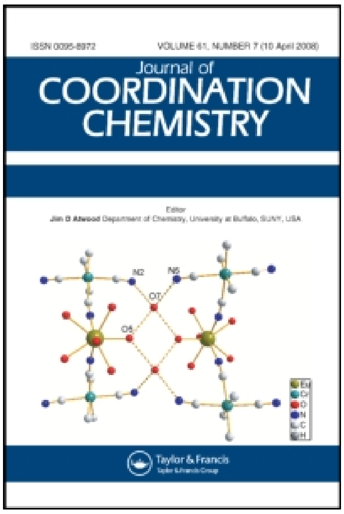

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# O,O'-DIETHYL DISELENOPHOSPHATE AS A LIGAND: Compounds of Some Transition Metals

V. Krishnan[a]; Ralph A. Zingaro[a]
[a] Department of Chemistry, Texas A&M University, College Station, Texas, U.S.A.

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# O,O′-DIETHYL DISELENOPHOSPHATE AS A LIGAND

## Compounds of Some Transition Metals

V. KRISHNAN and RALPH A. ZINGARO†
*Department of Chemistry, Texas A&M University, College Station, Texas* 77843, *U.S.A.*

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*O,O′*-Diethyl diselenophosphate (dsep) complexes of silver(I), copper(I), zinc(II), cadmium(II), nickel(II), cobalt(III), and rhodium(III) have been prepared and characterized. The infrared spectra of these complexes shed some light on the mode of attachment of the selenophosphate, $(C_2H_5O)_2P(Se)Se$, group to the metal ions. Results of electronic spectral studies and magnetic susceptibility measurements are reported and discussed.

## INTRODUCTION

In recent years there has been considerable interest shown in the investigation of organic selenium compounds as ligands in coordination chemistry.[1] Krishnan and Zingaro[1] studied the diethyl diselenophosphate complexes of nontransition metals, and discussed their spectral properties. As a logical extension of the study of this ligand, $(EtO)_2P(Se)Se^-$, hereafter referred to as dsep⁻, the preparation and properties of some transition metal complexes are described in this paper.

## EXPERIMENTAL

The experimental techniques and equipment, as well as the starting materials used in the synthesis of these compounds are described elsewhere.[1]

The magnetic susceptibilities were measured on a Gouy balance. The Gouy tube was calibrated for solids making use of $Hg[Co(CNS)_4]$ as a standard. The diamagnetic corrections for the paramagnetic substances were applied making use of the susceptibility values of either the diamagnetic zinc or cadmium complexes.

Analytical data were obtained by the Galbraith Laboratories, Knoxville, Tennessee and Schwarzkopf Microanalytical Laboratory, Woodside, New York.

*(O,O′-Diethyl diselenophosphato)silver(I)* An aqueous solution of potassium diethyl diselenophosphate (0.32 g in 20 ml) was added dropwise to an aqueous solution of silver(I) nitrate (0.17 g in 5 ml). A light yellow precipitate was formed immediately upon addition of the potassium salt. It was filtered, washed with water and dried *in vacuo* over $P_4O_{10}$. It was then dissolved in a minimum volume of chloroform and an equal volume of ligroin was added. On cooling, white crystals of the silver(I) complex separated. They were collected and dried over $P_4O_{10}$ *in vacuo.*

*Bis(O,O′-diethyl diselenophosphato)zinc(II), bis(O,O′-diethyl diselenophosphato)cadmium(II), bis(O,O′-diethyl diselenophosphato)nickel(II), and tris(O,O′-diethyl diselenophosphato)rhodium(III)* These compounds were prepared in absolute ethanol from solutions of the metal perchlorates and the potassium salt of the ligand. The rhodium(III) complex was prepared from the chloride. All were recrystallized from absolute ethanol.

*Bis(O,O′-diethyl diselenophosphato)dipyridinenickel(II)* A solution of pyridine (0.15 g in 10 ml) in absolute ethanol was added dropwise to bis(*O,O′*-diethyl diselenophosphato)nickel(II) (0.60 g in 20 ml), in the same solvent. The solution was stirred for 30 min. Under reduced pressure, and upon cooling, greenish yellow crystals of the pyridine complex separated. They were filtered and dried over $P_4O_{10}$ *in vacuo.*

*Tris(O,O′-diethyl diselenophosphato)cobalt (III)* A solution of potassium diethyl diselenophosphate in absolute ethanol (0.64 g in 30 ml) was added

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† Author to whom correspondence should be directed.

while stirring to cobalt(II) perchlorate (0.36 g in 15 ml of the same solvent). Upon addition of the selenophosphate, the pink color of cobalt(II) changed to green and, after a few minutes to brown. Following concentration of the solution under reduced pressure and cooling, brown needle-like crystals separated out. They were filtered and dried over $P_4O_{10}$ *in vacuo*.

The preparation of the cobalt(II) selenophosphate complex was attempted in a similar way. All of the solvents and reagents were constantly purged with nitrogen and the reaction was carried out under an atmosphere of this gas. The green color which is typical of the cobalt(II) complex was found to have only a transient existence. The solution turned brown in 30 min. The isolation of solid cobalt(II) complex was attempted by (1) concentration and cooling (2) addition of a nonpolar solvent, and (3) extraction into another immiscible solvent. All of these attempts proved to be unsuccessful.

*The reaction between copper(II) and O,O′-diethyl diselenophosphate* Attempts were made to isolate a copper(II) complex by mixing copper(II) perchlorate and the potassium salt of $dsep^-$ in 1 : 2 molar proportions in absolute ethanol under nitrogen. A yellow color was formed after the addition of two moles of the selenophosphate. This solution gradually deposited a green powder.

When one mole of the potassium salt was added to one mole of a copper(II) solution, an intense blue color was formed. An equal volume of $CHCl_3$ was added and, on concentration, a blue powder separated. This will be discussed subsequently.

The preparation of the copper(I) complex was accomplished by the gradual addition of two moles of Kdsep to one mole of copper(II) perchlorate in absolute ethanol. The addition of an equal volume of $CCl_4$ to the solution followed by concentration at reduced pressure yielded the green copper(I) salt. It was filtered, and dried over $P_4O_{10}$ *in vacuo*.

*Tris(O,O′-diethyl diselenophosphato)chromium(III)* This complex was prepared in a manner similar to that described by Kudchadker *et al.*[2]

## RESULTS

The analytical data for the transition metal compounds prepared are listed in Table I. In Tables II

TABLE I

Analytical data on transition metal diethyl diselenophosphates, (dsep)

| Compound | Color | M.P. | % Carbon | | % Hydrogen | | % Phosphorus | | % Selenium | | % Metal | | Molecular weight[a] | | Room temperature magnetic moment (BM) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | |
| Ag(dsep) | White | 168 | 12.56 | 12.42 | 2.60 | 2.58 | 7.74 | 8.00 | | | | | 1202[b] | 388 | |
| Cu(dsep) | Pale green | 200d | 13.83 | 14.03 | 2.80 | 2.92 | 8.79 | 9.04 | | | 18.90 | 18.48 | 996[b] | 343 | |
| $Zn(dsep)_2$ | White | 118 | 15.19 | 15.40 | 3.29 | 3.21 | 10.17 | 9.94 | | | 10.40 | 10.49 | 640 | 623 | Diamagnetic |
| $Cd(dsep)_2$ | White | 145 | 14.39 | 14.32 | 2.85 | 2.98 | 8.97 | 9.24 | | | 16.40 | 16.77 | 700 | 670 | Diamagnetic |
| $Ni(dsep)_2$ | Grey | 102 | 15.74 | 15.57 | 3.29 | 3.24 | 10.15 | 10.02 | | | 9.50 | 9.52 | 616 | 616 | Diamagnetic |
| $Co(dsep)_3$ | Grey | 145 | 15.67 | 16.07 | 3.29 | 3.34 | 10.03 | 10.38 | 53.33 | 52.89 | 6.10 | 6.58 | 702 | 895 | 1.9 (298°K)<br>1.77 (131.5°K) |
| $Co(dsep)_2$ | | | | 15.57 | | 3.24 | | 10.04 | | 51.00 | | 9.55 | | 616 | |
| $Rh(dsep)_3$ | Red | 178 | 15.52 | 15.38 | 3.35 | 3.20 | 9.54 | 9.91 | % Nitrogen | | | | | | Diamagnetic |
| $Ni(dsep)_2py_2$ | Greenish yellow | | 27.64 | 27.90 | 3.94 | 3.87 | 8.23 | 8.00 | 3.43 | 3.61 | | | | | 3.10 |

[a] Molecular weight determinations were done in $CHCl_3$ by vapor pressure osmometry.

[b] The concentrations of the compounds in $CHCl_3$ were: Cu(dsep), $7.89 \times 10^{-3}M$; Ag(dsep), $7.50 \times 10^{-3}M$. Some deposition of elemental selenium was observed during the course of the measurements.

and III are tabulated the infrared frequencies and electronic absorption maxima observed for these complexes.

TABLE II

Infrared absorption frequencies of metal *O,O′*-diethyl diselenophosphates in the region 600–300 cm$^{-1}$

| Compound | Freq.,$^a$ cm$^{-1}$ | | |
|---|---|---|---|
| | $\nu_1$ | $\nu_2$ | |
| K(dsep) | 585s | 525s | |
| Ag(dsep) | 570vs | 515s | |
| Cu(dsep) | 545vs | 470s | |
| Zn(dsep)$_2$ | 530vs, sp | 455w | |
| Cd(dsep)$_2$ | 570vs, b | 515s, 500w | |
| Ni(dsep)$_2$ | 530vs | 450s | 340m |
| Ni(dsep)$_2$py$_2$ | 555vs | 450s, 435m | 350m |
| Co(dsep)$_3$ | 545vw, 520s | 485m, 455s | 340m |
| Rh(dsep)$_3$ | 540vw, 515s | 480m, 450s | 340m |
| Cr(dsep)$_3$ | 555s, 540s, | 490m, 455s | 340m |

[a] Abbreviations: s = strong, vs = very strong, sp = split, b = broad, m = medium and w = weak.

TABLE III

Electronic absorption spectra of metal *O,O′*-diethyl diselenophosphates[a]

| Compound | Absorption max |
|---|---|
| K(dsep) | 36.63 (3.08) |
| Ag(dsep) | [31.25] (2.84) |
| Cu(dsep) | [31.75] (3.16) |
| Zn(dsep)$_2$ | 38.46 (3.46) |
| Cd(dsep)$_2$ | [37.74] (3.61) |
| Ni(dsep)$_2$ | [42.55] (4.03), 28.57 (4.10), 22.47 (3.03), 18.18 (2.01), 13.42 (1.93) |
| Co(dsep)$_3$ | 38.46 (4.10), 27.03 (4.21), 21.83 (2.75), 12.66 (2.60) |
| Rh(dsep)$_3$ | 40.32 (4.21), 35.09 (4.39), 27.40 (4.24), 20.20 (3.31) |
| Ni(dsep)$_2$ py$_2$ | 40.82 (4.16), 28.57 (3.51), 22.47 (3.10), 18.18 (2.05), 13.9 (1.20), 8.9 (1.10), 8.7 (1.00) |

[a] Band maxima are in kK; parentheses indicate log $\epsilon_{\text{mol}}$; brackets indicate shoulders. Solvents, used are absolute ethanol, chloroform and cyclohexane. py = pyridine.

A blue copper selenophosphate was isolated during the preparation of the green copper(I) complex. This compound was subjected to elemental analysis. The following values were reported C, 12.18; H, 2.59; P, 7.67; Cl, 3.21; Cu, 20.70. The infrared and electronic spectrum of this compound were taken. Its possible stoichiometry will be discussed subsequently.

The magnetic susceptibility of the cobalt complex was measured. The measured gram susceptibilities were 1.45 and 2.87 × $10^{-6}$ cgs units at 298.4° and 131.5° K, respectively.

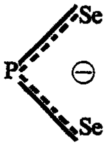
All of these complexes demonstrate chemical instability as is observed from their decomposition on standing. Noticeable decomposition was noted in all cases in 30 days, or less. The decomposed compounds, in addition to depositing the metal selenides, yield, as decomposition products, foul-smelling organoselenium compounds and elemental selenium.

The freshly prepared complexes are crystalline in nature and are easily soluble in the usual organic solvents. However, they are hydrolytically unstable.

## DISCUSSION

The reducing nature of the selenophosphate group is demonstrated by the formation of the copper(I) salt when the copper(II) perchlorate is mixed with the ligand. This is very similar to the earlier observation of the reduction of thallium(III) to thallium(I)[1] by this ligand.

The infrared spectra of various dialkyl diselenophosphates have been studied.[1,2] Potassium diethyl diselenophosphate absorbs at 585 and 525 cm$^{-1}$ and these two absorptions have been assigned to an asymmetric ($\nu_1$) and symmetric ($\nu_2$) stretching modes of the diselenophosphate group, respectively. This has been based on the assumption that there exists complete resonance,



in which the two selenium atoms are equivalent.[1] A similar observation was made in the case of diethyl diselenophosphinate[3] and dimethyl dithiophosphate.[4]

In the metal complexes studied, both $\nu_1$ and $\nu_2$ are observed at lower frequencies compared to those of the potassium salt. This suggests that the coordination of the selenophosphate group to the metal ions occurs through both of the selenium atoms of the ligand. Coordination of the selenophosphate to the metal ion through the selenium atom(s) will bring about a lowering in the approximately $C_{2v}$ symmetry (considering a tetrahedral arrangement about phosphorus in $Se_2P(OR)_2$ of the free ion. As a result, one, or both of the stretching vibrations will be split. Such splitting is clearly demonstrated in the presumably octahedral coordination about the Co(III), Rh(III), and Cr(III) ions in which both the antisymmetric, $\nu_1$ and symmetric, $\nu_2$, components are observed as doublets. It is interesting to note that in the case of the Zn(II) and Cd(II) complexes, which usually are tetrahedrally coordinated, that a splitting of $\nu_1$ is observed in the former case, while $\nu_2$ is observed as a doublet in the latter case. It is not at all unusual for Ni(II) to form square-coplanar complexes. The observation of the $\nu$(P=Se) vibrations as strong singlets in this molecule appears to reflect this higher degree of symmetry.

Although the lowering in $\nu$(P=Se) may be used as a measure of the strength of the coordinate bond, this can, at times, be misleading. Among metals having the same symmetry type, e.g. Co(III), Rh(III), Cr(III), the magnitude of the lowering is too small in each case to furnish a meaningful comparison. Furthermore, the observed frequencies may very well represent a coupling of the fundamental with lower frequency modes. Hence, we refrain from reaching any conclusions about the trends in strengths of the metal–selenium bonds without a larger amount of more meaningful data.

The weak absorption around 340 cm$^{-1}$ is assigned to one of the bending or scissoring modes of P—O—C or C—C—O or a combination of both.[1] The bands observed in the remaining portion of the spectra are characteristic of those usually observed for organophosphorus molecules and are not discussed further.

The molecular weight determinations of copper(I) and silver(I) (Table I) show that they very possibly exist as trimers in chloroform. Hesse[5] found that dithiocarbamate complexes of copper(I), silver(I) and gold(I) are associated in the solid state and in solution. The degree of association was found to depend upon the nature of the alkyl group. The (*N,N′*-diethyl dithiocarbamato)copper(I) exists as a tetramer in the crystalline state. The dithiophosphates of copper(I) and silver(I) are oligomers and have been found to be either dimers or tetramers.[3] Also, the trialkyl phosphine and arsine complexes of copper(I) and silver(I) are reported to be tetramers in solution.[6,7] It is not unusual to find association in the coordination compounds of copper(I) and silver(I). However, the coordination environments of copper(I) and silver(I) in the present case are not known with certainty. Crystal structure determinations on these complexes will be most informative.

The diamagnetic susceptibility of the nickel(II) complex is consistent with a low-spin, square planar configuration. The addition of pyridine to the brown nickel(II) complex brings about conversion to the high-spin octahedral $Ni(dsep)_2py_2$ complex, with a magnetic moment of 3.10 BM. This is quite similar to the behavior of the nickel(II) dithiophosphate[8] and diselenocarbamate[9] complexes. The diamagnetic susceptibility of the rhodium compound suggests a low-spin octahedral environment for rhodium(III).

The most interesting and not completely understood magnetic susceptibility of the cobalt compound merits additional discussion. The analytical data suggest octahedral coordination with three ligands attached to a cobalt(III) ion. However, octahedral Co(III) complexes are almost always diamagnetic, or, in a few cases, have a very high moment. The susceptibility measurements of the material prepared, however, is more consistent with a low-spin cobalt(II) ground state. Yet, the analytical data, notably that for cobalt (undertaken and checked independently by three laboratories, including our own) clearly require a $Co(dsep)_3$ stoichmetry. The molecular weight in $CHCl_3$ suggests that some dissociation occurs in this solvent. Because of the very limited solubility of this complex in all solvents tested, magnetic susceptibility measurements in solution were not carried out. It is difficult to compromise between cobalt(III), $^1A_1$, and cobalt(II) $^2E_g$ states in the complex. The possibility that some high-spin cobalt selenides might be present due to decomposition of the complex was considered. However, the susceptibility value seems to be too high to be attributable to impurity effects. In order to have an octahedral Co(II) complex, the presence of another cation is necessary in order to satisfy electroneutrality. The possibility of a double salt of the type $Co(dsep)_2 \cdot Kdsep$ would come close to satisfying the observed physical and chemical data. However, no potassium was detected in the compound. Additional studies of this compound, especially a single crystal structure determination, are planned.

The potassium salt absorbs in the ultraviolet region at 36.6 kK which has been assigned to a Rydberg excitation on selenium ($5p \rightarrow 6s$).[1] This absorption is observed at about the same frequency in the complexes. Because it does not overlap with the other absorptions, the identification of charge-transfer and *d–d* transitions in the complexes is possible. In the case of the nickel(II) compound, this absorption is shifted to a significantly higher frequency, 42.55 kK. This could be ascribed to strong interligand conjugation in the planar complex.

A detailed account of the electronic spectra of several diethyldithiophosphate (dtp) complexes has been given by Jorgensen.[8] The *d–d* transitions of the selenophosphates are very similar to those observed for the dithiophosphates but they are shifted towards lower frequencies in going from dithio- to diselenophosphates. Thus, the first spin-allowed transitions in the octahedral chromophores, chromium(III) and rhodium(III) occur at 12.60[10] and 20.20 kK. The corresponding values for the dithiophosphates are 13.1 and 21.3 kK. Recently, Jensen *et al.*[9] have discussed the electronic spectra of diselenocarbamate (dsec) complexes. This makes an interesting comparative study of the spectrochemical position of similar ligands (V shaped) of comparable sign and magnitude. The first spin allowed transition $^1A_{1g} \rightarrow {}^1T_{1g}$ of rhodium(III) diethyldiselenocarbamate[9] occurs at 22.2 kK which is higher than that observed in the dithiophosphate (21.3 kK) and the diselenophosphate (20.20 kK). The same trend is observed in low spin $d^8$ complexes. This suggests that the diselenophosphates impose a somewhat lower ligand field than the dithiophosphates. Hence, the position of $dsep^-$ in the spectrochemical series among the following related ligands is $dsep^- < dtp^- < dsec^-$.

The reducing character of the ligand is linearly related to the relative position of the occurrence of the first spin allowed transition and the first electron transfer transition. Jorgensen[10] calculated the optical electronegativity of $dsep^-$ as 2.6 which is close to that of dithiophosphate, 2.7. The electron transfer bands $\pi$–$\nu_{\tau 3}$ in nickel(II) and $\pi$–$\nu_3$ in cobalt(III) occur at 28.57 and 21.83 kK, respectively. The optical electronegativity calculated for $dsep^-$ in cobalt(III) compound is 2.6. This is in agreement with the value reported for the chromium(III) compound.[10]

The zinc(II) and cadmium(II) compounds exhibit only one internal ligand transition while the spectra of the copper(I) and silver(I) compounds are similar to that of thallium(I) and hence should be assigned accordingly.[1]

The bluish green solution which forms initially upon the addition of Kdsep to cobalt(II) was studied by visible spectroscopy. The electronic spectrum of this bluish green solution shows absorptions in the visible regions at 15.87 and 17.50 kK. There is a weak absorption around 5500 cm$^{-1}$ in the near infrared region which, however, was exceedingly weak and not always observed. This suggests that the cobalt(II) ion was present at least in the freshly prepared solutions. Jorgensen,[11] in his studies of cobalt diethyldithiophosphates, postulated the presence of $Co(dtp)_2$ and $Co(dtp)_2(EtOH)_2$ species in solution. The present results are in agreement with this suggestion. However, no definite assignments were possible because the bluish green color slowly turns brown and the absorptions at 15.87 and 17.50 kK disappeared. The oxidation to a cobalt(III) complex in the dark brown solutions was evident from the nature of the absorption spectra observed in the equilibrated solutions. Thus, the bands which appeared at 12.66, 21.83 and 27.03 kK are quite analogous to those reported for the dithiophosphate complex of cobalt(III).[11]

The spectrum of the cobalt(III) complex is the same in $CHCl_3$ as it is in alcohol. However, the molecular weight determinations suggest that there occurs some dissociation of the cobalt(III) complex in $CHCl_3$.

The octahedral, high spin, $Ni(dsep)_2py_2$ has absorption bands at 8.7, 8.9 and 13.9 kK. These absorptions are similar to the ones observed in $Ni(dtp)_2py_2$.[8] However, the $^3\Gamma_5 \rightarrow {}^3\Gamma_2$ absorption around 9 kK is split in the selenophosphate complex. The band at 13.9 kK is assigned to a $^3\Gamma_5 \rightarrow {}^3\Gamma_4$ transition.

One interesting compound, unexpectedly formed, was the blue copper complex. The elemental analysis of this compound is consistent with the formulation $Cu_4(dsep)_3ClO_4$. The infrared spectrum shows $ClO_4$ absorptions, however the $T_d$ symmetry of the perchlorate is lowered, possibly to either $C_{3v}$ or $C_{2v}$. The electronic absorption spectrum shows absorptions at 9.1, 15.27 and shoulders at 16.26 and 21.3 kK, respectively. It is not worthwile to suggest a structure for this compound without single crystal X-ray data.

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