Oxidation of Tris(dimethylamino)phosphine Sulphide to a New Type of Phosphorus–Sulphur Cation

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ALKYLPHOSPHINE SULPHIDES, $R_3P{=}S$, reduce Cu^{II} and Au^{III} ions[1-3] and form complexes. With tris(dimethylamino)phosphine sulphide, $(Me_2N)_3P{=}S$,[4] the novel cation $[(Me_2N)_3P{-}S{-}S{-}P(NMe_2)_3]^{2+}$ is formed by the Cu^{II} or bromine oxidation of $(Me_2N)_3P{=}S$.

Dissolution of the blue complex $[Cu(MeCN)_4](ClO_4)_2$ in liquid $(Me_2N)_3P{=}S$ at 30°, gives a nearly colourless solution (10 sec.) and white crystals. The i.r. spectrum of these is very similar to that of the original $(Me_2N)_3P{=}S$, except that the strong 565 cm.$^{-1}$ absorption ($P{=}S$ stretching frequency) is absent and two strong prechlorate bands at *ca.* 1100 and 625 cm.$^{-1}$ are present. The prechlorate bands indicate that a cation was formed. The compound is a bi-univalent electrolyte in nitromethane and its n.m.r. spectrum shows that all the methyl groups are equivalent and bonded to phosphorus. The J_{P-H} coupling constants and the downfield shift of the methyl doublet are comparable to those observed for $[(Me_2N)_3P{-}S{-}Me]^+I^-$. On the basis of the n.m.r. and i.r. spectral data, the analytical data, and the conductivity results, the structure of this new cation is suggested to be $[(Me_2N)_3P{-}S{-}S{-}P(NMe_2)_3]^{2+}$. Such a cation would result from the oxidation of $(Me_2N)_3P{=}\underset{\cdot\cdot}{S}$: to the free-radical $[(Me_2N)_3P{=}\overline{S}\cdot]^+$, followed by rapid coupling. The same species was isolated also as the tribromide salt after bromine oxidation of $(Me_2N)_3PS$ in acetonitrile.†

The above divalent cation also affords an explanation for the bright red crystals, $(Me_2N)_3PSCuCl_3$, which result from anhydrous copper(II) chloride or $Cu(MeCN)_4Cl_2$ and $(Me_2N)_3P{=}S$. The compound is a 2 : 2 electrolyte in nitromethane, exhibits a magnetic moment of 2·04 B.M. per copper ion, has an electronic spectrum remarkably similar to square-planar Cu^{II} anions,[5] and gives an i.r. spectrum identical to that of the above $[(Me_2N)_3P{-}S{-}S{-}P(NMe_2)_3]^{2+}$ salts. Thus, these red crystals should be formulated as $[(Me_2N)_3PS_2P(NMe_2)_3]$ $[Cu_2Cl_6]$, containing the known planar $[Cu_2Cl_6]^{2-}$ anion, rather than as any copper(II)–$(Me_2N)_3P{=}S$ coordination complex. As additional evidence, identical red crystals were prepared directly from $[(Me_2N)_3PS_2P(NMe_2)_3](ClO_4)_2$, anhydrous $CuCl_2$, and LiCl.

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† All the compounds discussed had satisfactory analyses.

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