in polar solvents. Typical spectra of octahedral palladium(II) complexes are unknown owing to the paucity of authentic complexes. However, [Pd(OP\(_2\)O\(_3\)]\(^{2+}\) does not appear to make any
FIGURE 13. ELECTRONIC SPECTRUM OF $[\text{Pd(O}_2\text{P})_3\text{][PdCl}_4]$; NUJOL MULL(—) and DMF SOLUTION(—)
noticeable contribution to the visible spectrum of the complex. The evidence suggests that the complex should be formulated as $[\text{Pd(OP}_2\text{O)}_3][\text{PdCl}_4]$ with a six-coordinate palladium cation probably in an octahedral environment. However, until further work with octahedral palladium complexes or an actual X-ray crystallographic structural analysis is done, the structural assignment of $[\text{Pd(OP}_2\text{O)}_3][\text{PdCl}_4]$ must remain tentative.

Cobalt(II) Complexes of Phosphine Sulfide and Selenide Ligands

Analytical and conductance data (Table 17) show that the cobalt halide complexes of tetramethyldiphosphine disulfide (TMD), dimethylphosphinothioic acid anhydride (DPTA), methylenebis(diphenylphosphino) disulfide(SP$_2$S) and diselenide (SeP$_2$Se) should be formulated as the non-electrolyte, monomeric CoLX$_2$ species. Although conductance measurements show that the cobalt halide complexes of tris(dimethylamino)phosphine sulfide (TDPS) dissociate somewhat in nitromethane, they can also be formulated as the molecular CoL$_2$X$_2$ species in the solid state. The cobalt perchlorate complexes of TDPS and SP$_2$S are bi-univalent electrolytes and contain the cations $[\text{Co(TDPS)}_4]^{2+}$ and $[\text{Co(SP}_2\text{S)}_2]^{2+}$ and two non-coordinated perchlorate anions.

The infrared spectra of Co(SP$_2$S)$_2$I$_2$, Co(SeP$_2$Se)Br$_2$; and Co(SeP$_2$Se)I$_2$ show two bands at 1060 and 900cm$^{-1}$ in addition to the ligand absorptions; these correspond to the two strongest infrared absorptions of THF. These complexes were isolated from THF solutions and the analytical data corresponds to Co(SP$_2$S)$_2$I$_2$·1/2THF,
Co(SeP₂Se)Br₂·1/2THF, and Co(SeP₂Se)I₂·3/4THF with THF trapped in the crystal lattice. As an additional proof (Fig. 7), the cobalt chloride complex of SeP₂Se also exhibited the 1060 and 900 cm⁻¹ bands and analyzed for Co(SeP₂Se)Cl₂·1/2THF. However, after the complex was heated overnight at 56° in vacuo, these bands disappeared and the complex analyzed for the unsolvated Co(SeP₂Se)Cl₂. The same procedure was performed on the above three THF-containing complexes, but little or no THF was removed under these conditions.

**TABLE 17**

CONDUCTANCE DATA FOR THE COBALT(II) COMPLEXES OF PHOSPHINE SULFIDE AND SELENIDE LIGANDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Λₐ cm²/ohm-mole</th>
<th>Compound</th>
<th>Λₐ cm²/ohm-mole</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="ClO%E2%82%84">Co(TDPS)₄</a>₂</td>
<td>164</td>
<td>Co(SP₂S)Br₂</td>
<td>7.7</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Co(SP₂S)₂</a>₂</td>
<td>151</td>
<td>Co(SeP₂Se)Br₂·1/2THF</td>
<td>8.4</td>
</tr>
<tr>
<td>Co(TDPS)₂Cl₂</td>
<td>23.8</td>
<td>Co(TDPS)₂I₂</td>
<td>25.9</td>
</tr>
<tr>
<td>Co(TMD)Cl₂</td>
<td>5.2</td>
<td>Co(TMD)I₂</td>
<td>11.5</td>
</tr>
<tr>
<td>Co(SeP₂Se)Cl₂</td>
<td>5.1</td>
<td>Co(DPTA)I₂</td>
<td>17.3</td>
</tr>
<tr>
<td>Co(TDPS)₂Br₂</td>
<td>24.1</td>
<td>Co(SP₂S)I₂·1/2THF</td>
<td>9.6</td>
</tr>
<tr>
<td>Co(TMD)Br₂</td>
<td>9.5</td>
<td>Co(SeP₂Se)I₂·3/4THF</td>
<td>10.7</td>
</tr>
<tr>
<td>Co(DPTA)Br₂</td>
<td>14.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ₐ Solutions were -10⁻³ M in nitromethane.
The electronic spectra of all the cobalt complexes (Table 18) exhibit visible $[\nu_3, ^4A_2 + ^4T_1(F)]$ and near infrared $[\nu_2, ^4A_2 + ^4T_1(F)]$ absorptions typical of known tetrahedral and pseudo-tetrahedral cobalt(II) compounds. Representative spectra of these complexes are illustrated in Figures 14-21 and in Table 18. Spectral parameters for the cobalt(II) complexes of phosphine sulfide and selenide ligands, as well as other tetrahedral and pseudo-tetrahedral cobalt complexes are presented in Table 19. The magnetic susceptibility values are consistent with tetrahedral cobalt(II) complexes (Table 22).

The ligand field strength modulus, $\Delta$, and the effective value of the Racah interelectronic repulsion term, $B'$ for the cobalt complexes were determined from the following relationships:

$$
\begin{align*}
\nu_1 &= \Delta \\
\nu_2 &= 1.5\Delta + 7.5B' - Q \\
\nu_3 &= 1.5\Delta + 7.5B' + Q \\
Q &= \frac{1}{2}[(0.6\Delta - 15B')^2 + 0.64\Delta^2]^{1/2}
\end{align*}
$$

**TABLE 18**

**ELECTRONIC SPECTRA DATA FOR THE COBALT(II) COMPLEXES OF PHOSPHINE SULFIDE AND SELENIDE LIGANDS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>$E_{\text{max.}}$ (cm$^{-1}$)</th>
<th>$\lambda_{\text{max.}}$ (mu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(TDPS)$_4$(ClO$_4$)$_2$</td>
<td>$5.0 \times 10^{-3}$ M in CH$_3$NO$_2$</td>
<td>15,250(480) 6,944(115)  656 1,440</td>
<td>$\nu_3$ $\nu_2$ $\nu_3$ $\nu_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,290(570) 5,473(124)  700 1,827</td>
<td>$\nu_3$ $\nu_2$ $\nu_3$ $\nu_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12,630(140)</td>
<td>$\nu_3$ $\nu_2$ $\nu_3$ $\nu_2$</td>
</tr>
</tbody>
</table>
**TABLE 18 — Continued**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>( E_{\text{max.}} ) (cm(^{-1})) ( v_3 )</th>
<th>( v_2 )</th>
<th>( \lambda_{\text{max.}} ) (mu) ( v_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Co(TDPS)}_2\text{Cl}_2 )</td>
<td>Nujol mull</td>
<td>14,370</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 1.0 \times 10^{-2} \text{M} )</td>
<td>17,000sh</td>
<td>7,010(51)</td>
<td>588</td>
</tr>
<tr>
<td></td>
<td>in ( \text{CH}_3\text{NO}_2 )</td>
<td>16,360sh</td>
<td>5,130</td>
<td>611</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15,720(388)</td>
<td></td>
<td>636</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,710sh</td>
<td></td>
<td>680</td>
</tr>
<tr>
<td></td>
<td>Nujol mull</td>
<td>16,580</td>
<td>6,830</td>
<td>603</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,770</td>
<td>4,940</td>
<td>677</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13,480</td>
<td></td>
<td>741</td>
</tr>
<tr>
<td></td>
<td>( 1.0 \times 10^{-2} \text{M} )</td>
<td>16,420(330)</td>
<td>6,670sh</td>
<td>609</td>
</tr>
<tr>
<td></td>
<td>in 2:3 TDPS: ( \text{CH}_2\text{Cl}_2 )</td>
<td>15,060(330)</td>
<td>5,060(80)</td>
<td>664</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13,370(220)</td>
<td></td>
<td>748</td>
</tr>
<tr>
<td>( \text{Co(TDPS)}_2\text{Br}_2 )</td>
<td>( 1.0 \times 10^{-2} \text{M} )</td>
<td>16,970sh</td>
<td>6,850(61)</td>
<td>590</td>
</tr>
<tr>
<td></td>
<td>in ( \text{CH}_3\text{NO}_2 ) (Fig. 14)</td>
<td>16,100sh</td>
<td>4,900(60)</td>
<td>621</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15,150(550)</td>
<td></td>
<td>660</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,610sh</td>
<td></td>
<td>684</td>
</tr>
<tr>
<td></td>
<td>( 1.0 \times 10^{-2} \text{M} )</td>
<td>15,550(390)</td>
<td>6,120sh</td>
<td>645</td>
</tr>
<tr>
<td></td>
<td>in 2:3 TDPS: ( \text{CH}_2\text{Cl}_2 )</td>
<td>14,550(470)</td>
<td>4,820(85)</td>
<td>688</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13,400(310)</td>
<td></td>
<td>746</td>
</tr>
<tr>
<td></td>
<td>Nujol mull (Fig. 15)</td>
<td>15,700</td>
<td>6,250</td>
<td>634</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,370</td>
<td>4,860</td>
<td>696</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13,070</td>
<td></td>
<td>765</td>
</tr>
</tbody>
</table>
FIGURE 14. ELECTRONIC SPECTRUM OF \( \text{Co(TDPS)}_2\text{Br}_2 \), \( \text{CH}_3\text{NO}_2 \) SOLUTION
FIGURE 15. ELECTRONIC SPECTRUM OF Co(TDPS)₂Br₂, NUJOL MULL
<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>$E_{\text{max.}}$ (cm$^{-1}$)</th>
<th>$\lambda_{\text{max.}}$ (m$\mu$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$v_3$</td>
<td>$v_2$</td>
</tr>
<tr>
<td>Co(TDPS)$_2$I$_2$</td>
<td>$1.0 \times 10^{-2} \text{M}$ in CH$_3$NO$_2$</td>
<td>15,150sh</td>
<td>6,600(86)</td>
</tr>
<tr>
<td></td>
<td>$1.0 \times 10^{-2} \text{M}$ in 2:3 TDPS: CH$_2$Cl$_2$</td>
<td>14,390(790)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nujol mull</td>
<td>13,820sh</td>
<td></td>
</tr>
<tr>
<td>Co(TMD)Cl$_2$</td>
<td>$5.4 \times 10^{-3} \text{M}$ in CH$_3$NO$_2$</td>
<td>14,680(540)</td>
<td>5,880(103)</td>
</tr>
<tr>
<td></td>
<td>Nujol mull (Fig. 16)</td>
<td>13,790(570)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>12,800(610)</td>
<td></td>
</tr>
<tr>
<td>Co(TMD)Br$_2$</td>
<td>$5.0 \times 10^{-3} \text{M}$ in CH$_3$NO$_2$</td>
<td>14,710</td>
<td>5,850</td>
</tr>
<tr>
<td></td>
<td>Nujol mull</td>
<td>13,600</td>
<td>4,710</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12,570</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>17,300(107)</td>
<td>9,090sh</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16,300(161)</td>
<td>6,670(21)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15,700(139)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,800sh</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>16,700</td>
<td>6,670</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,800</td>
<td>5,000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12,800</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>15,870(162)</td>
<td>6,840(22)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15,200(195)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,300sh</td>
<td></td>
</tr>
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</table>
FIGURE 16. ELECTRONIC SPECTRUM OF Co(TMD)Cl₂, NUJOL MULL
<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>$E_{\text{max.}}$ (cm$^{-1}$)$^a$</th>
<th>$\lambda_{\text{max.}}$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$v_3$ $v_2$</td>
<td>$v_3$ $v_2$</td>
</tr>
<tr>
<td>Nujol mull</td>
<td>15,870</td>
<td>6,450</td>
<td>630 1,550</td>
</tr>
<tr>
<td></td>
<td>14,430</td>
<td>4,880</td>
<td>693 2,050</td>
</tr>
<tr>
<td></td>
<td>12,700</td>
<td></td>
<td>788</td>
</tr>
<tr>
<td>Co(TMD)$_2$I$_2$</td>
<td>5.0×10$^{-3}$ M</td>
<td>15,100(183) 6,790(32)</td>
<td>663 1,473</td>
</tr>
<tr>
<td></td>
<td>in CH$_3$NO$_2$</td>
<td>14,300(197)</td>
<td>698</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13,500(200)</td>
<td>739</td>
</tr>
<tr>
<td>Nujol mull</td>
<td>14,790</td>
<td>6,170</td>
<td>676 1,620</td>
</tr>
<tr>
<td></td>
<td>13,560</td>
<td>4,760</td>
<td>738 2,100</td>
</tr>
<tr>
<td></td>
<td>12,220</td>
<td></td>
<td>818</td>
</tr>
<tr>
<td>Co(DPTA)Br$_2$</td>
<td>1.07×10$^{-2}$ M</td>
<td>15,700(380) 5,990(61)</td>
<td>636 1,670</td>
</tr>
<tr>
<td></td>
<td>in CH$_3$NO$_2$</td>
<td>15,200(402)</td>
<td>660</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,300(390)</td>
<td>698</td>
</tr>
<tr>
<td>Nujol mull (Fig. 17)</td>
<td>15,900</td>
<td>6,450</td>
<td>629 1,550</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,470 4,880</td>
<td>691 2,050</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12,900</td>
<td>775</td>
</tr>
<tr>
<td>Co(DPTA)I$_2$</td>
<td>1.0×10$^{-2}$ M</td>
<td>15,000(450) 6,670(70)</td>
<td>665 1,500</td>
</tr>
<tr>
<td></td>
<td>in CH$_3$NO$_2$</td>
<td>14,300(540)</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13,500(590)</td>
<td>739</td>
</tr>
<tr>
<td>Nujol mull</td>
<td>14,850</td>
<td>6,250</td>
<td>675 1,600</td>
</tr>
<tr>
<td></td>
<td>13,640</td>
<td>4,760</td>
<td>733 2,100</td>
</tr>
<tr>
<td></td>
<td>12,660</td>
<td></td>
<td>790</td>
</tr>
</tbody>
</table>
FIGURE 17. ELECTRONIC SPECTRUM OF Co(DPTA)Br$_2$, NUJOL MULL
<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>$E_{\text{max.}}$ (cm$^{-1}$)$^a$</th>
<th>$\lambda_{\text{max.}}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(Sp$_2$S)$_2$(ClO$_4$)$_2$</td>
<td>$1.0 \times 10^{-2}$ M in CH$_3$NO$_2$</td>
<td>15,430(285) 7,460(127)</td>
<td>684 1,340</td>
</tr>
<tr>
<td>(Fig. 18)</td>
<td>14,290(460) 5,760(81)</td>
<td>700 1,736</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13,120(210)</td>
<td>762</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nujol mull (Fig. 19)</td>
<td>15,290 7,520</td>
<td>654 1,329</td>
</tr>
<tr>
<td></td>
<td>14,080 5,790</td>
<td>710 1,728</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13,330</td>
<td>750</td>
<td></td>
</tr>
<tr>
<td>Co(Sp$_2$S)Br$_2$</td>
<td>$6.4 \times 10^{-3}$ M in THF</td>
<td>16,530sh 7,510(33)</td>
<td>605 1,331</td>
</tr>
<tr>
<td></td>
<td>14,640(730) 5,850(31)</td>
<td>683 1,708</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nujol mull</td>
<td>15,770 6,370</td>
<td>634 1,570</td>
</tr>
<tr>
<td></td>
<td>14,600 5,000</td>
<td>685 2,000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12,700</td>
<td>787</td>
<td></td>
</tr>
<tr>
<td>Co(Sp$_2$S)I$_2$·1/2THF</td>
<td>$2.1 \times 10^{-3}$ M in CH$_3$NO$_2$</td>
<td>15,040(470) 6,600(77)</td>
<td>665 1,515</td>
</tr>
<tr>
<td></td>
<td>14,390(450) 5,710(69)</td>
<td>695 1,750</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13,860(450)</td>
<td>722</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12,290(190)</td>
<td>814</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nujol mull</td>
<td>14,600 6,850sh</td>
<td>685 1,460</td>
</tr>
<tr>
<td></td>
<td>13,740 5,650</td>
<td>728 1,770</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12,200</td>
<td>820</td>
<td></td>
</tr>
<tr>
<td>Co(Sp$_2$Se)Cl$_2$</td>
<td>$1.1 \times 10^{-2}$ M in CH$_3$NO$_2$</td>
<td>17,150(110) 7,870(25)</td>
<td>583 1,270</td>
</tr>
<tr>
<td></td>
<td>15,690(160) 5,970(27)</td>
<td>638 1,675</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14,600(200)</td>
<td>685</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 18. ELECTRONIC SPECTRUM OF $[\text{Co(SPS)}_2](\text{ClO}_4)_2$, CH$_3$NO$_2$ SOLUTION
FIGURE 19. ELECTRONIC SPECTRUM OF [Co(SP₂S)₂][ClO₄]₂, NUJOL MULL
**TABLE 18 -- Continued**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>$E_{\text{max.}}$ (cm$^{-1}$)$^a$</th>
<th>$\lambda_{\text{max.}}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$v_3$</td>
<td>$v_2$</td>
</tr>
<tr>
<td>Co(Se$_2$Se)Br$_2 \cdot 1/2$THF</td>
<td>Nujol mull</td>
<td>16,390</td>
<td>6,670</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,350</td>
<td>4,940</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13,280</td>
<td></td>
</tr>
<tr>
<td>Co(Se$_2$Se)I$_2 \cdot 3/4$THF</td>
<td>1.0×10$^{-2}$M in CH$_3$NO$_2$ (Fig. 20)</td>
<td>16,670sh</td>
<td>7,620(35)</td>
</tr>
<tr>
<td></td>
<td>Nujol mull (Fig. 21)</td>
<td>14,750(380)</td>
<td>5,880(34)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,930</td>
<td>6,780sh</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,140</td>
<td>5,560</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12,480</td>
<td></td>
</tr>
<tr>
<td>Co(Se$_2$Se)I$_2 \cdot 3/4$THF</td>
<td>9.8×10$^{-3}$M in CH$_3$NO$_2$</td>
<td>16,130sh</td>
<td>7,230(58)</td>
</tr>
<tr>
<td></td>
<td>Nujol mull</td>
<td>14,350(550)</td>
<td>5,760(50)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,410</td>
<td>6,670sh</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13,390</td>
<td>5,220</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11,860</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Molar extinction coefficients in parenthesis. sh = shoulder.

The value for the $v_3$ transition was determined from the electronic spectra of the solid complex suspended in a Nujol mull and from the solution spectra of the [Co(TDPS)$_4$](ClO$_4$)$_2$ complex according to a method outlined by Drago.$^{200}$ The maximum for the $v_3$ band of the [Co(TDPS)$_4$](ClO$_4$)$_2$ complex was located at approximately the same
Figure 20. Electronic spectrum of Co(Se₂Se)Br₂ · 1/2THF, THF solution.
FIGURE 21. ELECTRONIC SPECTRUM OF Co(Se₂Se)Br₂·1/2THF, Nujol Mull
position in both the solid state and in solution, so both the \( \nu_2 \) and \( \nu_3 \) values for the calculations were taken from the spectrum of 
\[ \text{[Co(TDPS)}_4]\text{(ClO}_4\text{)}_2 \] in nitromethane. Fortunately the \( \nu_2 \) bands in the 
\text{Co(TDPS)}_2\text{X}_2 and \text{CoLX}_2 complexes were sufficiently resolved in the Nujol 
mull suspension to use, since both \( \nu_2 \) and \( \nu_3 \) are shifted to higher 
energy in solution. For the \text{Co(TDPS)}_2\text{X}_2 complexes, this solvation 
effect can be nullified effectively by adding a large excess of the free 
ligand to the solution. The value for the \( \nu_2 \) transition was determined 
by averaging the energy of the two broad bands or the maximum of the 
principal band observed in the 5,000-7,000cm\(^{-1}\) region.

To graphically illustrate the technique described in the 
preceding paragraphs, the spectral parameters of \[ \text{[Co(SP}_2\text{S)}_2]\text{(ClO}_4\text{)}_2 \] are 
determined here as a sample calculation. The \( T_1 \) states are split by 
spin-orbit coupling to the following extent \(-9/4\lambda'\), \(+6/4\lambda'\), and 
\(+15/4\lambda'\)^201 so that the energy of the \( \nu_3 \) transition, \( ^4A_2 \rightarrow ^4T_1 (P) \), is 
determined by using these weighting factors.

Calculation of \( \nu_3 \): \[ \frac{9}{4}(13,330) = 29,988 \]
\[ \frac{6}{4}(14,080) = 21,120 \]
\[ \frac{15}{4}(15,290) = \frac{57,330}{108,438} \]
\[ \nu_3 = 108,438 \div 30/4 \]
\[ \nu_3 = 14,460 \text{cm}^{-1} \]

Calculation of \( \nu_2 \): \[ \nu_2 = \frac{7,520 + 5,790}{2} \]
\[ \nu_2 = 6,655 \text{cm}^{-1} \]

Calculation of \( \Delta \) and \( B' \): \[ \Delta = 1/3(\nu_2 + \nu_3 - 15B') \]
\[ Q = 1/2(\nu_3 - \nu_2) \]
### Table 19

**Spectral Parameters for Tetrahedral and Pseudotetrahedral Cobalt Complexes**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta (\text{cm}^{-1}) )</th>
<th>( v_2 (\text{cm}^{-1}) )</th>
<th>( v_3 (\text{cm}^{-1}) )</th>
<th>( \beta = B'/B )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(TDPS)}_4] (\text{ClO}_4)_2)</td>
<td>3,620</td>
<td>6,208</td>
<td>14,270</td>
<td>0.66</td>
<td>d</td>
</tr>
<tr>
<td>([\text{Co(HMPA)}_4] (\text{ClO}_4)_2)</td>
<td>3,640</td>
<td>6,590</td>
<td>16,150</td>
<td>0.80</td>
<td>50</td>
</tr>
<tr>
<td>([\text{Co(Ph}_3\text{PO)}_4] (\text{ClO}_4)_2)</td>
<td>3,680</td>
<td>6,240</td>
<td>16,300</td>
<td>0.81</td>
<td>191</td>
</tr>
<tr>
<td>([\text{Co(Me}_3\text{PO)}_4] (\text{ClO}_4)_2)</td>
<td>3,800</td>
<td>6,600</td>
<td>16,890</td>
<td>0.83</td>
<td>43</td>
</tr>
<tr>
<td>([\text{Co(Me}_3\text{PS)}_4] (\text{ClO}_4)_2)</td>
<td>3,890</td>
<td>6,690</td>
<td>14,400</td>
<td>0.65</td>
<td>43</td>
</tr>
<tr>
<td>([\text{Co(Sp}_2\text{S)}_2] (\text{ClO}_4)_2)</td>
<td>3,900</td>
<td>6,655</td>
<td>14,460</td>
<td>0.65</td>
<td>d</td>
</tr>
<tr>
<td>(\text{CoCl}_4^{2-})</td>
<td>3,130</td>
<td>5,460</td>
<td>14,700</td>
<td>0.73</td>
<td>191</td>
</tr>
<tr>
<td>(\text{CoBr}_4^{2-})</td>
<td>2,850</td>
<td>4,980</td>
<td>14,000</td>
<td>0.72</td>
<td>191</td>
</tr>
<tr>
<td>(\text{CoI}_4^{2-})</td>
<td>2,645</td>
<td>4,600</td>
<td>13,250</td>
<td>0.69</td>
<td>191</td>
</tr>
<tr>
<td>([\text{Co(TDPS)}_2\text{Cl}_2)</td>
<td>3,390</td>
<td>5,880</td>
<td>15,290</td>
<td>0.76</td>
<td>d</td>
</tr>
<tr>
<td>([\text{Co(Me}_3\text{PS)}_2\text{Cl}_2)</td>
<td>3,340</td>
<td>5,810</td>
<td>14,990</td>
<td>0.74</td>
<td>43</td>
</tr>
<tr>
<td>([\text{Co(TMD)}\text{Cl}_2)</td>
<td>3,365</td>
<td>5,835</td>
<td>15,150</td>
<td>0.75</td>
<td>d</td>
</tr>
<tr>
<td>([\text{Co(SeP}_2\text{Se)}\text{Cl}_2)</td>
<td>3,340</td>
<td>5,810</td>
<td>15,170</td>
<td>0.75</td>
<td>d</td>
</tr>
<tr>
<td>([\text{Co(TDPS)}_2\text{Br}_2)</td>
<td>3,210</td>
<td>5,560</td>
<td>14,680</td>
<td>0.73</td>
<td>d</td>
</tr>
<tr>
<td>([\text{Co(Me}_3\text{PS)}_2\text{Br}_2)</td>
<td>3,280</td>
<td>5,700</td>
<td>14,540</td>
<td>0.72</td>
<td>43</td>
</tr>
<tr>
<td>([\text{Co(TMD)}\text{Br}_2)</td>
<td>3,270</td>
<td>5,670</td>
<td>14,500</td>
<td>0.71</td>
<td>d</td>
</tr>
<tr>
<td>([\text{Co(Dpta)}\text{Br}_2)</td>
<td>3,290</td>
<td>5,670</td>
<td>14,710</td>
<td>0.72</td>
<td>d</td>
</tr>
<tr>
<td>([\text{Co(SeP}_2\text{Se)}\text{Br}_2\text{1/2THF})</td>
<td>3,180</td>
<td>5,560</td>
<td>14,040</td>
<td>0.69</td>
<td>d</td>
</tr>
<tr>
<td>([\text{Co(Sp}_2\text{S)}\text{Br}_2)</td>
<td>3,270</td>
<td>5,690</td>
<td>14,610</td>
<td>0.72</td>
<td>d</td>
</tr>
<tr>
<td>([\text{Co(TDPS)}_2\text{I}_2)</td>
<td>3,290</td>
<td>5,280</td>
<td>13,840</td>
<td>0.68</td>
<td>d</td>
</tr>
</tbody>
</table>
TABLE 19 -- Continued

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta$(cm$^{-1}$)</th>
<th>$\nu_2$(cm$^{-1}$)</th>
<th>$\nu_3$(cm$^{-1}$)</th>
<th>$\beta$=B'/B</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(Me$_3$PS)$_2$I$_2$</td>
<td>3,260</td>
<td>5,650</td>
<td>13,710</td>
<td>0.66</td>
<td>43</td>
</tr>
<tr>
<td>Co(TMD)I$_2$</td>
<td>3,160</td>
<td>5,470</td>
<td>13,720</td>
<td>0.67</td>
<td>d</td>
</tr>
<tr>
<td>Co(DPTA)I$_2$</td>
<td>3,170</td>
<td>5,510</td>
<td>13,950</td>
<td>0.69</td>
<td>d</td>
</tr>
<tr>
<td>Co(SeP$_2$Se)I$_2$·3/4THF</td>
<td>3,030</td>
<td>5,220</td>
<td>13,470</td>
<td>0.66</td>
<td>d</td>
</tr>
<tr>
<td>Co(SP$_2$S)I$_2$·1/2THF</td>
<td>3,260</td>
<td>5,650</td>
<td>13,710</td>
<td>0.66</td>
<td>d</td>
</tr>
</tbody>
</table>

Values for tetrahalo cobalt complexes are average values for a number of cations.

Values are ±200 cm$^{-1}$.

$B$(free ion) = 967 cm$^{-1}$.

This work.

By substituting values for $\nu_2$ and $\nu_3$ and solving this equation, $4Q^2 = \Delta^2 - 18B\Delta + 225(B')^2$, the following values for $\Delta$ and B' for [Co(SP$_2$S)$_2$](ClO$_4$)$_2$ were determined.

$\Delta = 3,900$ cm$^{-1}$

$B' = 627$ cm$^{-1}$

The rule of average environment states that, for a set of mixed ligands, the cubic field magnitude is the weighted average of the cubic ligand fields associated with each of the complete set of ligands separately. From the spectral data of the tetrahedral CoX$_4^{2-}$, [Co(TDPS)$_4$](ClO$_4$)$_2$, and [Co(SP$_2$S)$_2$](ClO$_4$)$_2$ complexes it is possible to
check the applicability of the "average field" in the Co(TDPS)$_2$X$_2$ and Co(SP$_2$S)$_2$X$_2$ complexes. The spectral results are given in Table 20; the calculated and observed ligand field values agree very well.

### Table 20

**AVERAGE LIGAND FIELD APPROXIMATION FOR Co(TDPS)$_2$X$_2$ AND Co(SP$_2$S)$_2$X$_2$ COMPLEXES**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Observed Value $\Delta$(cm$^{-1}$)</th>
<th>Calculated Value $\Delta$(cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(TDPS)$_2$Cl$_2$</td>
<td>3,390</td>
<td>3,375</td>
</tr>
<tr>
<td>Co(TDPS)$_2$Br$_2$</td>
<td>3,210</td>
<td>3,235</td>
</tr>
<tr>
<td>Co(TDPS)$_2$I$_2$</td>
<td>3,050</td>
<td>3,132</td>
</tr>
<tr>
<td>Co(SP$_2$S)Br$_2$</td>
<td>3,270</td>
<td>3,375</td>
</tr>
<tr>
<td>Co(SP$_2$S)I$_2$·1/2THF</td>
<td>3,260</td>
<td>3,272</td>
</tr>
</tbody>
</table>

$^a$Values are calculated by averaging those for CoX$_4^{2-}$ from ref. 191 and the values for [Co(TDPS)$_4$](ClO$_4$)$_2$ and [Co(SP$_2$S)$_2$](ClO$_4$)$_2$ obtained in this study.

The general utility of the average environment rule in tetrahedral cobalt(II) complexes allows the ligand field strength of the phosphine sulfide and selenide ligands to be compared with other CoLX$_2$ complexes. The calculated ligand field strength of TMD, DPTA, and SeP$_2$Se in tetrahedral Co(II) complexes is 3,660, 3,720, and 3,490cm$^{-1}$, respectively. Thus, the position of phosphine sulfide and selenide ligands in a spectrochemical series for tetrahedral cobalt(II)
complexes may be deduced as: $I^- < Br^- < Cl^- < Ph_2P(Se)CH_2P(Se)Ph_2$
$\sim (Me_2N)_3PS < (Me_2N)_3PO < Me_2P(S)P(S)Me_2 < Ph_3PO < Me_2P(S)OP(S)Me_2$
$\sim Me_3PO < Me_3PS < Ph_2P(S)CH_2P(S)Ph_2$.

The $\beta$ values of all of these phosphine sulfide and selenide complexes of cobalt(II) are very low and approximately equal, suggesting appreciable and similar polarizability and covalency effects in the cobalt-sulfur or -selenium bonding. The order of $\beta$ values produces the following nephelauxetic series: $Ph_2P(Se)CH_2P(Se)Ph_2 \sim Ph_2P(S)CH_2P(S)Ph_2$
$\sim Me_3PS < Me_2P(S)P(S)Me_2 < Me_2P(S)OP(S)Me_2 < (Me_2N)_3PS < I^- < Br^- < Cl^-$
$\sim (Me_2N)_3PO < Ph_3PO < Me_3PO$.

Comparison of the parameters $D_q$ and $\beta$ for these phosphine sulfide and selenide cobalt complexes produces some interesting and surprising results. For example, the calculated $D_q$ value of TDPS is lower than the $D_q$ value of $Me_3PS$ but approximately the same as its oxygen analog, $(Me_2N)_3PO$ (HMPA). Wilkins et al. have also observed that analogous tertiary oxo and thioxo ligands of Group V elements produce similar ligand field effects. Although the $D_q$ values of TDPS and HMPA are nearly identical, the $\beta$ values are significantly lower in the TDPS complexes, as expected for the more polarizable thioxo group.

At first glance it is strange that the $D_q$ value of TDPS is smaller than that of $Me_3PS$, since the increased inductive character of the dimethylamino group should make the $\sigma$-donor strength of TDPS greater than $Me_3PS$. However, any ligand-ligand interaction between adjacent coordinated TDPS molecules would reduce the effective ligand field and lead to a smaller $D_q$ value. Accurate molecular models show that the
dimethylamino groups are certainly larger than methyl groups; thus ligand-ligand interaction would be more pronounced in TDPS and may account for its low Dq values. A steric interaction has been suggested previously for coordinated amides and nitriles where the observed Dq values did not increase with increasing N-substitution and relative basicities toward the reference acids, iodine and phenol. The steric argument might also explain why TDPS and HMPA exhibit comparable Dq values toward cobalt(II). That is, the shorter Co-O and O-P bond distances for coordinated HMPA would show a greater ligand-ligand repulsion than in the TDPS case, and the effective field would be lower than expected for the oxo ligand.

The Dq values of TMD and Me₃PS are also very similar. The effect of removing a methyl group from Me₃PS to form TMD should decrease the basicity of the ligand slightly, whereas the chelate effect of the bidentate ligand should compensate somewhat. The data indicate that these two effects have nullified each other so no difference in ligand field strength of Me₃PS and TMD toward cobalt(II) is observed.

As mentioned before (see p. 52), ligands of the type \((\text{Me}_2\text{N})_2\text{P(O)XP(O)(NMe}_2\text{)_2}\) where \(X = 0\) or NMe, are more basic than when \(X = \text{CH}_2\), at least toward nickel(II). However, the insertion of an oxygen atom between the two phosphorous atoms in TMD to form DPTA does not have any noticeable effect on the spectral properties of the ligand toward cobalt(II). In this study, both disulfide ligands have almost identical Dq and \(\beta\) values. The effect of increasing the chelate ring
size from five to six members appears to offset the inductive effect of the oxygen. At present it is impossible to determine just what magnitude these two competing effects assert individually on the ligand properties.

The ligand field strength of $\text{SP}_2\text{S}$ is remarkably high when one considers that the similar monodentate, triphenylphosphine sulfide, shows no interaction with cobalt(II) in similar solvents. In fact, on the basis of spectral data, $\text{SP}_2\text{S}$ is as good a ligand toward cobalt as $\text{Me}_3\text{PS}$ and better than TDPS. Likewise, the ligand field strength of $\text{SeP}_2\text{Se}$ is also remarkably high and is comparable to TDPS and $\text{Ph}_3\text{PO}$ toward cobalt(II). The $\text{Dq}$ value of $\text{SP}_2\text{S}$ is greater than that of $\text{SeP}_2\text{Se}$. It is unfortunate that the analogous phosphine oxide, $\text{OP}_2\text{O}$, did not give tetrahedral cobalt complexes to complete this series. In any case, it is evident that the electron withdrawing effects of the phenyl rings is compensated adequately by the chelate effect of these bidentate ligands.

Tetrahedral cobalt(II) complexes with other sulfur and selenium ligands have not been studied extensively. Work in this area has been generally confined to thiourea and substituted thioureas, although Jorgensen has determined the spectral parameters for a tetrahedral cobalt complex with diethylthiophosphate (Table 21). Other sulfur ligands such as diethylthiocarbamate rapidly oxidize cobalt(II) to cobalt(III). A comparison of the $\text{Dq}$ values for tetrahedral cobalt(II) complexes of phosphine sulfides with those of thiourea, ethylenethiourea, and diethylthiophosphate gives the following spectrochemical series: $\text{TDPS} < \text{etu} < \text{Me}_3\text{PS} < \text{SP}_2\text{S} < \text{dtp}$
Moreover, the $\beta$ values give the nephelauxetic series: $tu < SP_2S \sim Me_3PS \sim TDPS < etu \sim dtp \sim I^-$. 

**TABLE 21**

SPECTRAL PARAMETERS FOR SOME TETRAHEDRAL AND PSEUDO-TETRAHEDRAL COBALT(II) COMPLEXES CONTAINING SULFUR LIGANDS

<table>
<thead>
<tr>
<th>Compound $^a$</th>
<th>$\Delta$(cm$^{-1}$)</th>
<th>$v_2$(cm$^{-1}$)</th>
<th>$v_3$(cm$^{-1}$)</th>
<th>$\beta=B/B^*$</th>
<th>$\mu_{\text{eff.}}$(BM)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$<a href="%5Ctext%7BClO%7D_4">\text{Co(tu)}_4</a>_2$</td>
<td>4,250</td>
<td>7,200</td>
<td>14,500</td>
<td>0.62</td>
<td>4.50</td>
<td>206</td>
</tr>
<tr>
<td>$\text{Co(dtp)}_2$</td>
<td>4,000</td>
<td>6,900</td>
<td>15,100</td>
<td>0.68</td>
<td>-</td>
<td>208</td>
</tr>
<tr>
<td>$<a href="%5Ctext%7BClO%7D_4">\text{Co(etu)}_4</a>_2$</td>
<td>3,780</td>
<td>6,480</td>
<td>14,600</td>
<td>0.67</td>
<td>4.73</td>
<td>207</td>
</tr>
<tr>
<td>$\text{Co(tu)}_2\text{Cl}_2$</td>
<td>3,480</td>
<td>6,000</td>
<td>15,000</td>
<td>0.73</td>
<td>4.45</td>
<td>206</td>
</tr>
<tr>
<td>$\text{Co(etu)}_2\text{Cl}_2$</td>
<td>3,390</td>
<td>5,870</td>
<td>14,700</td>
<td>0.71</td>
<td>4.51</td>
<td>207</td>
</tr>
<tr>
<td>$\text{Co(tu)}_2\text{Br}_2$</td>
<td>3,390</td>
<td>5,900</td>
<td>14,700</td>
<td>0.72</td>
<td>4.49</td>
<td>206</td>
</tr>
<tr>
<td>$\text{Co(etu)}_2\text{Br}_2$</td>
<td>3,320</td>
<td>5,740</td>
<td>14,200</td>
<td>0.69</td>
<td>4.54</td>
<td>207</td>
</tr>
<tr>
<td>$\text{Co(etu)}_2\text{I}_2$</td>
<td>3,210</td>
<td>5,560</td>
<td>13,510</td>
<td>0.65</td>
<td>4.58</td>
<td>207</td>
</tr>
</tbody>
</table>

$^a$dtp = diethylidithiophosphate, tu = thiourea, and etu = ethylenethiourea.

Since the mode of bonding is somewhat related, the coordinating ability of phosphine sulfides, $R_3P=S$, might be comparable to that of thioureas, $R_2C=S$, and this seems to be the case. The $Dq$ values for the cobalt complexes of phosphine sulfides and ethylenethiourea, as well as the cobalt halide complexes including thiourea, are very similar. The $\beta$ values also show that both types of sulfur ligands have a high degree of covalency in the cobalt-sulfur bond. The high $Dq$
value of the tetrahedral cobalt(II) complex of thiourea may be a reflection of a smaller steric interaction (as previously mentioned with phosphine sulfides). This would be attributed to the fact that hydrogens are smaller than methyl or phenyl groups in addition to the fact that thioureas are nearly planar. In contrast, the phosphine sulfides studied all have large, bulky organic substituents on phosphorous as well as being tetrahedral in structure. Interestingly, when organic groups are substituted for the hydrogens in thiourea, even in a "pinned-back" position of ethylenethiourea, the $Dq$ value for the tetrahedral cobalt(II) complex, $(\text{CoL}_4)(\text{ClO}_4)_2$, is markedly reduced from that of the thiourea complex. However, there is little change in the $Dq$ values for the pseudo-tetrahedral cobalt halide complexes, $\text{CoL}_2X_2$.

The $Dq$ and $\beta$ values for $(\text{EtO})_2\text{PS}_2^-$ and $\text{Ph}_2\text{P(S)CH}_2\text{P(S)Ph}_2$ cobalt(II) complexes are comparable, however, it is dangerous to conclude that dtp is a better ligand than SP$_2$S or that SP$_2$S is more covalently bound to cobalt than dtp on the basis of only one complex. In fact, just the opposite results would be expected if these ligands are compared to thioethers, thiols, and other anionic sulfur ligands. Work with thiols and thioethers shows that the coordinating ability increases, while polarizability decreases, from RS$^-$ to $R_2S$.\textsuperscript{121} Likewise, Jorgensen\textsuperscript{120} has pointed out that as the number of lone pairs on sulfur increases, the $\Delta$ value decreases. Thus, SP$_2$S should be a better ligand than dtp. The $Dq$ values show just the opposite effect. However, all the available chemical evidence points to extensive delocalization of electron density when dtp bonds with metals\textsuperscript{122} but little or none with
Therefore, increased ligand field strength by delocalization as well as a difference in the size of the chelate ring (four versus six-membered) may account for the increased $Dq$ value of dtp over $SP_2S$.

The magnetic moments (Table 22) of the phosphine sulfide and selenide cobalt complexes are in good agreement with a tetrahedral structure. A comparison of the moments for these cobalt complexes shows some rather marked differences for ligands with similar coordinating units and mode of bonding with cobalt. The values for the TDPS-cobalt complexes seem abnormally high, whereas those for the $Me_3PS$-cobalt complexes are very low. Wilkins et al.\textsuperscript{43} have attributed the low moments of the $Me_3PS$-cobalt complexes to the higher covalency (and correspondingly lower spin-orbit coupling constant) in the metal-sulfur bond as compared to the metal-oxygen bond of analogous oxo ligands. Since the magnetic moments of the TDPS-cobalt complexes are consistently higher than those of $Me_3PS$, the implication of this data is that delocalization (or covalent bonding) effects are less important for TDPS than for $Me_3PS$. The other phosphine sulfide and selenide ligands would then be intermediate in covalent bonding. This may be rationalized on the basis of more severe steric interactions in the case of TDPS, as discussed on p. 103.

Other factors such as differences in ligand field strengths and steric interactions may also cause variations of the magnetic moments. Cotton has proposed\textsuperscript{198} that in $K_2[Co(NCO)_4]$ the low moment of 4.32BM and low spin-orbit coupling constant of $-115\text{cm}^{-1}$ is due to a
distortion of the complex in the solid state. By replacing the small potassium cation with a bulky cation, Ph$_3$C$_4$H$_9$P$^+$, the magnetic moment of [Co(NCO)$_4$]$_{2-}$ was 4.44BM. Thus various degrees of distortion of the tetrahedral structure in the solid state as well as slight differences in covalent bonding and ligand field strength would cause a wider range of magnetic moments than otherwise might be expected for the phosphine sulfide and selenide cobalt complexes.

**TABLE 22**

MAGNETIC DATA FOR THE PHOSPHINE SULFIDE AND SELENIDE AND SOME PHOSPHINE OXIDE COBALT(II) COMPLEXES

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\chi_{corr.}$</th>
<th>Diamagnetic Correction</th>
<th>TIP</th>
<th>$\mu_{eff.}$</th>
<th>$\lambda (\text{cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="CIO$_4$">Co(TDPS)$_4$</a>$_2$</td>
<td>8,852</td>
<td>-499</td>
<td>578</td>
<td>4.59</td>
<td>162</td>
</tr>
<tr>
<td><a href="CIO$_4$">Co(HMPA)$_4$</a>$_2$</td>
<td>8,627(30°)</td>
<td>-550</td>
<td></td>
<td>4.58</td>
<td>150</td>
</tr>
<tr>
<td><a href="CIO$_4$">Co(Ph$_3$PO)$_4$</a>$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.53</td>
<td>147</td>
</tr>
<tr>
<td><a href="CIO$_4$">Co(Me$_3$PO)$_4$</a>$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.56</td>
<td>164</td>
</tr>
<tr>
<td><a href="CIO$_4$">Co(Me$_3$PS)$_4$</a>$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.31</td>
<td>105</td>
</tr>
<tr>
<td><a href="CIO$_4$">Co(SP$_2$S)$_2$</a>$_2$</td>
<td>8,223</td>
<td>-435</td>
<td>536</td>
<td>4.45</td>
<td>140</td>
</tr>
<tr>
<td>Co(Me$_3$PS)$_2$Cl$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.32</td>
<td>92</td>
</tr>
<tr>
<td>Co(TDPS)$_2$Cl$_2$</td>
<td>8,703</td>
<td>-271</td>
<td>629</td>
<td>4.54</td>
<td>144</td>
</tr>
<tr>
<td>Co(IMD)Cl$_2$</td>
<td>8,364</td>
<td>-172</td>
<td>621</td>
<td>4.46</td>
<td>126</td>
</tr>
<tr>
<td>Co(SeP$_2$Se)Cl$_2$</td>
<td>8,857</td>
<td>-421</td>
<td>626</td>
<td>4.60</td>
<td>155</td>
</tr>
<tr>
<td>Co(Me$_3$PS)$_2$Br$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.41</td>
<td>111</td>
</tr>
<tr>
<td>Co(TDPS)$_2$Br$_2$</td>
<td>8,800</td>
<td>-293</td>
<td>651</td>
<td>4.57</td>
<td>145</td>
</tr>
<tr>
<td>Compound</td>
<td>( \chi_{\text{corr.}} \times 10^6 ) (cgsu)</td>
<td>Diamagnetic Correction ( \times 10^6 ) (cgsu)</td>
<td>TIP ( \times 10^6 ) (cgsu)</td>
<td>( \mu_{\text{eff.}} ) ( \text{(BM)}^a ) ( \lambda \text{(-cm}^{-1})^b )</td>
<td>Ref.</td>
</tr>
<tr>
<td>--------------------------</td>
<td>---------------------------------------------</td>
<td>-----------------------------------------------</td>
<td>-----------------------------</td>
<td>---------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Co(TMD)Br(_2)</td>
<td>8,547</td>
<td>-194</td>
<td>639</td>
<td>4.52</td>
<td>135</td>
</tr>
<tr>
<td>Co(DPTA)Br(_2)</td>
<td>8,591</td>
<td>-198</td>
<td>635</td>
<td>4.52</td>
<td>136</td>
</tr>
<tr>
<td>Co(SeP(_2)Se)Br(_2) ( \cdot ) ( \text{1/2THF} )</td>
<td>8,539</td>
<td>-470</td>
<td>657</td>
<td>4.52</td>
<td>131</td>
</tr>
<tr>
<td>Co(SP(_2)S)Br(_2)</td>
<td>8,592</td>
<td>-261</td>
<td>628</td>
<td>4.52</td>
<td>132</td>
</tr>
<tr>
<td>Co(Me(_3)PS)(_2)I(_2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.42</td>
<td>110</td>
</tr>
<tr>
<td>Co(TDPS)(_2)I(_2)</td>
<td>9,011</td>
<td>-325</td>
<td>688</td>
<td>4.64</td>
<td>147</td>
</tr>
<tr>
<td>Co(TMD)I(_2)</td>
<td>8,809</td>
<td>-213</td>
<td>661</td>
<td>4.57</td>
<td>141</td>
</tr>
<tr>
<td>Co(DPTA)I(_2)</td>
<td>8,623</td>
<td>-218</td>
<td>659</td>
<td>4.54</td>
<td>135</td>
</tr>
<tr>
<td>Co(SeP(_2)Se)I(_2) ( \cdot ) ( \text{3/4THF} )</td>
<td>8,600</td>
<td>-515</td>
<td>690</td>
<td>4.53</td>
<td>127</td>
</tr>
<tr>
<td>Co(SP(_2)S)I(_2) ( \cdot ) ( \text{1/2THF} )</td>
<td>8,688</td>
<td>-293</td>
<td>639</td>
<td>4.54</td>
<td>138</td>
</tr>
</tbody>
</table>

\(^a\)Values are \( \pm 0.05\)BM. The magnetic moment of \([\text{Co(HMPA)}\(_4\)](\text{ClO}_4)\(_2\)\) is not corrected for TIP.

\(^b\)Calculated from \( \mu_{\text{obs.}} = \mu_{\text{s.o.}} - 15.56\lambda'/\Delta \). Values are \( \pm 20\text{cm}^{-1} \); \( \lambda\text{(free ion)} = -172\text{cm}^{-1} \).

\(^c\)This work.

The orbital contribution of the \( ^4T_2 \) state to the total magnetic moment is expected to increase from chloride to iodide, as observed for all the cobalt halide complexes except Co(SeP\(_2\)Se)Cl\(_2\). However, since the bromide and iodide complexes of SeP\(_2\)Se have THF molecules tightly held in the crystal lattice, these complexes may be
more distorted than Co(SeP₂Se)Cl₂. Interestingly, the marked similarity of the TMD and DPTA ligands is also exhibited in their magnetic moments, as both the cobalt bromide and iodide complexes of these ligands have identical magnetic moments, within experimental error.

**Nickel(II) Complexes of (Me₂N)₃PS and Ph₂P(S)CH₂P(S)Ph₂**

The conductivity values (Table 23) as well as elemental analysis indicate that the nickel complexes of SP₂S should be formulated as [Ni(SP₂S)₂](CIO₄)₂ and the monomeric Ni(SP₂S)X₂ species. The nickel bromide complex is formulated as Ni(SP₂S)Br₂·1/2THF which is based on its infrared spectrum and elemental analysis in an analogous fashion to some of the cobalt halide complexes. The nickel iodide complex crystallizes with 1/2 mole of dichloromethane in the crystal lattice. Although the conductivity value for [Ni(TDPS)₄](CIO₄)₂ could not be obtained due to its rapid decomposition in solution, the infrared spectrum showed no splitting of the perchlorate bands and the perchlorate anions are assumed to be uncoordinated. The complex is thus formulated as containing the [Ni(TDPS)₄]²⁺ cation.

The electronic spectra and extinction coefficients for [Ni(TDPS)₄](CIO₄)₂ (Fig. 22) in a 1:1 volume mixture of TDPS-nitromethane and for the SP₂S-nickel halide complexes (Fig. 23) are consistent with a tetrahedral or pseudo-tetrahedral nickel(II) complex (Table 24). The solid state spectrum of [Ni(TDPS)₄](CIO₄)₂ could not be obtained for comparison owing to the rapid decomposition of the complex, even when
FIGURE 22. ELECTRONIC SPECTRUM OF [Ni(TDPS)$_4$](ClO$_4$)$_2$, CH$_3$NO$_2$-TDPS SOLUTION
FIGURE 23. ELECTRONIC SPECTRUM OF Ni(SP\textsubscript{2}S)Br\textsubscript{2}·1/2THF, CH\textsubscript{3}NO\textsubscript{2} SOLUTION
coated with mineral oil. The solid state spectra of the \( \text{SP}_2\text{S} \)-nickel halide complexes were obtained as Nujol mulls and showed essentially no differences in the absorption maxima from those obtained in solution, in contrast to the behavior of the cobalt(II) complexes.

**TABLE 23**

**CONDUCTIVITY AND MAGNETIC DATA FOR THE NICKEL(II) COMPLEXES OF TRIS(DIMETHYLAMINO)PHOSPHINE SULFIDE AND METHYLENEBIS(DIPHENYLPHOSPHINO) DISULFIDE**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Lambda_a^M ) ( \text{cm}^2/\text{ohm-mole} )</th>
<th>( \chi_{\text{corr.}}^M \times 10^6 ) (cgsu)</th>
<th>Diamagnetic ( \chi_{\text{corr.}}^M \times 10^6 ) (cgsu)</th>
<th>( \mu_{\text{eff.}} ) (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni(TDPS)}_4]\text{(ClO}_4\text{)}_2)</td>
<td>b</td>
<td>5,417</td>
<td>-499</td>
<td>3.59</td>
</tr>
<tr>
<td>([\text{Ni(SP}_2\text{S)}_2]\text{(ClO}_4\text{)}_2)</td>
<td>132</td>
<td>3,335</td>
<td>-435</td>
<td>2.82</td>
</tr>
<tr>
<td>([\text{Ni(SP}_2\text{S)}Br_2\cdot1/2\text{THF})</td>
<td>7.3</td>
<td>4,660</td>
<td>-290</td>
<td>3.35</td>
</tr>
<tr>
<td>([\text{Ni(SP}_2\text{S)}I_2\cdot1/2\text{CH}_2\text{Cl}_2)</td>
<td>29.5</td>
<td>4,770</td>
<td>-300</td>
<td>3.38</td>
</tr>
</tbody>
</table>

\( ^a \text{Solutions were -}10^{-3}\text{M in nitromethane.} \)

\( ^b \text{Decomposes in solution.} \)

\( ^c \text{Values are \pm 0.05BM.} \)

The magnetic moment of \([\text{Ni(TDPS)}_4]\text{(ClO}_4\text{)}_2\) is at the low end of the range observed (3.49-4.00BM) for tetrahedral nickel(II) complexes. The low moment may possibly be due to a distortion from a strictly tetrahedral structure. A similar explanation was given for the magnetic moment of \( \text{NiI}_4^{2-} \), whereby the structural distortion causes considerable splitting and separation of the ground state multiplet (a \( ^3\text{T}_1 \) term) that exists for a Td nickel(II) complex.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>$E_{\text{max.}} (\text{cm}^{-1})$\textsuperscript{a}</th>
<th>$\lambda_{\text{max.}} (\mu\text{m})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ni(TDPS)}_4\text{]}(\text{ClO}_4)_2$</td>
<td>$1.2 \times 10^{-2} \text{M}$ in 1:1 TDPS: CH$_3$NO$_2$ (Fig. 22)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>26,850 (1,830)</td>
<td>372</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,400 (179)</td>
<td>694</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13,080 (163)</td>
<td>765</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10,000 (35)</td>
<td>1,000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8,660 (34)</td>
<td>1,155</td>
</tr>
<tr>
<td>$[\text{Ni(SP}_2\text{S)}_2\text{]}(\text{ClO}_4)_2$</td>
<td>$1.87 \times 10^{-2} \text{M}$ in CH$_3$NO$_2$ (Fig. 24)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>27,200 (910)</td>
<td>368</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13,020 (28)</td>
<td>768</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7,770 (17)</td>
<td>1,287</td>
</tr>
<tr>
<td></td>
<td>$5.4 \times 10^{-3} \text{M}$ in CH$_2$Cl$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>26,320 (1,610)</td>
<td>380</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13,000 (20)</td>
<td>769</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7,920 (9)</td>
<td>1,262</td>
</tr>
<tr>
<td></td>
<td>Nujol mull</td>
<td>26,900</td>
<td>371</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12,970</td>
<td>771</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7,690</td>
<td>1,300</td>
</tr>
<tr>
<td>$\text{Ni(SP}_2\text{S)}\text{Br}_2 \cdot 1/2\text{THF}$</td>
<td>$9.3 \times 10^{-3} \text{M}$ in CH$_3$NO$_2$ (Fig. 23)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>27,590 (1,890)</td>
<td>363</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15,530 (116)</td>
<td>644</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,430 (127)</td>
<td>693</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9,640sh</td>
<td>1,037</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8,450 (43)</td>
<td>1,184</td>
</tr>
</tbody>
</table>
TABLE 24 — Continued

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>$E_{\text{max.}}$ (cm$^{-1}$)$^a$</th>
<th>$\lambda_{\text{max.}}$ (µ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nujol mull</td>
<td>16,000sh</td>
<td>625</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14,100</td>
<td>709</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9,610sh</td>
<td>1,040</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8,460</td>
<td>1,182</td>
<td></td>
</tr>
<tr>
<td>$\text{Ni(SP}_2\text{S)}\text{I}_2\cdot1/2\text{CH}_2\text{Cl}_2$</td>
<td>$5.2\times10^{-3}$ M in $\text{CH}_3\text{NO}_2$</td>
<td>19,510(1,210)</td>
<td>513</td>
</tr>
<tr>
<td></td>
<td>14,550(104)</td>
<td>688</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13,070(147)</td>
<td>765</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8,330(48)</td>
<td>1,200</td>
<td></td>
</tr>
<tr>
<td>Nujol mull</td>
<td>19,300</td>
<td>518</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14,620sh</td>
<td>684</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13,000</td>
<td>768</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8,330</td>
<td>1,200</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Molar extinction coefficients in parenthesis; sh = shoulder.

The magnetic moments of the $\text{SP}_2\text{S}$-nickel halide complexes are also low, lower than most pseudo-tetrahedral nickel(II) complexes. However, the experimental results with cobalt(II) show that $\text{SP}_2\text{S}$ is certainly a much better ligand than the halides, so that, as in the case of the triphenylphosphine-nickel halide complexes,$^{210}$ an effective symmetry lower than "Td" would be expected. The low symmetry of the ligand field would cause a further splitting of the ground state
multiplet, produced by the action of spin-orbit coupling on the $^3T_1$ orbital ground state, and consequently the magnetic moments would be lower than for Td examples.

In conclusion, the combined magnetic and spectral data indicate that $[\text{Ni(TDPS)}_4](\text{ClO}_4)_2$, $\text{Ni(SP}_2\text{S})\text{Br}_2\cdot\text{1/2THF}$, and $\text{Ni(SP}_2\text{S})\text{I}_2\cdot\text{1/2CH}_2\text{Cl}_2$ have tetrahedral and pseudo-tetrahedral structures. The $[\text{Ni(TDPS)}_4](\text{ClO}_4)_2$ complex, as well as the nickel complex of its oxygen analog, $[\text{Ni[OP(\text{NMe}_2}_3\text{)}_4](\text{ClO}_4)_2]$, are, to date, the only known cationic tetrahedral nickel(II) complexes.

The nickel perchlorate complex of $\text{SP}_2\text{S}$ does not appear to fit into this trend of tetrahedral nickel(II) complexes for phosphine sulfide ligands. Although conductivity and analytical data indicate that the complex contains the $[\text{Ni(SP}_2\text{S})_2]^{2+}$ cation, the electronic spectra and extinction coefficients (Fig. 24 and Table 24) as well as magnetic moment precludes a tetrahedral structure. The electronic spectra and extinction coefficients are more compatible for nickel(II) in a square planar environment. However, the magnetic moment of 2.82BM is too high for a planar nickel(II) complex, but too low for a tetrahedral one. A structure intermediate between a square planar and tetrahedral environment is proposed to explain this inconsistency between the spectra and magnetic data. Similar reasoning has been used for the $[\text{Ni(Ph}_3\text{PO)}_4](\text{ClO}_4)_2$ complex.
FIGURE 24. ELECTRONIC SPECTRUM OF [Ni(S₂P₂)₂](ClO₄)₂, CH₃NO₂ SOLUTION
Palladium(II) Complexes of (Me₂N)₃PS, PhP(S)CH₂P(S)Ph₂, and Ph₂P(Se)CH₂P(Se)Ph₂

The palladium(II) complexes of TDPS, SP₂S, and SeP₂Se are non-electrolytes in solution and exhibit electronic spectra typical of known square planar palladium complexes (Table 25). The electronic spectra are essentially the same in solution as in the solid state indicating that little or no structural change occurs in solution. The complexes are thus formulated as the square planar Pd(TDPS)₂Cl₂, Pd(SP₂S)X₂, and Pd(SeP₂Se)X₂ molecular species.

TABLE 25
CONDUCTIVITY AND ELECTRONIC SPECTRA DATA FOR THE PALLADIUM(II) COMPLEXES OF TRIS(DIMETHYLAMINO)PHOSPHINE SULFIDE AND METHYLENEBIS(DIPHENYLPHOSPHINO) DISULFIDE AND DISELENIIDE

<table>
<thead>
<tr>
<th>Compound</th>
<th>Aₘa</th>
<th>Medium</th>
<th>E max. (cm⁻¹)b</th>
<th>λ max. (μμ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(TDPS)₂Cl₂</td>
<td>13.5</td>
<td>1.0x10⁻³M in CH₃NO₂</td>
<td>26,670(2,920)</td>
<td>375</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nujol mull</td>
<td>27,160</td>
<td>369</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20,160sh</td>
<td>496</td>
</tr>
<tr>
<td>Pd(SP₂S)Cl₂</td>
<td>1.6</td>
<td>1.98x10⁻⁴M in DMF</td>
<td>31,200(7,780)</td>
<td>321</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nujol mull</td>
<td>30,770</td>
<td>325</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>23,920</td>
<td>418</td>
</tr>
</tbody>
</table>
Table 25 — Continued

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda^a _m</th>
<th>$E_{\text{max.}}^{(\text{cm}^{-1})}</th>
<th>\lambda_{\text{max.}}(\mu)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Pd(SP}_2\text{S)}\text{Br}_2$</td>
<td>1.8</td>
<td>2.01x$10^{-4}$ M in DMF</td>
<td>28,300 (7,410) 353</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nujol mull</td>
<td>24,000 (1,970) 416</td>
</tr>
<tr>
<td>$\text{Pd(SP}_2\text{S)}\text{I}_2$</td>
<td>2.5</td>
<td>1.98x$10^{-4}$ M in DMF</td>
<td>30,100 (11,400) 332</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25,400 (4,360) 394</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18,800 (2,270) 531</td>
</tr>
<tr>
<td>$\text{Pd(SeP}_2\text{Se)}\text{Cl}_2$</td>
<td>11.6</td>
<td>1.0x$10^{-3}$ M in DMF</td>
<td>31,400 (4,300) 318</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nujol mull</td>
<td>24,600 (1,460) 406</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30,300 330</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>23,900 418</td>
</tr>
<tr>
<td>$\text{Pd(SeP}_2\text{Se)}\text{Br}_2$</td>
<td>14.6</td>
<td>1.0x$10^{-3}$ M in DMF</td>
<td>26,900 (4,900) 372</td>
</tr>
</tbody>
</table>

$^a$ Solutions were $10^{-3}$ M in DMF, except $\text{Pd(TDPS)}_2\text{Cl}_2$ which was $10^{-3}$ M in nitromethane.

$^b$ Molar extinction coefficients in parenthesis; sh = shoulder.

The position of the first band in the visible spectrum has been suggested as a means of comparing the ligand field strength of various ligands toward palladium(II). Although this is a less accurate means of developing a spectrochemical series than in the case of cobalt, it does illustrate some interesting trends. The order of
ligand-palladium interaction observed in palladium chloride complexes is:
TDPS < Ph3PSe ~ Ph3PS138 < SeP2Se ~ SP2S. By comparison, the order of
ligand-palladium interaction developed by displacement reaction is:
Cl− < Br− < Ph3PSe, Ph3PS < I− < SP2S < SCN−. The ordering of this
series is quite compatible with the more inclusive and developed
spectrochemical series.

The greater ligand field strength of SP2S and SeP2Se over
Ph3PS and Ph3PSe toward palladium(II) is not surprising and is probably
due to the chelate effect as well as to a slightly better inductive
effect of the methylene bridge as compared to a phenyl ring. Moreover,
there is a marked similarity between the two sets of analogous sulfide
and selenide ligands. With cobalt(II), which is considered a borderline
metal, SP2S was a better ligand than SeP2Se; however, with the "soft"
metal, palladium(II), they are almost identical. It appears that the
better σ-bonding ability of SP2S compared to SeP2Se with cobalt(II) is
nullified by the larger size and greater polarizability of the selenium
atoms in SeP2Se. This may make SeP2Se a better π-bonder than SP2S with
palladium(II). Polarizability and π-bonding will be discussed more
fully in a following section on the bonding in the phosphine
chalcogenide complexes.
Silver(I) and Group IIB Metal Complexes of \((\text{Me}_2\text{N})_3\text{PS}\), \(\text{Ph}_3\text{PS}\), \(\text{Ph}_2\text{P(S)CH}_2\text{P(S)Ph}_2\) and \(\text{Ph}_2\text{P(O)CH}_2\text{P(S)Ph}_2\)

The conductivity data (Table 26) indicate that the silver perchlorate complexes of TDPS, \(\text{SP}_2\text{S}\), and \(\text{OP}_2\text{S}\) are typical uni-univalent electrolytes in nitromethane. Since the infrared spectra shows all the \(\text{P=S}\) and \(\text{P=O}\) groups coordinated and only ionic perchlorate groups, the complexes are formulated as \([\text{Ag(TDPS)}_2]\text{ClO}_4\), with two-coordinate silver(I) in the complexes with monodentate ligands, and as \([\text{Ag(SP}_2\text{S})_2]\text{ClO}_4\) and \([\text{Ag(OP}_2\text{S})_2]\text{ClO}_4\), with four-coordinate silver(I) in the cases of bidentates.

The stoichiometry, infrared spectra (Fig. 25), and low conductance value of the \(\text{Ag(TDPS)NO}_3\) complex all suggest that the nitrate group is coordinated. The infrared spectrum of \(\text{Ag(TDPS)NO}_3\) in a Nujol mull shows two sharp, medium intensity peaks at 1035 and 1030 cm\(^{-1}\), which are assigned to the \(-\text{ONO}_2\) symmetric stretch of coordinated nitrate groups. However, the infrared spectrum cannot be used to differentiate between monodentate and bidentate \(\text{NO}_3^-\) groups, owing to overlap of strong ligand bands in the 1200-1500 cm\(^{-1}\) region.

The conductivity values for the \(\text{SP}_2\text{S}\) and \(\text{OP}_2\text{S}\) Group IIB metal iodide complexes and the \(\text{SP}_2\text{S}\)-perchlorate complexes indicate that they are non-electrolytes and bi-univalent electrolytes, respectively. Together with elemental analysis and infrared spectra, these complexes are formulated as \(\text{M(SP}_2\text{S})\text{I}_2\), \(\text{M(OP}_2\text{S})\text{I}_2\), and \([\text{M(SP}_2\text{S})_2]\text{ClO}_4\) where the four-coordinate Group IIB metal ion probably has a tetrahedral or pseudo-tetrahedral structure.
### TABLE 26

CONDUCTIVITY VALUES AND NMR SPECTRA OF SILVER(I) AND GROUP IIB COMPLEXES OF TRIS(DIMETHYLAMINO)PHOSPHINE SULFIDE AND METHYLENEBIS(DIPHENYLPHOSPHINO) DISULFIDE AND OXIDE SULFIDE

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Lambda_M$</th>
<th>$-\text{CH}_2-$</th>
<th>$J_{P-H}$</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm$^2$/ohm-mole</td>
<td>Triplet($\tau$)</td>
<td>(cps)</td>
<td></td>
</tr>
<tr>
<td>[Ag(TDPS)$_2$]ClO$_4$</td>
<td>75.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ag(TDPS)NO$_3$</td>
<td>38.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Hg(TDPS)Br$_2$]$_2$</td>
<td>18.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SP$_2$S</td>
<td>-</td>
<td>5.97</td>
<td>13.0</td>
<td>CDC$_3$</td>
</tr>
<tr>
<td>[Ag(SP$_2$S)$_2$]ClO$_4$</td>
<td>80.7</td>
<td>5.78</td>
<td>13.0</td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td><a href="ClO$_4$">Zn(SP$_2$S)$_2$</a>$_2$</td>
<td>168</td>
<td>5.61</td>
<td>13.0</td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td><a href="ClO$_4$">Cd(SP$_2$S)$_2$</a>$_2$</td>
<td>173</td>
<td>5.49</td>
<td>13.0</td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td><a href="ClO$_4$">Hg(SP$_2$S)$_2$</a>$_2$</td>
<td>168</td>
<td>5.45</td>
<td>13.0</td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td>SP$_2$S</td>
<td>-</td>
<td>5.69</td>
<td>13.5</td>
<td>CH$_3$COCH$_3$</td>
</tr>
<tr>
<td>Zn(SP$_2$S)I$_2$</td>
<td>4.0</td>
<td>5.28</td>
<td>13.5</td>
<td>CH$_3$COCH$_3$</td>
</tr>
<tr>
<td>Cd(SP$_2$S)I$_2$</td>
<td>6.4</td>
<td>5.00</td>
<td>13.5</td>
<td>CH$_3$COCH$_3$</td>
</tr>
<tr>
<td>Hg(SP$_2$S)I$_2$</td>
<td>5.4</td>
<td>b</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Ag(OP$_2$S)$_2$]ClO$_4$</td>
<td>89.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn(OP$_2$S)I$_2$</td>
<td>6.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cd(OP$_2$S)I$_2$</td>
<td>11.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hg(OP$_2$S)I$_2$</td>
<td>3.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Solutions were $10^{-3}$ M in nitromethane.

$^b$Not sufficiently soluble.
FIGURE 25. INFRARED SPECTRUM OF Ag(TDPS)NO₃
Previously the Lewis acid strength of a metal halide has been correlated with the shift in the phosphoryl stretching frequency\(^3\) or the shift in the carbonyl frequency of ethyl acetate.\(^{214}\) For triphenylphosphine oxide complexes, the shift of the P=O frequency to lower energy was 39, 35, and 34\,\text{cm}^{-1} for the ZnL\(_2\)Br\(_2\), CdL\(_2\)Br\(_2\), and HgL\(_2\)Br\(_2\) complexes, respectively. This trend might be expected for an interaction of a "hard" base with a series of borderline to "soft" metals. However, a similar comparison of the P=S stretching frequency in OP\(_2\)S and SP\(_2\)S Group IIB metal complexes (Tables 12 and 13) does not give analogous trends. For example, the P=S stretching frequencies in the SP\(_2\)S-metal iodide complexes, M(SP\(_2\)S)I\(_2\), M = Zn, Cd, or Hg, are at 572, 573, and 570\,\text{cm}^{-1}, respectively, whereas in the metal perchlorate complexes, [M(SP\(_2\)S)\(_2\)](ClO\(_4\))\(_2\), they appear at 568, 568, and 565\,\text{cm}^{-1}. From these values one might be tempted to attribute the magnitude of the interaction of this phosphine sulfide with Group IIB metals in the order Hg > Cd ~ Zn, which is the expected trend of a "soft" base with "soft" to borderline metals. However, the significance of a three \,\text{cm}^{-1} difference is questionable considering that a number of variables such as mass effects and \(\pi\)-bonding have been ignored.

The NMR spectra of the SP\(_2\)S Group IIB metal complexes were examined in order to determine the relative strength of the metal-sulfur interaction by measuring the shift of the methylene triplet on coordination. The triplet should shift to lower field, that is, the electron density of the hydrogens of the methylene group should decrease in forming the metal-sulfur bond, thus the amount of shielding would be
less in the complex as compared to the free ligand and the triplet would be shifted to lower field. Examination of the NMR spectral data, then, for the $\text{SP}_2\text{S}$ Group IIB metal iodide and perchlorate complexes (Table 26) does show a trend of $\text{Zn} < \text{Cd} < \text{Hg}$. This trend fits the expected interaction of these metals with a "soft" base and is consistent with stability constant measurements of Group IIB complexes with other sulfur donors.\textsuperscript{105,215} Moreover, cadmium(II) and mercury(II), both considered "soft" metals, have similar shifts and noticeably greater than zinc(II), a borderline metal. The NMR spectrum of $[\text{Ag(SP}_2\text{S})_2]\text{ClO}_4$ also shows a shift of the methylene triplet to lower field, however, since the charge on silver is +1, a direct quantitative comparison with Group IIB metals, which have a +2 charge, is not possible.

The mercuric bromide complex of TDPS is a non-electrolyte in nitromethane; in order to have a four-coordinate mercuric ion that is consistent with the elemental analysis, the complex is formulated as a dimer. Likewise, the elemental analysis of the cadmium iodide complex of triphenylphosphine sulfide also suggests a dimer. The infrared spectra show that TDPS and $\text{Ph}_3\text{PS}$ retain their normal bonding, so halogen bridges between the two metal ions are proposed. Dimeric $\text{L}_X^X\text{M}_M^X$ complexes have been proposed for mercury(II) and cadmium(II) with other phosphine sulfide and selenide ligands.\textsuperscript{138,143} The formula of the mercuric complex is especially interesting, since the compound was always recrystallized in the presence of excess TDPS ligand; however no $\text{Hg(TDPS)}_2\text{Br}_2$ complex was isolated.
Oxidation of \((\text{Me}_2\text{N})_3\text{PS}\)

The copper(I) complex \([\text{Cu(TDPS)}_4]\text{ClO}_4\) was obtained from the reduction of \([\text{Cu(\text{CH}_3\text{CN})}_4]\text{ClO}_4)_2\) by excess TDPS. The conductance and magnetic data (Table 27), elemental analyses, and infrared spectrum all support a four-coordinate copper(I) complex. There are previous examples of copper(II) being reduced to copper(I) by alkyl phosphine sulfides.\textsuperscript{136,138} In addition, alkyl and aryl phosphine sulfides have been shown to reduce Au(III) and Pt(IV) to lower oxidation states.\textsuperscript{138,143} No attempt was made in the previous studies to identify the oxidized material, although in those cases with alcohols as solvents, it is possible that the alcohol may have been oxidized to the aldehyde. However, in the present study, no solvent other than excess TDPS was used; thus, it was of considerable interest to identify the material that was oxidized when Cu(II) was reduced spontaneously to Cu(I) in TDPS.

In the preparation of \([\text{Cu(TDPS)}_4]\text{ClO}_4\), a white compound precipitated when \([\text{Cu(\text{CH}_3\text{CN})}_4]\text{ClO}_4)_2\) was dissolved in TDPS. The infrared spectrum of the recrystallized material (Fig. 26) was very similar to that of TDPS except that the 565\text{cm}^{-1} infrared band (P=S stretching frequency) was absent and two new peaks at 655 and 515\text{cm}^{-1} were present in addition to the strong perchlorate bands at ~1100 and 625\text{cm}^{-1}. The same cation was also isolated as the \text{Br}_3^- salt after bromine oxidation of TDPS in acetonitrile. Both salts behave as bi-univalent electrolytes in nitromethane.
FIGURE 26. INFRARED SPECTRA OF \((\text{Me}_2\text{N})_3\text{PS}(-)\) and \(\left[(\text{Me}_2\text{N})_3\text{P-S-S-P(NMe}_2\right)_3\right)(\text{ClO}_4)_2(-)\)
TABLE 27
CONDUCTANCE, MAGNETIC, AND ELECTRONIC SPECTRAL DATA FOR
THE COPPER(I) COMPLEX AND OXIDATION PRODUCTS OF
TRIS(DIMETHYLAMINO)PHOSPHINE SULFIDE

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Lambda_m^a ) ( \text{cm}^2/\text{ohm-mole} )</th>
<th>( \mu_{\text{eff.}} ) ( \text{BM}^b )</th>
<th>Visible Spectrum ( c ), ( \text{E max. (cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cu(TDPS)}_4]\text{ClO}_4)</td>
<td>112</td>
<td>Diamagnetic</td>
<td>CH(_3)NO(_2) Soln.</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BClO%7D_4">\text{(Me}_2\text{N)}_3\text{PS}_2\text{P(NMe}_2\text{)_3}</a>_2)</td>
<td>193</td>
<td>-</td>
<td>26,770(790)</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BBr%7D_3">\text{(Me}_2\text{N)}_3\text{PS}_2\text{P(NMe}_2\text{)_3}</a>_2)</td>
<td>146</td>
<td>-</td>
<td>21,380(1,860)</td>
</tr>
<tr>
<td>([\text{(Me}_2\text{N)}_3\text{PS}_2\text{P(NMe}_2\text{)_3}][\text{Cu}_2\text{Cl}_6])</td>
<td>126, 2.04/Cu(II)</td>
<td>-</td>
<td>11,200(105)</td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>8,470sh</td>
<td></td>
</tr>
</tbody>
</table>

\( a \) Solutions are \(-10^{-3}\) M in nitromethane.

\( b \) Values are \( \pm 0.05\) BM

\( c \) Molar extinction coefficients in parenthesis; sh = shoulder.

The NMR spectra of the perchlorate and tribromide salts show a sharp doublet at 7.10\( \tau \) and 7.02\( \tau \) with the \( J_{\text{P-H}} \) values of 11.3 and 11.5cps, respectively (CD\(_3\)NO\(_2\) solution with TMS as an internal standard). The above values are to be compared with 7.32\( \tau \) and \( J_{\text{P-H}} = 11.0\) cps for TDPS. The NMR spectra show that all the methyl groups are equivalent and the dimethylamino groups are bonded to phosphorous. The magnitude of the downfield shift of the methyl resonance is approximately the same.
as was observed for the methyl iodide derivative of TDPS,
\[
[(\text{Me}_2\text{N})_3\text{P-S-CH}_3]^{+}\text{I}^-, \quad 7.06\tau \text{ (N-CH}_3) \text{ and } J_{\text{P-H}} = 11.2\text{cps}.
\]
The infrared spectra also suggest that little change has occurred in the dimethylamino groups, but a major change in the bond order of the phosphorous-sulfur bond is apparent. On the basis of NMR and infrared spectral data, analytical data, and conductivity results, the structure of this new cation is proposed as \([(\text{Me}_2\text{N})_3\text{P-S-P(}\text{NMe}_2\text{)_3}]^{2+}\). Such a cation would result from the oxidation of \((\text{Me}_2\text{N})_3\text{P=S}\) to the positive free radical \([(\text{Me}_2\text{N})_3\text{P=S}^\cdot]^+\) followed by rapid coupling with another radical unit. The overall formulas for the oxidation reactions of TDPS with copper(II) and bromine may, then, be written as:

\[
\begin{align*}
10(\text{Me}_2\text{N})_3\text{PS} + 2[\text{Cu(CH}_3\text{CN})_4](\text{ClO}_4)_2 & \rightarrow [(\text{Me}_2\text{N})_3\text{PS}_2\text{P(}\text{NMe}_2\text{)_3}]\text{(ClO}_4)_2 \\
& + 2\text{Cu[SP(}\text{NMe}_2\text{)_3]}_4\text{ClO}_4 \\
2(\text{Me}_2\text{N})_3\text{PS} + 3\text{Br}_2 & \rightarrow [(\text{Me}_2\text{N})_3\text{PS}_2\text{P(}\text{NMe}_2\text{)_3]}\text{(Br}_3)_2.
\end{align*}
\]

This is not, however, without precedence in phosphorous-sulfur or sulfur chemistry. Dithiophosphinic acids are oxidized by \text{Cu(II)}, \text{Au(III)}, and \text{Ti(III)} to give the sulfane, with the metal ion being reduced to the +1 oxidation state.\textsuperscript{216} The +1 metal ion is then isolated

\[
6\text{R}_2\text{PS}_2^- + 4\text{Cu(II)} \rightarrow \text{R}_2\text{P(S)-S}_2\text{P(S)}\text{R}_2 + [\text{R}_2\text{PS}_2\text{Cu}]_4
\]
as the dithiophosphinic acid complex. Iodine oxidizes thiosulfate, \(\text{S}_2\text{O}_3^{2-}\), to form the tetrathionate \([\text{O}_3\text{S-S}_2\text{-SO}_3]^{2-}\).\textsuperscript{217} Moreover, thiourea
spontaneously reduces Cu(II) to Cu(I), Au(III) to Au(I), and Pt(IV) to Pt(II). In the case of the Cu(II) reduction in acetonitrile, the oxidation product was proposed as the disulfide cation $[\{(H_2N)_2C-S-S-C(NH_2)_2\}]^{2+}$. This is analogous to the oxidation product of selenourea in the presence of silver chloride, which was shown by an X-ray crystallographic study to contain the cation $[\{(H_2N)_2C-Se-Se-C(NH_2)_2\}]^{2+}$. The cation was isolated as the dichloride and a free radical mechanism was proposed.

The divalent cation of TDPS also affords an explanation for the bright red crystals, Cu(TDPS)Cl$_3$, which result from adding CuCl$_2$ or Cu(CH$_3$CN)$_2$Cl$_2$ to TDPS. These crystals are electrolytes in nitromethane, exhibit a magnetic moment of 2.04Bohr magnetons per copper ion, have an electronic spectrum very similar to square planar copper(II) anions, and give an infrared spectrum identical to the $[(\text{Me}_2N)_3\text{PS}_2\text{P(NMe}_2)_3]\text{Cu}_2\text{Cl}_6$ salts. Thus, these red crystals should be formulated as $[(\text{Me}_2N)_3\text{PS}_2\text{P(NMe}_2)_3]\text{Cu}_2\text{Cl}_6^2$ containing the known planar $[\text{Cu}_2\text{Cl}_6]^2$ anion, rather than as any copper(II)-TDPS coordination complex. As additional evidence, these red crystals were prepared independently from $[(\text{Me}_2N)_3\text{PS}_2\text{P(NMe}_2)_3]\text{ClO}_4_2$, anhydrous CuCl$_2$, and LiCl.

Interestingly, although copper(II) and bromine in acetonitrile would oxidize TDPS, iodine in acetonitrile did not. Therefore the oxidation potential of TDPS in acetonitrile must lie somewhere between iodine, 0.396 volt versus Ag/Ag$^+$ electrode, and bromine or copper(II), 0.96 volt versus aqueous S.C.E.
Bonding in Phosphine Chalcogenide Complexes

Livingstone\(^{121}\) has pointed out that for the formation of a complex between a metal ion \(M^+\) and an uncharged ligand \(L\), the bond strength (\(-\Delta H\)) will be given by:

\[
-\Delta H = \frac{Ze(P + p')}{r_1^2}
\]

where \(Ze\) = effective nuclear charge on \(M\), \(r_1\) = distance from center of \(M^+\) to center of dipole, \(P\) = the permanent dipole moment of the ligand, \(p'\) = the induced dipole moment which is equal to the polarizability factor times the inducing electrostatic field.

For phosphine chalcogenides, then, the expected interaction with "hard" metals, which have a low field strength, would be \(O > S > Se\), based on the decreasing size of the donor atom \((r_1\) decreasing) and increasing permanent dipole moment of the ligand. Although the measured dipole moments actually increase from oxide to selenide, it is questionable whether this is an actual measure of the separation of charge or merely reflecting the lengthening of the phosphorous-chalcogenide bond. In any case, such a study on the bond strengths of phosphine chalcogenides with "hard" metals has not been done. However, the difficulty in obtaining phosphine sulfide and selenide complexes with "hard" metals compared to the abundance of phosphine oxide complexes suggests, at least qualitatively, that the expected order is correct.

The borderline metals, however, are intermediate between "hard" and "soft" metals in bonding characteristics and it is
impossible to say a priori anything quantitatively about the expected order of bond strengths in phosphine chalcogenide complexes. However, the results with cobalt(II) show that the differences in the permanent polarity and polarizabilities of the phosphine chalcogenide ligands must compensate each other in bonding to cobalt since their $D_q$ values are nearly identical. It is evident from the $\beta$ values and magnetic moments that the phosphine sulfide and selenide ligands are much more polarizable and are more covalently bound to cobalt than are the phosphine oxide ligands.

For "soft" metals, which have a high field strength, polarizability would favor stronger bonds with phosphine sulfides and selenides over phosphine oxides. However, again it is difficult to say a priori whether the sulfide or the selenide will show a stronger spectrochemical interaction with "soft" metals, since competing factors of size and permanent polarity favor the sulfide whereas polarizability favors the selenide. Moreover, the contributions from $\pi$-bonding have been neglected and, at least, for complexes of "soft" metals, may be a significant factor.

It is difficult to separate polarizability from $\pi$-bonding and the extent that each exerts in bonding phosphine sulfide and selenide ligands with a "soft" acceptor is a matter of some conjecture. Both sulfur and selenium atoms have vacant d-orbitals which can be used for $d\pi$-$d\pi$ bonding with the latter transition metals in their normal oxidation states [e.g. Pd(II), Pt(II), Hg(II)] and with the early transition metals in low oxidation states [e.g. Mo(0), Re(I)]. In fact, it has
been suggested that the principal difference between thiols and thioethers as ligands is that the former are more highly polarizable but not as effective d\textpi electron acceptors as the latter.\textsuperscript{222} Studies with substituted metal carbonyls show that thioethers, thiourea, and thioacetamide all show a tendency to function as \pi-acceptors.\textsuperscript{223} There seems little doubt that in favorable circumstances, \pi-bonding does occur with sulfur and selenium ligands. In principle, then, it is quite possible for phosphine sulfide and selenide ligands to show some \pi-bonding tendencies.

Zingaro et al.\textsuperscript{134,135,224} have determined a number of equilibrium quotients for some 1:1 adducts of phosphine chalcogenides with iodine (Table 28). It is apparent that the interaction of the phosphine chalcogenides with iodine follows the order 0 < S < Se. This trend has been explained on the basis of the relative amount of \pi-bonding between iodine and the chalcogenide.\textsuperscript{135} The chalcogenide has two lone-pair orbitals, an sp hybrid \sigma and a p\textpi orbital, not involved in bonding to phosphorous which are available for overlap with the lowest energy unfilled orbital of the acceptor molecule – the \sigma^* (5p_z) level in the case of iodine. Such a model would imply a linear P-X-I bond angle. Back donation of p\textpi acceptor electrons to the 3d orbital of sulfur or 4d of selenium may take place, which would result in an increase in the chalcogenide-iodine interaction. P\textpi-d\textpi back donation is impossible between iodine and phosphine oxide because of the lack of a suitable d orbital on the oxygen atom. Thus, there is no enhancement of the phosphine oxide-iodine interaction due to \pi-bonding.
TABLE 28

EQUILIBRIUM QUOTIENTS FOR 1:1 IODINE-PHOSPHINE CHALCOGENIDE COMPLEXES.135

<table>
<thead>
<tr>
<th>Donor K, 1/mole</th>
<th>Donor K, 1/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{C}<em>6\text{H}</em>{11})_3\text{PO}) 39</td>
<td>((\text{CH}_3)_3\text{PS}) 604</td>
</tr>
<tr>
<td>((\text{C}<em>6\text{H}</em>{11})_3\text{PS}) 1,820</td>
<td>((\text{C}_4\text{H}_9)_3\text{PS}) 59</td>
</tr>
<tr>
<td>((\text{C}<em>6\text{H}</em>{11})_3\text{PSe}) 46,600</td>
<td>((\text{C}_2\text{H}_5)_3\text{PO})^a 6.2</td>
</tr>
<tr>
<td>((\text{C}_6\text{H}_5)_3\text{PS}) 106</td>
<td>((\text{C}_2\text{H}_5)_3\text{PS})^a 10</td>
</tr>
<tr>
<td>((\text{C}_6\text{H}_5)_3\text{PSe}) 3,370</td>
<td></td>
</tr>
</tbody>
</table>

^aSee reference 225.

An X-ray crystallographic study of the triphenylphosphine sulfide-iodide complex, \((\text{Ph}_3\text{PS})_2(\text{I}_2)_3\), shows the P-S bond length to be 2.02Å with a P-S-I bond angle of 107°.226 Such an acute bond angle would tend to rule out the bonding scheme proposed by Zingaro and suggests that sulfur is sp\(^3\) hybridized with little or no π-interaction with phosphorous or iodine. However, the P-S bond length is significantly shorter than that of a P-S single bond, 2.08-2.10Å, \(^8\) so that even though the P-S bond is lengthened on coordination (the 2.02 value is longer than for the P-S bond length in uncoordinated phosphine sulfides, see Tables 3 and 4), it still retains some multiple bond character. This is consistent with infrared data which shows a decrease in the P-S bond order on coordination with iodine.227 Thus the orbitals used by sulfur in bonding must be intermediate between sp\(^2\) and sp\(^3\) to account for the bond angle of 107° as well as to allow some multiple bonding with phosphorous. Moreover, the S-I bond length of 2.69Å is significantly shorter than those reported for thioether-iodine complexes: for example \(\text{C}_4\text{H}_8\text{S}_2\cdot\text{I}_2\), S-I = 2.87Å, \(^2\) and \((\text{C}_6\text{H}_5\text{CH}_2)_2\text{S} \cdot\text{I}_2\), S-I = 2.78Å.229 This
suggests that there is some multiple bonding by back donation from a filled iodine p orbital to an empty sulfur d orbital between iodine and sulfur in triphenylphosphine sulfide.

Keen has proposed, however, that there is no synergic σ-π bonding between the sulfur and gold in Au(Ph₃PS)Cl. In fact, there is a repulsion between non-bonded sulfur electrons and gold d-orbitals. This argument is also used to explain the instability of the diethylsulfide complex of gold(I) chloride.

Dalziel et al. also agrees with Keen that there is no appreciable π-bonding in triphenylphosphine sulfide complexes, at least with copper(I) and mercury(II). The infrared spectra of these complexes show little change in the carbon-phosphorous symmetric and asymmetric frequencies or in the "X-sensitive" frequency from that of the free triphenylphosphine sulfide. The "X-sensitive" frequency in the infrared spectrum of R₃PX is reported to be very sensitive to changes in the mass and electronegativity of the phosphorous atom (it is assigned to the strong band at 1121, 1105, and 1098 cm⁻¹ for the triphenylphosphine oxide, sulfide, and selenide, respectively). The lack of change in the infrared spectra of triphenylphosphine sulfide on coordination was interpreted by Dalziel et al. to mean that the electronegativity of the phosphorous and hence the pπ-dπ interaction in the P=S bond is not significantly changed on coordination. Together with the instability of the copper(I) halide complexes, it was concluded that there is no appreciable contribution from π-bonding in the donor properties of triphenylphosphine sulfide. Thus any difference in the donor properties of phosphine sulfides and oxides must be related to differing polarizabilities of the donor atoms.
The evidence for differences in stabilities of complexes between phosphine chalcogenides and "soft" acceptors based on π-bonding or polarizability is not conclusive. Either effect may be used to explain differences in bond strengths or formation constants. The argument for polarizability based on infrared spectra is not convincing. In fact, the shift of the P=S stretching frequency to lower energy shows that there is a change in the P=S bond on coordination and especially in the π-dπ bond between phosphorous and sulfur. Thus it is questionable whether the so-called "X-sensitive" frequency is as sensitive to changes in the electronegativity of phosphorous as suggested. Unfortunately, only one X-ray crystallographic study has been made with a phosphine sulfide complex and it did indicate a short sulfur-iodine bond and possibly some multiple bonding. However, until further X-ray crystallographic studies have been made, it is impossible to say whether the differences in stabilities of phosphine oxide, sulfides, and selenide complexes with "soft" metals is due primarily to differences in polarizabilities or whether π-bonding ability must also be included.

Conclusion

Phosphine sulfide and selenide ligands can be classified as "soft" or class b donors. They exhibit a very high nephelauxetic effect and a marked preference for "soft" metals such as Pd(II), Cd(II), or Hg(II). The ligand field strength of phosphine sulfide and selenide ligands with borderline metals is very similar to their phosphine oxide analogues and to other sulfur ligands and higher than the halide anions.
Phosphine sulfides exhibit a higher ligand field strength but slightly lower covalent bonding with borderline metals than the analogous phosphine selenides. With "soft" metals, they are comparable in ligand field strength. This may be due to the difference in \( \sigma \)-versus \( \pi \)-bonding ability of the ligands or merely reflects the differences in polarity and polarizabilities of the donor atoms.
APPENDIX

Attempted Complexes with Secondary Phosphine Sulfides

Coordination of secondary phosphine oxides with "soft" or class b metals has led to some rather unusual complexes. For example, diethylphosphine oxide reacts with \([\text{Pt(PEt}_3\text{Cl}_2]_2\) to form the complex \((\text{Et}_2\text{P})\text{Et}_3\text{PPtCl}_2\) and diphenylphosphine oxide reacts slowly with silver salts to form \(\text{Ph}_2\text{P-O-Ag}\). Both of these reactions may be explained on the basis that secondary phosphine oxides exist in two tautomeric forms, I and II. Thus the coordination of the enol form with platinum

\[
\begin{align*}
\text{O} \\
\text{R}_2\text{PH} \leftrightarrow \text{R}_2\text{POH} \\
\text{I} \quad \text{II}
\end{align*}
\]

simply reflects the preferred interaction of a "soft" metal with a "soft" base.

A similar tautomeric equilibrium is thought to exist with secondary phosphine sulfides. It would be of some interest then to determine if secondary phosphine sulfides undergo similar rearrangements in coordinating with class a metals. In addition since complexes of secondary phosphine sulfide have not been reported, coordination with class b metals was also attempted to confirm the "soft" character of these ligands.
Experimental. Dimethylphosphine sulfide was prepared\textsuperscript{176} by heating a slurry of 26.0g (0.14 mole) of tetramethyldiphosphine disulfide with 5.6g (0.14 mole) of sodium hydroxide in 120ml of water to 90° for one hour with vigorous stirring under nitrogen. The reaction

\[ \text{Me}_2\text{P(S)}\text{P(S)}\text{Me}_2 + \text{NaOH} \rightarrow \text{Me}_2\text{P(S)}\text{H} + \text{Me}_2\text{P(S)ONa} \] \hspace{1cm} (30)

mixture was extracted with chloroform, and the chloroform was dried and stripped off under nitrogen. The resulting residue was vacuum distilled to give 8.2g (0.087 mole) of dimethylphosphine sulfide, bp\textsubscript{1.0} 50-52° (lit. value 50° at 0.5mm\textsuperscript{176}), yield 62%.

Diphenylphosphine sulfide was prepared\textsuperscript{234} by adding dropwise a solution of 5.1g (0.16 mole) of sulfur in 200ml of benzene to 29.0g (0.16 mole) of diphenylphosphine in 50ml benzene while stirring the

\[ \text{Ph}_2\text{PH} + \frac{1}{8}\text{S}_8 \rightarrow \text{Ph}_2\text{P(S)}\text{H} \] \hspace{1cm} (31)

solution under nitrogen. The reaction mixture was refluxed two hours, the benzene stripped off, and the solid residue was recrystallized twice from ethanol to give 23.5g (0.11 mole) of white, crystalline diphenylphosphine sulfide, mp 98-99° (lit. value 95-97°\textsuperscript{234}) yield 69%.

In general, the complexes of Ph\textsubscript{2}P(S)H were attempted in the following manner. The anhydrous metal chloride was dissolved in absolute ethanol and added dropwise with vigorous stirring under nitrogen to four equivalents of Ph\textsubscript{2}P(S)H in a mixture of ethanol-dichloromethane. The deep blue cobalt(II) solution showed no color change or precipitate after stirring overnight with Ph\textsubscript{2}P(S)H. However, after the solution
stood one day exposed to air, green crystals began to form. After a few days, the green crystals were collected on a filter from a violet colored solution. They were insoluble in water and most organic solvents but sparingly soluble in boiling acetonitrile. Subsequent experiments showed that green crystals formed only when the reaction mixture was exposed to air.

Anal. Calc. for $C_{24}H_{20}CoP_2S_4$:

$\begin{align*}
\text{C}, & \quad 51.74; \text{H}, \quad 3.44; \text{P}, \quad 11.10; \text{S}, \quad 22.98; \text{Cl}, \quad 0.00 \\
\text{Found:} & \quad C, 52.24; \text{H}, \quad 3.84; \text{P}, \quad 11.27; \text{S}, \quad 22.61; \text{Cl}, \quad 0.00
\end{align*}$

The nickel(II) chloride reaction mixture turned deep red almost immediately and a precipitate formed after the mixture stood overnight. The red crystalline precipitate was collected on a filter and the red filtrate rapidly turned yellow when it was exposed to air. Attempts to recrystallize the initial material from dichloromethane-ether failed and yielded only intractable oils.

Anal. Calc. for $C_{24}H_{20}NiP_2S_4$:

$\begin{align*}
\text{C}, & \quad 51.74; \text{H}, \quad 3.44; \text{Cl}, \quad 0.00 \\
\text{Found:} & \quad C, 60.41; \text{H}, \quad 4.20; \text{Cl}, \quad 0.00
\end{align*}$

Complexes of Pd(II) and Pt(II) were attempted from $Na_2PdCl_4$ and $Na_2PtCl_4$. The $Na_2PtCl_4$ was dissolved in acetonitrile. An orange precipitate formed after a few minutes with Pd(II) and a yellow precipitate formed with Pt(II) after the mixture stood overnight. Although both precipitates were soluble in dichloromethane,
reccrystallization failed and only a precipitate could be isolated. The precipitates were then dissolved in dichloromethane, filtered, and reprecipitated with ether several times (3 for Pd, 8 for Pt).

**Anal. Calcd. for C$_{24}$H$_{20}$P$_2$PdS$_4$:**

C, 47.64; H, 3.00; Cl, 0.00

Found: C, 47.57; H, 3.02; Cl, 0.00

**Anal. Calcd. for C$_{24}$H$_{20}$P$_2$PtS$_4$:**

C, 42.05; H, 3.00; Cl, 0.00

Found: C, 43.26; H, 4.17; Cl, 1.80

A white precipitate formed immediately when HgCl$_2$ was added to Ph$_2$P(S)H but it turned yellow after stirring overnight; the yellow precipitate was collected on a filter. The precipitate was insoluble in all organic solvents tried.

**Anal. Calcd. for C$_{12}$H$_{10}$ClHgPS$_2$:**

C, 29.90; H, 2.28; Cl, 7.30

Found: C, 33.77; H, 2.87; Cl, 5.61

A nickel(II) chloride complex Me$_2$P(S)H was also attempted. An excess of Me$_2$P(S)H was added to a solution of NiCl$_2$, [Ni(H$_2$O)$_6$](ClO$_4$)$_2$, or [Ni(H$_2$O)$_6$](ClO$_4$)$_2$ dehydrated with 2,2'-dimethoxypropane, in ethanol. The reaction mixture slowly turned deep red and a black material precipitated; the black compound was removed by filtration and its infrared spectrum showed little
organic material. The deep red filtrate was concentrated to give only a small amount of flaky purple crystals after standing several days.

Anal. Calcd. for $\text{C}_4\text{H}_{12}\text{NiP}_2\text{S}_4$:

\[
\begin{align*}
\text{C}, & \ 15.55; \ \text{H}, \ 3.91; \ \text{P}, \ 20.05; \ \text{S}, \ 41.50; \ \text{Cl}, \ 0.00 \\
\text{Found:} & \ \ \text{C}, \ 16.97; \ \text{H}, \ 4.53; \ \text{P}, \ 18.54; \ \text{S}, \ 38.00; \ \text{Cl}, \ 0.00
\end{align*}
\]

Discussion. The infrared spectra of the complexes of $\text{Ph}_2\text{P(S)H}$ are markedly different from that of the free ligand (Fig. 27). In the complexes, the $\text{P-H}$ stretch at $2330\text{cm}^{-1}$ as well as the bands between $950-1050\text{cm}^{-1}$ present in the free ligand have disappeared and additional bands between $500-600\text{cm}^{-1}$ have appeared. There is no evidence for a $\text{S-H}$ bond in the infrared spectra. The position of these bands may be compared with the reported spectra of metal complexes of diphenylthiophosphinic acid in Table 29. The $\nu_1$ frequency was assigned to the asymmetric $\text{P-S}$ stretching frequency while $\nu_2$ was assigned to the symmetrical stretching frequency.

**TABLE 29**

THE $\text{P-S}$ STRETCHING FREQUENCIES FOR THE METAL COMPLEXES OF DIPHENYLDITHIOPHOSPHINIC ACID

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_1$ (cm$^{-1}$)</th>
<th>$\nu_2$ (cm$^{-1}$)</th>
<th>$\nu_1$ (cm$^{-1}$)</th>
<th>$\nu_2$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Co}$</td>
<td>565, 553</td>
<td>490</td>
<td>562, 552</td>
<td>490</td>
</tr>
<tr>
<td>$\text{Ni}$</td>
<td>575, 550</td>
<td>497</td>
<td>574</td>
<td>485</td>
</tr>
<tr>
<td>$\text{Pd}$</td>
<td>550</td>
<td>495</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The infrared spectrum of the nickel complex of Me₂P(S)H is also different from that of the free ligand (Fig. 28). In the complex, the strong P-H frequency at 2340 cm⁻¹ present in the free ligand has disappeared, the bands between 850-1000 cm⁻¹ have been shifted to lower energy, and two bands now appear in the 500-600 cm⁻¹ region at 588 and 512 cm⁻¹. This spectrum is very similar to that reported for dimethyl-dithiophosphinic acid metal complexes. The P-S frequencies in (Me₂PS₂)GaMe₂ and (Me₂PS₂)InMe₂ are at 590 and 503 and 596 and 496 cm⁻¹, respectively.

The infrared spectra together with the elemental analysis suggests that these secondary phosphine sulfides undergo oxidation and/or disproportionation in the presence of metal ions to give the dithiophosphinic acid. The acid then coordinates with the metal ion to give the complexes that were isolated.

**TABLE 29 -- Continued**

<table>
<thead>
<tr>
<th>Compound</th>
<th>vP-S(cm⁻¹)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>v₁</td>
<td>v₂</td>
<td>v₁</td>
<td>v₂</td>
<td></td>
</tr>
<tr>
<td>(Ph₂PS₂)₂Pt</td>
<td>550</td>
<td>540</td>
<td>480</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Ph₂PS₂)HgCl</td>
<td>565</td>
<td>495</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Ph₂PS₂)₂AlMe</td>
<td>-</td>
<td>-</td>
<td>566</td>
<td>485</td>
<td></td>
</tr>
<tr>
<td>(Ph₂PS₂)Cu</td>
<td>-</td>
<td>-</td>
<td>562</td>
<td>492</td>
<td></td>
</tr>
</tbody>
</table>

*See references 235 and 236.*
FIGURE 27. INFRARED SPECTRA OF Co(S₂PPh₂)₂(--) and Ph₂P(S)H(-)
FIGURE 28. INFRARED SPECTRA OF $\text{Me}_2\text{P(S)H}$ (--$-$) and $\text{Ni(S}_2\text{PMe}_2)_2$ (--)
The fact that air and/or moisture was necessary to give the 
(Ph₂PS₂)₂Co complex may indicate that a reaction similar to the 
following occurs:

$$2\text{Ph}_2\text{P(S)H} + \text{O}_2 \rightarrow \text{Ph}_2\text{P(O)OH} + \text{Ph}_2\text{P(S)SH}.$$ \hspace{1cm} (32)

This has been observed for the oxidation of dibutylphosphine sulfide 
with hydrogen peroxide or iodine. However, considerably more work 
is necessary before any definitive statements may be made concerning 
the conversion of $\text{R}_2\text{P(S)H}$ compounds to complexes of $\text{R}_2\text{P(S)SH}$. 
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