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Ligating Properties of Tertiary Phosphine/Arsine Sulphides or Selenides: Part IV—Complexes of Ditertiary Phosphine Disulphides & Diselenides with Cadmium(II) Halides

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Ditertiary phosphine disulphides and diselenides form 1:1 (metal-ligand) adducts of the type CdX_2 (L-L) [where X=Cl, Br and I; L-L=1,2-ethylenebis(diphenylphosphine sulphide or selenide) (EDPS or EDPSe); 1,3-propylenebis(diphenylphosphine sulphide or selenide) (PDPS or PDPSe); 1,4-butylenebis(diphenylphosphine sulphide or selenide) (BDPS or BDPSe) and 1,6-hexamethylenebis(diphenylphosphine selenide) (HDPSe)]. A 2:1 adduct, Cd_2X_4BDPSe , has also been prepared. The adducts have been characterized on the basis of elemental analyses and infrared spectra and have been assigned tetrahedral bridged structures.

VERY few adducts of Cd(II) with tertiary phosphine sulphides or selenides are reported in literature as compared with those of other class *b* metal ions¹⁻¹². In the present note we are reporting adducts of ditertiary phosphine disulphides or diselenides with Cd(II) halides.

The ligands, 1,2-ethylenebis(diphenylphosphine sulphide or selenide) (EDPS or EDPSe), 1,3-propylenebis(diphenylphosphine sulphide or selenide) (PDPS or PDPSe), 1,4-butylenebis(diphenylphosphine sulphide or selenide) (BDPS or BDPSe) and

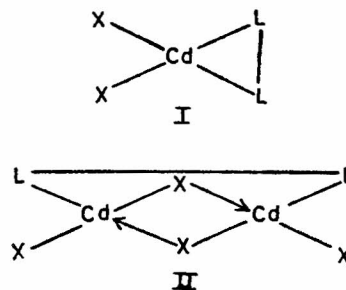
1,6-hexamethylenebis(diphenylphosphine selenide) (HDPSe), were prepared by procedures analogous to those reported in literature^{8,13}. The analytical data for the ligands have been already reported¹⁴.

The adducts were isolated by mixing the hot solutions of the ligands in benzene or ethanol with those of cadmium(II) halides in ethanol. The white solids obtained after either scratching or refluxing were filtered and washed with warm ethanol or benzene and dried *in vacuo*. The elemental analyses for the adducts (Table 1) were carried out by the Australian Microanalytical Service, Melbourne. The infrared spectra in the range 4600-200 cm^{-1} were recorded using Specord 71 IR and Beckman IR-12 spectrophotometers.

Infrared spectra indicate that the $\nu P-C$ (aromatic) modes occurring in the ligands EDPS, PDPS, BDPS, EDPSe, PDPSe, BDPSe and HDPSe respectively at 1090, 1080, 1090, 1090, 1080, 1080 and 1100 cm^{-1} remain practically unaffected after complex formation.

The $\nu P=S$ modes decrease by 38-53 cm^{-1} while $\nu P=Se$ modes decrease by 10-16 cm^{-1} after coordination to Cd(II). However, the $\nu P=Se$ for $CdX_2 \cdot PDPSe$ remains practically unchanged. These observations are in agreement with similar changes reported in literature^{8-11,15}. Further, $\nu Cd-Cl$ occurs at 266 cm^{-1} in $CdCl_2 \cdot PDPSe$ and 274 cm^{-1} in $CdCl_2 \cdot PDPS$ which is very strong in intensity. This may be due to overlapping with $\nu Cd-S$ as the range for the latter bands is 236-74 cm^{-1} . $\nu Cd-Br$ and $\nu Cd-Se$ occur in the ranges 215-225 and 240-262 cm^{-1} respectively. $\nu Cd-I$ and frequencies due to bridging halogens fall below 200 cm^{-1} (ref. 16-20).

All the adducts have been assigned tetrahedral structures. Structures of types I and II may be assigned to the 1:1 and 2:1 (metal-ligand) complexes.



In the BDPSe adduct with $CdBr_2$ the ligand has been found to act as a bridge between the two metal ions. The bridging behaviour of the ligand is evident from the fact that there is no increase in the number of $-CH_2-$ (bending) bands in the IR spectrum of the complex. The other alternative, chelate formation, would lead to the lowering of the symmetry of the ligand and hence an increase in the number of bands due to $-CH_2-$ (bending). Also, on chelation, high membered rings will be formed which are less stable.

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TABLE 1 — MELTING POINT AND ANALYTICAL DATA OF CADMIUM(II) HALIDE ADDUCTS

Complex	Found (Calc.), %			m.p. (°C)
	C	H	P/S	
CdCl ₂ .PDPS	49.09 (49.15)	4.14 (3.94)	10.6(S) (9.71)	225(d)
CdCl ₂ .PDPSe	43.28 (43.03)	3.69 (3.45)	7.20(P) (8.52)	240
CdBr ₂ .PDPS	43.86 (43.18)	3.82 (3.47)	8.2(S) (8.55)	228-30
CdBr ₂ .EDPSe	37.78 (37.70)	2.95 (3.00)	7.8(P) (7.7)	232(d)
CdBr ₂ .PDPSe	38.85 (38.48)	3.21 (3.09)	7.20(P) (7.36)	250(d)
Cd ₂ Br ₄ .BDPSe	30.77 (29.79)	2.66 (2.48)	5.5(P) (5.5)	275(d)
CdBr ₂ .HDPSe	41.86 (40.70)	3.69 (3.60)	6.3(P) (7.0)	75(d)
CdI ₂ .EDPS	37.59 (37.70)	2.87 (3.00)	7.7(P) (7.7)	250-52
CdI ₂ .BDPS	40.72 (39.25)	3.51 (3.27)	6.7(S) (7.48)	240(d)
CdI ₂ .PDPS	39.15 (38.48)	3.15 (3.09)	—	242-44
CdI ₂ .EDPSe	34.52 (33.80)	2.67 (2.60)	6.5(P) (6.70)	260(d)
CdI ₂ .PDPSe	36.15 (34.61)	3.50 (2.78)	5.6(P) (6.62)	275(d)
CdI ₂ .BDPSe	36.24 (35.37)	3.18 (2.95)	6.5(P) (6.53)	265(d)

cated Instrumentation Centre, IIT, Madras, for recording far infrared spectra in the range 650-200 cm⁻¹.

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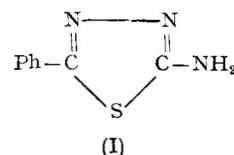
Complexes of 2-Amino-5-phenyl-1,3,4-thiadiazole with Cu(II), Ni(II), Co(II), Fe(II) & Zn(II) Sulphates

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Complexes of Cu(II), Ni(II), Co(II), Fe(II) and Zn(II) sulphates with 2-amino-5-phenyl-1,3,4-thiadiazole have been prepared and characterized on the basis of analytical, magnetic susceptibility, infrared and electronic spectral, TGA, DTA and DTG data. The ligand shows bidentate behaviour in all the complexes except in the case of Ni(II) complex where it acts as a monodentate ligand. All the complexes reported have octahedral stereochemistry except [Cu(2-amino-5-phenyl-1,3,4-thiadiazole)₂]₂SO₄ which is square-planar.

THE ligand, 2-amino-5-phenyl-1,3,4-thiadiazole (I) has four potential donor sites, viz. three nitrogen atoms and one sulphur atom. It will therefore be of interest to investigate the nature of bonding in the complexes formed by 2-amino-5-phenyl-1,3,4-thiadiazole. In this note, we report the results of our studies on the Cu(II), Ni(II), Co(II), Fe(II) and Zn(II) sulphate complexes.



All the chemicals used for the preparation of the complexes were of AR or chemically pure grade. The ligand, 2-amino-5-phenyl-1,3,4-thiadiazole (hereafter denoted as APTH) was prepared by the literature method¹.

The complexes were prepared by mixing aqueous solutions of metal sulphate hydrates with the ethanolic solution of ligand in (1:1) ratio and refluxing the mixture for 30 min, 1 hr, 2-3 hr in the case of Cu(II); Ni(II), Co(II) and Fe(II), Zn(II) complexes respectively. The complexes obtained were filtered and washed with hot ethanol and water and dried *in vacuo*.

Elemental analyses and magnetic measurements were carried out using standard methods. Electronic and IR spectra, TGA, DTA and DTG of complexes were also recorded using standard methods.

The molecular formulae and the elemental analyses are given in Table 1. On comparing the infrared spectra of the ligand with those of the complexes, it was found that the positions of most of the bands had shifted. The asymmetric and symmetric νNH observed at 3350 and 3270 cm⁻¹ in the ligand were shifted to 3360-3430 and 3280-3330 cm⁻¹ respectively in the spectra of the complexes. νC-S observed at 648 cm⁻¹ in the ligand was shifted to a position below 600 cm⁻¹ in the spectra of the complexes. These evidences indicate that the complexation is taking place through the sulphur atom and nitrogen atom of the NH₂ group.

From the analytical data and molecular formulae of the complexes, it is apparent that, in the case of Ni(II), the APTH behaves as a monodentate