Inorganic Heterocycles. The Reaction of 1,1′-Bi(1-phospholan-1-thione) with Some Transition-metal Salts

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The title compound (L) forms copper(I) complexes, [{CuL(X)}$_n$] (X = Cl or Br), on reaction with the appropriate copper(II) halide. These probably contain dimeric units, each copper being in a S_3X environment produced by a chelating L, one bridging sulphur atom from the second L ligand, and a terminal halide. These species contain the novel multi-heterocyclic rings C_4P, $Cu_2S_2P_2$, and Cu_2S_2 in the same molecule. Palladium(II) and platinum(II) chlorides produce [$Pd_2L_2Cl_2$][$PdCl_4$] and [$PtLCl_2$]. Insoluble [Hg_2LCl_4] has also been isolated.

SULPHUR is a very important donor atom in co-ordination chemistry, and complexes of phosphine sulphide ligands are attracting increasing attention.[1-11]

We embarked on the present study for several reasons. First to prepare new complexes of chelating diphosphine disulphide ligands. Secondly with 1,1′-bi(1-phospholan-1-thione), L,† there is the intriguing possibility of synthesising heterocycles which already contain a heterocyclic phosphorus; thus in the same molecule we would obtain both inorganic and organic heterocyclic rings. Thirdly we were interested in the complex of Meek and Nicpon [1] formulated as [$Cu(Me_4P_2S_2)_2$][$CuCl_2$] containing the rare [$CuCl_2$]$^-$ ion, and hoped to prepare further examples. However, while our work was in progress Cotton *et al.*[6] showed that this complex is in fact binuclear with each Cu^I in an S_3Cl tetrahedral environment provided by one chelating $Me_4P_2S_2$ ligand, a terminal chloride, and a bridging sulphur from the second phosphine sulphide ligand.

TABLE

Analytical data and physical properties

Complex	Colour	M.p. (θ_c/°C)	Λ [a] S cm² mol⁻¹	Analysis (%) [b] C	H	S	X	M	ν(P=S) cm⁻¹
[$Cu_2L_2Cl_2$]	White	130	138	28.0 (28.4)	4.9 (4.7)	18.1 (18.4)	10.5 (10.5)	19.1 (18.8)	608, 588
[$Cu_2L_2Br_2$]	White	150—160	127	25.5 (25.1)	4.1 (4.2)	16.6 (16.8)	21.0 (20.8)	16.3 (16.6)	603, 580
[$Pd_2L_2Cl_2$][$PdCl_4$]	Brown		147	19.0 (19.1)	3.6 (3.2)	12.9 (12.7)	21.7 (21.2)	20.7 (21.1)	595, 555
[$PtLCl_2$]	Yellow-brown	*ca.* 260	4	18.9 (19.0)	3.5 (3.2)	12.8 (12.7)	14.4 (14.1)	38.2 (38.7)	590, 545
[Hg_2LCl_4]	White	*ca.* 210	Insoluble	2.6 (2.1)	2.6 (2.1)	8.4 (8.2)	18.4 (18.2)		545

[a] In 10^{-3} mol dm^{-3} MeCN. 1 : 1 Electrolytes have $\Lambda \sim 120\sim160$ S cm² mol^{-1} in this solvent. [b] Calculated values are given in parentheses.

RESULTS AND DISCUSSION

We obtain yields of [{CuL(X)}$_n$] (X = Cl or Br) of *ca.* 50% when copper(II) halides and the ligand L react in a 1 : 1 molar ratio in deoxygenated absolute ethanol. The resulting precipitates were rinsed thoroughly with diethyl ether to remove any free ligand. The initial green colour of the solutions was lost after *ca.* 10 min and white complexes precipitated. This suggests that a copper(II) intermediate is formed initially and is then reduced to Cu^I. Slinkard and Meek [4] found that with tris(dimethylamino)phosphine sulphide the reaction with copper(II) chloride proceeds as in (1). We found no

$$4CuCl_2 + 8P(NMe_2)_3S \longrightarrow 2[Cu\{P(NMe_2)_3S\}_4]Cl + [(Me_2N)_3PSSP(NMe_2)_3][Cu_2Cl_6] \quad (1)$$

evidence for an oxidation product analogous to the last species in (1), and neither does oxidation of the ethanol solvent to acetaldehyde seem to occur since we were unable to detect MeCHO by g.l.c. or by treatment by phenylhydrazine. Thus the mechanism of this reaction remains obscure.

1,2-Dithioxodi-λ^5-phosphanes $R_2(S)PP(S)R_2$, which in the free state exist in a *trans* conformation and exhibit one ν(P=S) vibration in the i.r. spectra, necessarily adopt a *cis* conformation when behaving as chelating ligands and this is revealed by the presence of two ν(P=S) frequencies, one at higher and one at lower frequency than in the free ligand.[12,13] In free L, ν(P=S) occurs at 595 cm^{-1}, and in [{CuL(X)}$_n$] two bands are evident (Table) confirming the *cis* conformation of L and con-

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† A trivial name for this compound is bis(cyclotetramethylene)-diphosphine disulphide.

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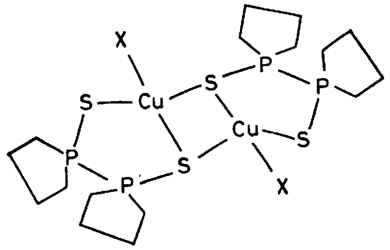
[11] M. G. Newton, H. D. Caughman, and R. C. Taylor, *Chem. Comm.*, 1970, 1227.

sistent with chelation to the copper. Careful examination of the i.r. spectra also reveals a weak absorption, not present in the ligand, at *ca.* 430 cm^{-1} which is probably ν(P–P) which becomes weakly i.r. active on co-ordination. We have been unable to assign ν(Cu–X) unambiguously in the far-i.r. spectra, but the electronic-reflectance spectra show a shift of the absorptions to lower energy from the chloro- to the bromo-complex, consistent with co-ordination of X. The complexes are 1 : 1 electrolytes in 10^{-3} mol dm^{-3} acetonitrile solution (Table), probably due to reaction (2), but are insufficiently soluble in non-polar solvents for molecular-weight measurements. In view of the similar steric properties of L to $Me_2(S)PP(S)Me_2$, and the generally similar properties of their complexes,[1,6,10] it is very likely that the complexes of L are dimeric in the solid state with a similar structure to $[\{Cu(Me_4P_2S_2)Cl\}_2]$ as revealed by the previous[6] *X*-ray study. Thus we propose structure (1) for these complexes containing multi-heterocyclic rings, C_4P, CuS_2P_2, and Cu_2S_2.

$$[\{CuL(X)\}_n] \rightleftharpoons \frac{n}{2}\{[CuL_2][CuX_2]\} \qquad (2)$$



(1)

Sodium tetrachloropalladate(II) and L produced a brown complex $Pd_3L_2Cl_6$ which is a 2 : 2 electrolyte in acetonitrile and is probably the dichloride-bridged $[Pd_2L_2Cl_2][PdCl_4]$. In contrast, sodium tetrachloroplatinate(II) yielded $[PtLCl_2]$, a non-electrolyte. Both complexes exhibited two ν(P=S) (Table) consistent with chelating L, but again the large number of absorptions in the far-i.r. region prevented assignment of the metal-chloride vibrations.

Mercury(II) chloride yielded insoluble white $[Hg_2LCl_4]$ on stirring with L in cold ethanol. On refluxing this mixture, ill defined yellow solids of low carbon content were produced suggesting decomposition of the ligand. In contrast to the other complexes, $[Hg_2LCl_4]$ exhibits only a single ν(P=S) at 545 cm^{-1} suggesting that the ligand is present in the *trans* conformation and hence bridging rather than chelating.[12,13] There are numerous examples of incorrect structures assigned to mercury(II) complexes on the basis of only vibrational spectra,[14] and speculation about the structure of this complex is not justified.

We were unable to isolate any complexes of L with nickel(II) or cobalt(II) salts and, in contrast to $Me_4P_2S_2$,[1,11,12] L did not yield complexes with zinc or cadmium halides and reduced silver nitrate to metallic silver. This suggests that, although generally similar to $Me_4P_2S_2$, L is a rather poorer ligand.

EXPERIMENTAL

1,1′-Bi(1-phospholan-1-thione), L, was prepared as previously described.[15]

Reactions.—Copper(II) chloride (0.083 g, 0.48 mmol) and L (0.26 g, 1.1 mmol) were mixed together in deoxygenated anhydrous ethanol (20 cm^3), and the green mixture was stirred and heated under reflux for 20 min. The green colour gradually faded and, on cooling, white crystals were deposited. The solid was filtered off and washed with anhydrous diethyl ether (3 × 10 cm^3), yield 0.16 g. The complex derived from L and $CuBr_2$ was similarly prepared.

Sodium tetrachloropalladate(II) (0.192 g, 0.055 mmol) in deoxygenated anhydrous ethanol (15 cm^3) was added to a stirred suspension of L (0.121 g, 0.51 mmol) in deoxygenated anhydrous ethanol (10 cm^3). The colour of the resulting solution changed rapidly from orange to dark brown and a brown solid was deposited. After stirring for another 2 h the solid was filtered off and washed with water (20 cm^3), ethanol (20 cm^3), and anhydrous diethyl ether (20 cm^3), yield 0.1 g. The reaction between L and $Na_2[PtCl_4]$ was similar.

Mercury(II) chloride (0.254 g, 0.93 mmol) and L (0.225 g, 0.945 mmol) were mixed in deoxygenated anhydrous ethanol (20 cm^3). After *ca.* 5 min the clear solution deposited a white powder, but stirring was continued for 1 h. The solid was filtered off and washed with anhydrous diethyl ether (20 cm^3). All the complexes slowly evolve H_2S on exposure to air, but appear to be stable under dry conditions.

Physical measurements were made as previously described.[16]

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