Ligating Properties of Tertiary Phosphine/Arsine Sulphides or Selenides: Part IV—Complexes of Tertiary 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 CdX₂ (L-L) [where X=Cl, Br and I; L-L=1,2-ethylenedibis(diphenylphosphine sulphide or selenide) (EDPS or EDPSe); 1,3-propylenedibis(diphenylphosphine sulphide or selenide) (PDPS or PDPSe); 1,4-butylenedibis(diphenylphosphine sulphide or selenide) (BDPS or BDPSe) and 1,6-hexamethylenebis(diphenylphosphine selenide) (HDPSe), were prepared by procedures analogous to those reported in literature. The analytical data for the ligands have been already reported.

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 I) 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 νP=C (aromatic) modes occurring in the ligands EDPS, PDPS, BDPS, EDPSe, PDPSe, BDPSe and HDPSe respectively at 1090, 1080, 1090, 1080, 1080 and 1100 cm⁻¹ remain practically unaffected after complex formation.

The νP=S modes decrease by 38-53 cm⁻¹ while νP=Se modes decrease by 10-16 cm⁻¹ after coordination to Cd(II). However, the νP=Se for CdBr₂-PDPSe remains practically unchanged. These observations are in agreement with similar changes reported in literature.

Further, νCd–Cl occurs at 266 cm⁻¹ in CdCl₄-PDPSe and 274 cm⁻¹ in CdCl₄-PDPS which is very strong in intensity. This may be due to overlapping with νCd–S as the range for the latter bands is 236-74 cm⁻¹. νCd–Br and νCd–Se occur in the ranges 215-225 and 240-262 cm⁻¹ respectively. νCd–I and frequencies due to bridging halogens fall below 200 cm⁻¹.

All the adducts have been assigned tetrahedral bridged 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 CdBr₂ 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 νCH₂—(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 νCH₂—(bending). Also, on chelation, high membered rings will be formed which are less stable.

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References

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

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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 bidistal 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)₂SO₄], which is square-planar.