Metal Complexes of Tertiary Arsine Sulphides and Phosphine Selenides

By PHILIP NICPON and DEVON W. MEEK

(*Department of Chemistry, The Ohio State University, Columbus, Ohio* 43210)

IN contrast to numerous metal complexes of phosphine oxides and arsine oxides, few phosphine sulphide[1–4] and only one arsine sulphide[5] complexes have been reported. Although two triphenylphosphine selenide complexes have been noted[1] previously, no infrared data were given. Recently we[3,6] have been investigating the co-ordinating properties of $R_3P{=}S$, $R_3P{=}Se$, and $R_3As{=}S$ compounds toward a variety of metallic ions. We have isolated a number of "class b"[7] or "soft"[8] metal complexes with each of the three types of molecules. This Communication reports the first triphenylarsine sulphide complexes and the first infrared data for tertiary phosphine selenide complexes.

Crystalline triarylphosphine selenide and tri-n-butylphosphine selenide complexes of Hg^{II}, Ag^{I}, Pd^{II}, and Pt^{II} may be obtained by the direct reaction of the appropriate metal salt with the ligand in ethanol or methanol. Satisfactory analytical data were obtained for all the compounds reported. Their physical properties are given in the Table.

Triphenylphosphine selenide, tri-*p*-tolylphosphine selenide, and tri-*m*-tolyphosphine selenide all form square-planar PdL_2Cl_2 complexes. Although the value of the P=Se stretching vibration varies with the three ligands, this peak is shifted 16 cm.$^{-1}$ toward lower energy in each of the palladium complexes, compared with the free phosphine selenide.

Triphenylarsine sulphide forms stable, crystalline complexes of Cd^{II}, Hg^{II}, Ag^{I}, and Pd^{II}. Ethanolic solutions of copper(II) salts are reduced rapidly by triphenylarsine sulphide to yield copper(I) complexes, *e.g.*, $[CuLBr]_x$.

No triphenylarsine sulphide or tertiary phosphine selenide complexes of "class a" or "hard" metal ions such as Co^{II}, Ni^{II}, or Cu^{II} have been isolated in this study.

The position of the P=Se band in the infrared spectrum of each complex is shifted to lower energy compared with the value for the uncomplexed ligand, indicating that the P=Se group co-ordinates with the metal ions through selenium. The magnitude of this shift was 15—20 cm.$^{-1}$ The As=S stretching vibration for uncomplexed triphenylarsine sulphide was found at 497 cm.$^{-1}$, clearly above strong ligand absorptions at 450—475 cm.$^{-1}$ The As=S vibration in the complexes

TABLE

Properties of some complexes

Complex	Colour	Conductance[a] (cm.^{2} ohm^{-1} M^{-1})	$\nu_{P=Se}$ (cm.$^{-1}$)	$\Delta\nu_{P=Se}$ (cm.$^{-1}$)
HgI_2,Ph_3PSe	Light yellow	[b]	542	−20
$PdCl_2,2(m\text{-}Me{\cdot}C_6H_4)_3PSe$	Pale orange	3·2,MeCN	558	−16
$PtCl_2,2Ph_3PSe$	Light tan	[b]	544	−18
$CdI_2,2(C_4H_9)_3PSe$	Colourless	6·8,MeCN	480	−15
$AgClO_4,2Ph_3PSe$	Colourless	132,MeCN	551[c] 542	−11[c] −20
$PdBr_2,2Ph_3AsS$	Orange-brown	<2,acetone	—	—
$AgClO_4,2Ph_3AsS$	Colourless	140,MeCN	—	—

[a] Approximately 10^{-3}M in acetonitrile.
[b] Not sufficiently soluble in MeCN, $MeNO_2$, or acetone.
[c] The $\nu_{P=Se}$ band is split in the Ag^{I} complexes.

was not distinguishable, presumably due to its shift to lower energy and coincidental overlap with the ligand bands. That the arsine sulphide linkage probably remained intact is shown by the fact that satisfactory carbon, hydrogen, and halogen analyses were obtained, and, most important, the theoretical amount of sulphur was found in all of the triphenylarsine sulphide complexes.

(*Received, May 6th,* 1966; *Com.* 299.)

---

[1] E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 1960, 1959.
[2] I. M. Keen, *J. Chem. Soc.*, 1965, 5751.
[3] D. W. Meek and P. Nicpon, *J. Amer. Chem. Soc.*, 1965, **87**, 4951.
[4] H. Teichmann, *Angew. Chem.*, 1965, **77**, 809.
[5] A. Merijanian and R. A. Zingaro, *Inorg. Chem.*, 1966, **5**, 187.
[6] P. Nicpon and D. W. Meek, Paper presented at 151st American Chemical Society Meeting, Pittsburgh, Pa., March, 1966.
[7] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.
[8] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.