water and cannot be stored over desiccants. If exposed to the atmosphere for prolonged periods of time, these five-coordinate bromo complexes take on additional water to form mixtures of six-coordinate octahedral complexes, which were not further investigated at this time.

(3) **Complexes of the General Formula $M(L^+)(NH_3)X_3$.**—The preparation of these complexes requires rigorously anhydrous solvents to prevent the formation of hydroxo species. Ethanol solutions of the ligand halides and metal halides were dried over 4A molecular sieves for several days and then used to prepare the $M(L^+)X_3$ complexes as previously described.[12] A solution of $NH_3$ in anhydrous ethanol was added dropwise to the freshly prepared $M(L^+)X_3$ complexes suspended in their mother liquor, with vigorous stirring at 50°. The reactants were mixed in a 1:1 $NH_3$-to-metal ratio. The reaction was generally complete within 5 min provided the initial particle size of the $M(L^+)X_3$ complexes was sufficiently small. As the reaction progressed, the color of the suspended solid changed from blue to lavender for Co(II), from deep blue to golden brown for Ni(II), and from deep yellow to golden for Cu(II). The $M(L^+)(NH_3)X_3$ complexes were filtered, washed with anhydrous ethanol, and dried *in vacuo*. It was necessary to control the addition of the ammonia solution, because a considerable excess over a 1:1 $NH_3$-to-metal ratio leads to the formation of a mixture of ammine complexes which were not further investigated.

**Characterization of the Complexes.**—The complexes prepared were characterized by analyses, visible and infrared spectra (30,000–250 $cm^{-1}$), magnetic susceptibility, and X-ray powder diffraction measurements. For details, see ref 12.

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# O,O′-Diethyl Diselenophosphate as a Ligand. Compounds of Nontransition Elements[1]

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O,O′-Diethyl diselenophosphate ($dsep^-$) complexes of Tl(I), Pb(II), Sn(II), As(III), Sb(III), Bi(III), and In(III) have been prepared and their spectral properties have been investigated. The infrared spectra give some evidence of the nature of bonding between the >P(Se)Se group and the central ion. Some electronic transitions of these complexes have been tentatively assigned. Powder X-ray patterns have also been obtained.

## Introduction

The investigation of organic selenium compounds as ligands in coordination chemistry is of relatively recent interest.[2–11] Recently Jørgensen[12] studied the electronic spectra of some transition metal diethyl diselenophosphates. Kudchadker, *et al.*,[13] prepared various dialkyl diselenophosphates and their potassium and chromium salts and studied their spectral properties.

## Experimental Section

The organic solvents used in this study were of reagent grade and they were dried and distilled before use. The chemicals were of analytical reagent grade and they were used without further purification.

The infrared spectra of the compounds were measured as KBr pellets on a Beckman model IR-12 spectrometer. The electronic spectra were recorded on the Cary model 14-R spectrometer. The X-ray powder diffraction patterns were measured on a General Electric XRD-5 X-ray diffraction unit using Cu K$\alpha$ radiation ($\lambda$ 1.54050 Å).

Phosphorus pentaselenide and the potassium salt of O,O′-diethyldiselenophosphoric acid were prepared in the manner described by Kudchadker, *et al.*[13] The melting point of the potassium salt was found to be 134–136°; lit.[13] 132–136°.

**(O,O′-Diethyl diselenophosphato)thallium(I).**—An aqueous solution of potassium diethyl diselenophosphate (0.32 g in 20 ml) was added dropwise to an aqueous solution of thallium(I) chloride (0.20 g in 100 ml). A white precipitate was formed immediately upon addition of the potassium salt. It was filtered, washed with water, and dried *in vacuo* over $P_4O_{10}$. The thallium(I) compound was recrystallized from chloroform in the form of white flakes.

**Bis(O,O′-diethyl diselenophosphato)lead(II).**—An ethanolic solution of potassium diethyl diselenophosphate (0.64 g in 20 ml) was added dropwise to a solution of lead acetate (0.33 g in 40 ml) in ethanol. A creamy yellow compound separated which was crystallized from absolute ethanol and dried over $P_4O_{10}$ *in vacuo*.

**Bis(O,O′-diethyl diselenophosphato)tin(II).**—This compound was prepared from $SnCl_2 \cdot 2H_2O$ in the manner just described. The compound was crystallized from ligroin.

**Tris(O,O′-diethyl diselenophosphato)arsenic(III).**—A solution of potassium diethyl diselenophosphate (1.02 g in 30 ml) in absolute ethanol was added dropwise in a solution containing 0.20 g of arsenic trichloride in 25 ml of the same solvent. During the course of the addition, the color of the arsenic(III) solution changed from pale yellow and the separation of elemental col-

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TABLE I

ANALYTICAL DATA ON DIETHYL DISELENOPHOSPHATE ($dsep^-$) COMPOUNDS

| | | | % carbon | | % hydrogen | | % phosphorus | | % selenium | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Color | Mp, °C | Found | Calcd | Found | Calcd | Found | Calcd | Found | Calcd |
| Tl(dsep) | White | 89–90 | 9.36 | 9.94 | 2.18 | 2.01 | 6.19 | 6.41 | 33.03 | 32.68 |
| $Pd(dsep)_2$ | Yellow | 80 | 12.55 | 12.66 | 2.61 | 2.62 | | | | |
| $Sn(dsep)_2$ | Yellow | 79–80 | 14.36 | 14.19 | 3.06 | 2.95 | | | | |
| $As(dsep)_3$ | Pale yellow | 103 | 15.96 | 15.80 | 3.38 | 3.29 | 10.25 | 10.19 | 52.08 | 51.97 |
| $Sb(dsep)_3$ | Yellow | 92 | 14.66 | 15.03 | 3.05 | 3.13 | 9.30 | 9.69 | | |
| $Bi(dsep)_3$[a] | Orange | 113 | 13.36 | 13.78 | 2.85 | 2.87 | 8.84 | 8.88 | 45.46 | 45.26 |
| $In(dsep)_3$[b] | Yellow | 114–115 | 15.28 | 15.14 | 3.24 | 3.15 | | | | |

[a] Bi analysis: calcd, 20.00; found, 19.60. [b] In analysis: calcd, 12.06; found, 11.80.

loidal selenium was observed during the final stages of the addition. The precipitated selenium was separated by filtration and the filtrate, on concentration and cooling, gave light yellow crystals. These were filtered and recrystallized from absolute ethanol.

**Tris(O,O′-diethyl diselenophosphato)antimony(III) and Tris(O,O′-diethyl diselenophosphato)bismuth(III).**—These compounds were prepared from antimony(III) and bismuth(III) chlorides in a manner similar to that described for the arsenic(III) compound.

**Tris(O,O′-diethyl diselenophosphato)indium(III).**—Indium metal (0.30 g) was dissolved in 20 ml of 9 *M* nitric acid. It was kept over a steam bath and evaporated until the evolution of oxides of nitrogen ceased. The indium salt which separated was dissolved in 20 ml of water. To 10 ml of the solution was added 30 ml of an aqueous solution containing potassium diethyl diselenophosphate (2.50 g). A yellow precipitate was formed which was filtered, washed with water, and dried over $P_4O_{10}$ *in vacuo*. Final recrystallization was carried out from chloroform.

**Attempted Preparation of Tris(O,O′-diethyl diselenophosphato)thallium(III).**—To a solution of $TlCl_3 \cdot 2H_2O$ in acetonitrile (0.30 g in 20 ml) was added an aqueous solution of potassium diethyl diselenophosphate (1.0 g in 20 ml). A yellow precipitate was formed and this was extracted into chloroform. The chloroform layer was separated and it was concentrated and cooled. Very light yellow crystals separated. These crystals were identified as the thallium(I) salt. The analytical data for these diethyl diselenophosphate compounds are given in Table I.

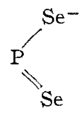
None of the compounds was found to be very hygroscopic. They are stable in air. The thallium(I) compound is light sensitive. They are soluble in common organic solvents and decompose in aqueous solutions. The tin(II) compound was found to decompose slowly over a period of 30 days, possibly to tin selenide.

## Results and Discussion

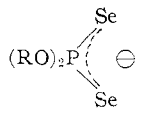
The formation of the thallium(I) compound during the attempted preparation of the thallium(III) compound clearly demonstrates that O,O′-diethyl diselenophosphate may behave as a reducing ligand.

**Infrared Studies.**—The infrared spectra of O,O′-diethyl dithiophosphate complexes of transition and nontransition metals have been studied recently.[14,15] This makes a comparison with the corresponding selenium derivatives more meaningful. Kudchadker, *et al.*,[13] observed a pair of strong bands in the region 600–450 cm$^{-1}$ in bis(dialkyl diselenophosphate) and in potassium and chromium(III) dialkyl diselenophosphates. Chittenden and Thomas[16] also observed a pair of bands in the compounds of the types $(RO)_3PSe$, $R(RO)_2PSe$, and $(RO)(OH)(R)PSe$ and these were ascribed to $\nu$(P–Se). However, in phosphine selenides, Zingaro[17] observed only one band due to $\nu$(P–Se).

The infrared frequencies of the diethyl diselenophosphate compounds observed in the present study are given in Table II in the region 600–300 cm$^{-1}$. Absorption above 600 cm$^{-1}$ can be assigned by comparison with relevant phosphorus compounds to various modes arising from the $P–OC_2H_5$ group, such as $\nu$(P–O), $\nu$(C–H), $\nu$(C–O), *etc.* Absorptions below 300 cm$^{-1}$ are not listed because of the KBr cutoff. Potassium diethyl diselenophosphate absorbs at 584 and 520 cm$^{-1}$. These two bands can be ascribed to asymmetric ($\nu_1$) and symmetric ($\nu_2$) stretching vibration of the >P(Se)Se group of the diethyl diselenophosphate. The possibility that the higher frequency arises from the P–Se bond of higher order in



and that the lower frequency corresponding to P–Se of lower bond order seems unlikely if one assumes a complete resonance as



Similar resonance was observed in diethyl diselenophosphinate[18] and in O,O′-dimethyl dithiophosphate.[19]

The infrared spectrum of one of the $dsep^-$ compounds, $As(dsep)_3$, has been compared in Figure 1 with that of the corresponding O,O′-diethyl dithiophosphate, $As(dtp)_3$, for the purpose of isolating the P–Se stretching frequencies. It is to be noted that the $\nu_1$ and $\nu_2$ of the P–Se stretching frequencies occur at different positions than the $\nu_1$ and $\nu_2$ of the P–S stretching frequencies although $\nu_2$ of P–S occurs very near $\nu_1$ of P–Se.

There is observed a decrease in both the $\nu_1$ and $\nu_2$ frequencies in going from lead(II) to tin(II) to arsenic(III), antimony(III), bismuth(III), and indium(III) $dsep^-$ compounds compared to that of potassium

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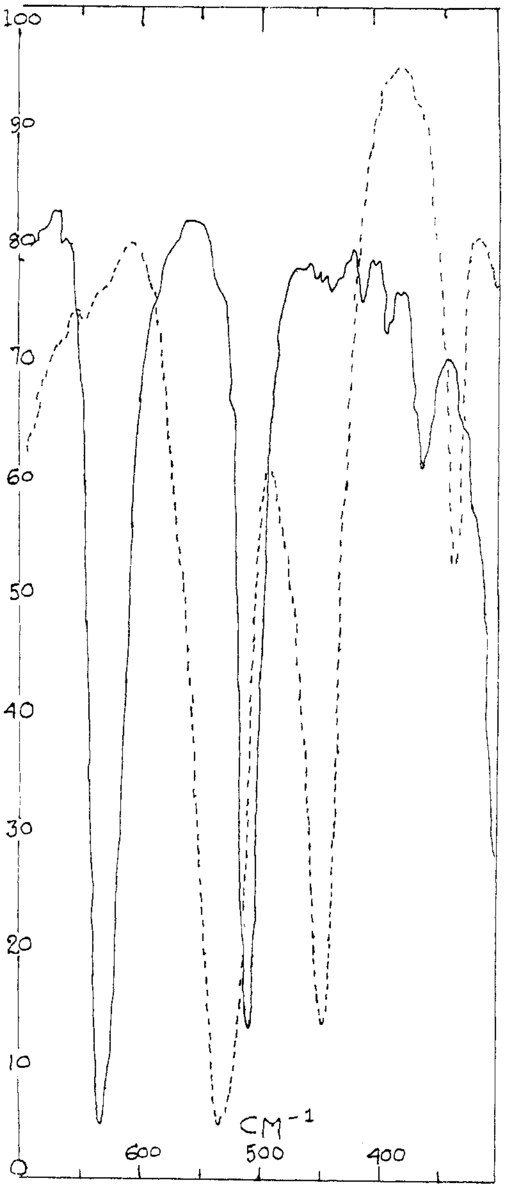

Figure 1. Infrared spectra of As(dtp)$_3$ (——) and As(dsep)$_3$ (- - - -).

TABLE II
INFRARED ABSORPTION FREQUENCIES OF O,O′-DIETHYL DISELENOPHOSPHATE (dsep$^-$) DERIVATIVES IN THE REGION 600–300 CM$^{-1}$

| Compound | Freq,$^a$ cm$^{-1}$ | | |
|---|---|---|---|
| | $\nu_1$ | $\nu_2$ | |
| Tl(dsep) | 570 s | 520 m | |
| Pb(dsep)$_2$ | 540 s | 480 m | 345 w |
| Sn(dsep)$_2$ | 535 s | 445 m | 335 w |
| As(dsep)$_3$ | 535 s | 450 m | 340 w |
| Sb(dsep)$_3$ | 515 s | 450 m | 340 w |
| Bi(dsep)$_3$ | 510 s, 475 vw | 450 m | 340 w |
| In(dsep)$_3$ | 555 s, 525 m | 480 m, 445 m | 335 w |

$^a$ Abbreviations: s strong; m, medium; w, weak; vw, very weak.

diethyl diselenophosphate. In the bismuth(III) compound, the $\nu_1$ is split into a doublet whereas in the indium(III) compound both $\nu_1$ and $\nu_2$ are split into doublets similar to that of the chromium(III) compound.[13] This decrease in $\nu_1$ and $\nu_2$ relative to that of the potassium salt suggests bonding through both of the selenium atoms of the selenophosphate to the metal ions. The reason for the splitting of $\nu_1$ and $\nu_2$ in indium(III) and chromium(III) is not understood.

One interesting feature of the infrared spectra of these compounds is the occurrence of a weak absorption band around 340 cm$^{-1}$. This band is absent in potassium and thallium(I) compounds. The possibility that this band might be due to a metal–selenium stretching mode is ruled out because such absorptions should occur at frequencies lower than 300 cm$^{-1}$. In the corresponding dtp$^-$ complexes the $\nu$(M–S) (M = Bi, In, Pb) stretching frequencies occur in the region of 250 cm$^{-1}$. The intensity and position of the absorption band around 340 cm$^{-1}$ in dsep$^-$ compounds suggests that it may involve one of the bending or scissoring modes of P–O–C or C–C–O or a combination of both.

The infrared spectrum of the thallium(I) compound differs from the rest of the spectra of the dsep$^-$ compounds. In the thallium(I) compound, only the $\nu_1$ of P–Se is lowered compared to that of the potassium salt and the band around 340 cm$^{-1}$ is absent. This could be due to the bridged structure of the thallium(I) compound.

TABLE III
SPECTRAL DATA ON O,O′-DIETHYL DISELENOPHOSPHATE (dsep$^{-1}$) DERIVATIVES$^a$

| Compound | Absorption max |
|---|---|
| Tl(dsep) | [33.90] (3.40) |
| Pb(dsep)$_2$ | [31.75] (3.16), [39.76] (3.77), [45.45] (4.64) |
| Sn(dsep)$_2$ | 32.79 (3.79), 38.99 (3.95) |
| As(dsep)$_3$ | [30.77] (3.62), [34.48] (3.92), 40.82 (4.28) |
| Sb(dsep)$_3$ | [23.81] (3.10), [30.77] (3.68) |
| Bi(dsep)$_3$ | 22.91 (3.48), 27.78 (4.04), 33.16 (4.59), 37.74 (4.59) |
| In(dsep)$_3$ | 35.71 (3.80), 43.19 (4.19) |

$^a$ Cyclohexane solvent. Band maxima are in kK; parentheses indicate log $\epsilon_{mol}$; brackets indicate shoulders.

It is difficult to infer the relative measure of the bond strength of M–Se in these compounds from the decrease in $\nu_1$ and $\nu_2$ of P–Se alone.

**Electronic Spectra.**—The absorption maxima and the intensities of the bands of the dsep$^-$ compounds studied are given in Table II. The first band of K(dsep) in the ultraviolet region occurs at 36.63 kK,[13] close to that observed for $P_2Se_5$ at 36.00 kK.[20] This may be ascribed to a 3p → 4s Rydberg excitation in Se. It is reasonable to expect charge-transfer bands to occur in this region.

It is found that the absorptions of the dsep$^-$ compounds fall very close to those observed for the bromide complexes.[21–23] Also, the absorptions observed for dsep$^-$ compounds occur at frequencies lower than those

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TABLE IV

X-RAY POWDER DATA ON DIETHYL DISELENOPHOSPHATE (dsep⁻) COMPOUNDS: *d* SPACINGS (Å)[a]

| As(dsep)$_3$ | Sb(dsep)$_3$ | Bi(dsep)$_3$ | In(dsep)$_3$ | Cr(dsep)$_3$ | Sn(dsep)$_2$ | Pb(dsep)$_2$ | Tl(dsep) |
|---|---|---|---|---|---|---|---|
| | | 11.777 | | | 11.334 | 11.936 | 12.617 |
| | 10.773 | 10.773 | | | 10.782 | 10.517 | 12.267 |
| | | | 9.604 | 9.408 | 9.509 | 9.604 | |
| 8.838 | 8.926 | | | | 9.212 | | |
| | | | 8.838 | 8.425 | | | |
| | | 7.893 | | | | | |
| 7.557 | | | 7.493 | 7.493 | | | |
| | | 5.98 | | | 7.138 | | 6.103 |
| 5.466 | 5.534 | | | | 5.405 | | |
| | | | | | 4.599 | | |
| | | | | | 4.332 | | 4.018 |
| 3.897 | 3.897 | | | 3.738 | 4.076 | | |
| 3.476 | 3.490 | 3.545 | | | 3.493 | 3.424 | 3.490 |
| 3.348 | | | | 3.284 | | | |
| 3.275 | 3.275 | 3.287 | | | | | |
| | | | 3.129 | 3.094 | | 3.015 | 3.015 |
| 3.139 | | | | | | | |
| | | | | | 2.959 | | |
| | | | | | 2.940 | 2.680 | |
| 2.554 | | | 2.575 | 2.535 | | 2.547 | 2.396 |

[a] Only the strong lines are listed.

observed for dtp⁻ compounds.[24] This could be due to the greater reducing property of dsep⁻ than dtp⁻. The indium(III) compound shows only one internal ligand transition. The exact assignment of the bands is complicated because of the considerable overlap of the internal transitions of the ligand with the $s^2 \rightarrow sp$ transitions of the central ions. The absorption bands of Bi(dsep)$_3$ at 22.91 and 27.78 kK may be assigned to a $^1\Gamma_1 \rightarrow \Gamma_4$ transition by analogy with the corresponding transition in Bi(dtp)$_3$.[25]

**X-Ray Powder Studies.**—*d* spacings observed for the different compounds calculated from the X-ray powder diffraction patterns are listed in Table IV. There is a closer correspondence in the *d* values of the dsep⁻ compounds of Cr(III) and In(III). In the case of the other metal ions the *d* values differ. Arsenic(III) N′,N′-diethyldithiocarbamate[26] has a trigonal-antiprismatic structure in which the bonding of sulfur atoms to arsenic is not equivalent. A similar situation may exist in dsep⁻ compounds also. The *d* values of the Tl(I)–dsep compound are quite different from other dsep⁻ compounds. It is difficult to draw any conclusions from the *d* values regarding the stereochemistry of the central ions studied.

Work on the preparation and properties of transition metal complexes with this ligand is currently in progress and will be reported shortly.

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