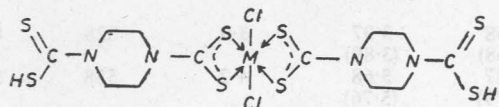


(I)



(M=Ge, Si, Ti)

(II)

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Complexes of Triphenylphosphine Sulphide with Some Lewis Acids

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Adducts of triphenylphosphine sulphide with boron trifluoride and chlorides of Al(III), Sn(IV), Ti(IV), Zr(IV) and Sb(V) have been prepared and characterized on the basis of elemental analyses, molar conductances, molecular weights and IR spectral data.

IN continuation of our studies on the complexes of triphenylphosphine sulphide with halides of zinc, cadmium and mercury¹, we now report the preparation of some new complexes of triphenylphosphine sulphide with boron trifluoride and chlorides of aluminium(III), tin(IV), titanium(IV), zirconium(IV) and antimony(V).

The Lewis acids were purified by standard methods.

The preparation of the adducts involved refluxing of metal halides with triphenylphosphine sulphide in dry benzene. Solid adducts thus obtained were recrystallized from anhydrous ethanol. Infrared spectra of the compounds under study were recorded in nujol mulls in teflon sheets on Perkin-Elmer model 337 and 621. The mulls were prepared in a dry box to avoid contact with moisture.

The elemental analyses of the adducts are reported in Table 1. Molar conductance values of $10^{-3} M$ solutions in nitrobenzene, determined at $25^{\circ} \pm 0.1^{\circ}$ using a cell of cell constant 0.543 cm^{-1} are far below the values expected for a 1:1 electrolytes (Table 1). Molecular weight of the adducts of aluminium and boron trihalides determined cryoscopically show that they are monomers (Table 1) while those of the halides of group IVA are dimers.

IR bands (ν_{max} in cm^{-1}) of the ligand assigned to the phenyl ring² do not undergo change on adduct formation, so also the carbon-phosphorus bands observed at 518 (asymmetric) and 430 cm^{-1} (symmetric). Out of two ligand bands at 690 and 546, assigned to $\nu\text{P-S}$ only the higher frequency band is perturbed and appears at a lower frequency on adduct formation. In the compound $2\text{BF}_3 \cdot (\text{C}_6\text{H}_5)_3\text{PS}$, a new band is observed at 580 which is assigned to $\nu\text{B-S}$. A broad band at 528 analogous to degenerate $\nu\text{B-F}$ bending mode in BF_4^- is also observed³. A new band at 1150 is observed which may be assigned⁴ to $\nu\text{B-F}$. In the case of $2\text{AlCl}_3 \cdot (\text{C}_6\text{H}_5)_3\text{PS}$ and $2\text{AlBr}_3 \cdot (\text{C}_6\text{H}_5)_3\text{PS}$ an intense absorption band, independent of the halide used is observed at 512 which may be assigned to $\nu\text{Al-S}$. In the far IR spectra of these adducts, intense bands at 492 and 418 are also observed which may be assigned⁵ to aluminium-halogen stretching mode.

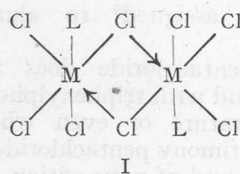
Phosphorus pentachloride does not form any addition compound with triphenylphosphine sulphide at room temperature or even when refluxed in benzene while antimony pentachloride forms a yellow crystalline compound of composition $(\text{C}_6\text{H}_5)_3\text{PS} \cdot \text{SbCl}_5$ at room temperature. The compound is stable in dry atmosphere but changes its colour when exposed to moisture. The $\nu(\text{P-S})$ observed at 690 in the pure ligand is shifted slightly to 668 on adduct formation. This is indicative of extensive back donation from the filled *p*-orbitals of antimony into the empty *d*-orbitals of sulphur. Appearance of antimony-sulphur stretching mode at 386 not present in the ligand indicates the metal coordination to the ligand. Appearance of the intense bands at 636 and 328 due to $\nu(\text{Sb-Cl})$ in $\text{SbCl}_5 \cdot (\text{C}_6\text{H}_5)_3\text{PS}$ indicates an octahedral environment around antimony^{6,7}.

Adducts of triphenylphosphine sulphide with tetrachlorides of tin, titanium and zirconium having com-

TABLE 1 — ANALYTICAL DATA FOR THE ADDUCTS OF TRIPHENYLPHOSPHINE SULPHIDE WITH LEWIS ACIDS

Adduct	Colour and state	m.p. °C	Reqd (%) (Found)			ΔM ohm ⁻¹ cm ² mol ⁻¹	Mol wt	
			Halogen	Metal	S		Reqd	Found
Ph ₃ PS.2AlBr ₃	Brown liquid	—	58.10 (58.17)	6.68 (6.68)	3.97 (3.89)	3.9	828	802
Ph ₃ PS.2AlCl ₃	White	230°	50.48 (50.39)	7.87 (7.79)	5.68 (5.76)	4.2	558	574
Ph ₃ PS.2BF ₃	Brown liquid	—	26.87 (26.72)	5.21 (5.19)	7.68 (7.69)	3.8	428	438
Ph ₃ PS.SbCl ₅	Yellow	230°	31.69 (31.79)	22.06 (21.98)	5.39 (5.29)	5.6	—	—
Ph ₃ PS.TiCl ₄	Light brown	230°	29.58 (29.49)	9.73 (9.68)	6.67 (6.70)	4.9	968	1972
Ph ₃ PS.SnCl ₄	White	230°	25.56 (25.62)	21.32 (21.29)	8.38 (8.29)	4.6	1110	2229
Ph ₃ PS.ZrCl ₄	Yellow	110°	26.97 (26.89)	17.23 (17.10)	6.07 (6.12)	5.2	1054	2126

positions Ph₃PS.SnCl₄, Ph₃PS.TiCl₄ and Ph₃PS.ZrCl₄ have been isolated. In the case of silicon tetrachloride, no reaction takes place due to weak donor and acceptor character of both the components. These compounds are slightly soluble in various aprotic solvents. Molecular weights in dilute solutions show them to be dimer. In the case of the compound TiCl₄·(C₆H₅)₃PS, possibility of the titanium metal acquiring hexacoordination through chlorine bridging is indicated by the appearance of an intense band at 308 apart from the bands observed at 338 due to terminal Ti—Cl band^{8,9}. Appearance of a strong band at 362 assigned to ν Ti—S suggests metal-sulphur coordination. It is interesting to note that in these compounds ν P—S is lowered by about 90 cm⁻¹ which is quite high as compared to the values observed for other Lewis acids. Similar observations have been recorded for other metal chloride adducts. Structure (I) may be proposed for the compounds where each metal acquires hexacoordination.



where M = Ti, Zr, Sn
L = Ph₃PS

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α -Picoline & Ethylenediamine Adducts of Ni(II), Cu(II), Pd(II) & Pt(II) Complexes with *o*-(2-Pyrrolideneimino)benzoic Acid & 3-(2-Pyrrolideneimino)propionic Acid

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α -Picoline & Ethylenediamine Adducts of the bivalent metal complexes of the type [M(PA)L] and [M(PA)L.H₂O] have been synthesized, where H₂PA = *o*-(2-pyrrolideneimino)benzoic acid or 3-(2-pyrrolideneimino)propionic acid, and when L = α -picoline, M = Ni(II), Cu(II), Pd(II) or Pt(II) and when L = ethylenediamine, M = Ni(II) or Cu(II). Molecular weights, elemental analyses, magnetic moments, conductance and spectral data suggest that the α -picoline adducts of Ni(II) and Cu(II) complexes display distorted square-planar configuration whereas those of Pd(II) and Pt(II) complexes possess normal square-planar geometry. The ethylenediamine adducts of Ni(II) and Cu(II) complexes exhibit distorted octahedral stereochemistry.

A SURVEY of the literature¹⁻⁴ shows that no work has been done on the α -picoline and ethylenediamine adducts of Ni(II), Cu(II), Pd(II) and Pt(II) complexes with *o*-(2-pyrrolideneimino)benzoic acid (H₂PB) and 3-(2-pyrrolideneimino)propionic acid (H₂PP). These are biprotic tridentate ligands possessing >C=N-, -COOH and =N- groups. We report here the preparation and characterization of the α -picoline and ethylenediamine adducts of these complexes.

All the chemicals used were of AR grade. The apparatus employed were the same as reported earlier⁵.

The ligands H₂PB and H₂PP were prepared by the condensation of pyrrole-2-carboxaldehyde with anthranilic acid and β -alanine, respectively,