445. *Phosphine Oxide Complexes. Part IV.*[1] *Tetrahedral, Planar, and Binuclear Complexes of Copper*(II) *with Phosphine Oxides, and Some Arsine Oxide Analogues.*

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Some phosphine oxide complexes of copper(II) have been prepared, along with the arsine oxide analogues of two of them, and physical measurements made in order to determine the co-ordination symmetries. It appears that the co-ordination is tetrahedral in $[Cu(Ph_3PO)_2Cl_2]$ and $[Cu(Ph_3PO)_2Br_2]$, as in the analogous manganese(II), cobalt(II), and nickel(II) compounds. The triphenylarsine oxide analogues of these complexes do not seem to be tetrahedral. The complex cation $[Cu(Me_3PO)_4]^{2+}$ appears to be square, and the complex $CuCl_2,4(HO{\cdot}CH_2)_3PO$ also appears to contain tetragonally co-ordinated copper(II). The complex $Cu(CH_3{\cdot}CO_2)_2,Ph_3PO$ is very probably a carboxylate-bridged dimer.

THE factors which determine the relative stabilities of the tetrahedral and planar configurations for four-co-ordinate complexes of manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), and other ions are imperfectly understood. It is true that some contributing factors are recognized. For example, the effect of ligand field stabilization energies,[2] known in a semiquantitative way, would by itself probably lead to the following order of preference for the tetrahedral as compared with the planar configuration: Mn(II) $\approx$ Zn(II) $>$ Co(II) $>$ Cu(II) $>$ Ni(II). Since other factors—steric effects, additional electrostatic forces, covalency in the metal–ligand bonds, and perhaps others—may be expected to vary more or less regularly with atomic number of the metal ion in a series of stoicheiometrically analogous complexes, it is not surprising that the above order is fairly consistent with observations although the latter are not extensive.

However, the predictive capabilities of present theory do not appear to extend much

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[1] Part III, Bannister and Cotton, *J.*, 1960, 2276.

[2] George and McClure, *Progr. Inorg. Chem.*, 1959, **1**, 381.

further. In particular, it is difficult to know exactly what properties of ligands, or what combination of properties, cause certain complexes of a given ion to be tetrahedral while others are planar. For example, with nickel(II), $[Ni(Ph_3P)_2Cl_2]$ is tetrahedral[3] while no other $[Ni(R_3P)_2Cl_2]$ complex has yet been prepared which is tetrahedral even when R is cyclohexyl.[4] Thus the steric factor alone does not seem decisive. It is probable, perhaps even likely, that a close balance of various factors determines the result so that simple predictive theory may remain beyond reach. In any event, the more experimental data which are available, the more likely it is that some general patterns may become evident. In this work, a very primitive and empirical hypothesis was tested. We have previously reported[5] the preparation of triphenylphosphine oxide complexes of nickel(II) halides, $[Ni(Ph_3PO)_2X_2]$ (X = Cl, Br, I), the bromide having also been reported by Issleib and Mitscherling,[6] and detailed evidence was presented to show that they are tetrahedral.[5] It has also been shown that the corresponding triphenylarsine oxide complexes containing chloride and bromide are tetrahedral,[7] and that the analogous triphenylphosphine oxide and triphenylarsine oxide complexes of manganese(II) are tetrahedral.[8] In view of the relative scarcity of tetrahedral nickel(II) complexes and, in particular, of the tendency of most other complexes of the type $[NiL_2X_2]$ to be planar, the hypothesis that triphenylphosphine oxide and its arsenic analogue might have an optimum set of properties favouring the tetrahedral configuration was considered. On this assumption, it seemed plausible that analogous copper(II) complexes might also be tetrahedral, since copper(II) should not be significantly more reluctant than nickel(II) to form tetrahedral complexes.

Few phosphine oxide or arsine oxide complexes of copper(II) have been reported before. Pebal[9] reported pale green $CuSO_4,3Et_3PO$; Pickard and Kenyon[10] reported light brown $CuCl_2,Et_3PO$; and Bannister and Cotton have reported $[Cu(Ph_3PO)_4](ClO_4)_2$[11] and $[Cu(Ph_3PO)_2(NO_3)_2]$.[1] For the last two compounds the spectral data were explicitly interpreted as indicating square-planar configurations, and the colour of the sulphate complex leaves little doubt that it, too, has a planar or distorted octahedral configuration. The nature of the brown $CuCl_2,Et_3PO$ compound remains uncertain. Nyholm[12] has reported the perchlorate and $[CuCl_2]^-$ salts of $[Cu(Ph_2MeAsO)_4]^{2+}$ which also appear to contain square-planar copper(II), as does $[Cu(dimethyl\text{-}2\text{-}picolylarsine\ oxide)_2](ClO_4)_2$ reported by Goodwin and Lions.[13]

TABLE 1. *Magnetic moments of the complexes.*

No.	Complex	Temp. (K)	$\chi^{M}_{corr.}$ ($\times 10^6$)	Diamagnetic corrn. ($\times 10^6$)	μ (B.M.) ($\pm 0{\cdot}02$)
1	$[Cu(Ph_3PO)_2Cl_2]$	299·1°	1797	405	2·08
2	$[Cu(Ph_3PO)_2Br_2]$	299·5	1664	426	2·01
3	$[Cu(Ph_3AsO)_2Cl_2]$	298·8	1539	449	1·92
4	$[Cu(Ph_3AsO)_2Br_2]$	300·7	993	470	1·56
5	$Cu(CH_3{\cdot}CO_2)_2,Ph_3PO$	299·2	959	246	1·52
6	$[Cu(Me_3PO)_4](ClO_4)_2$	298·4	1790	339	2·07 [a]
7	$CuCl_2,4(HO{\cdot}CH_2)_3PO$	297·8	1656	330	1·99

[a] Some indication of dependence of susceptibility on field strength.

Knowledge of the behaviour and properties of tetrahedrally co-ordinated copper(II) is also limited. Golden-yellow cæsium tetrachlorocuprate(II) containing the tetrahedral

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[3] Venanzi, *J.*, 1958, 719.

[4] Issleib and Brack, *Z. anorg. Chem.*, 1954, **277**, 258; Turco, Scatturin, and Giacometti, *Nature*, 1959, **183**, 601; Turco and Giacometti, *Ricerca sci.*, 1959, **29**, 1057.

[5] Cotton and Goodgame, *J. Amer. Chem. Soc.*, 1960, **82**, 5771.

[6] Issleib and Mitscherling, *Z. anorg. Chem.*, 1960, **304**, 73.

[7] Goodgame and Cotton, *J. Amer. Chem. Soc.*, 1960, **82**, 5774.

[8] Goodgame and Cotton, unpublished work.

[9] Pebal, *Annalen*, 1862, **120**, 202.

[10] Pickard and Kenyon, *J.*, 1906, **89**, 270.

[11] Bannister and Cotton, *J.*, 1960, 1878.

[12] Nyholm, *J.*, 1951, 1767.

[13] Goodwin and Lions, *J. Amer. Chem. Soc.*, 1959, **81**, 311.

Table 2. *Electronic absorption spectra of the complexes.*

Compound	Medium	Colour	Absorption bands (mμ) (molar extinction coefficients for solutions)					
[Cu(Ph$_3$PO)$_2$Cl$_2$]	Solid	Yellow	345,	375,	425,			>1100
	10^{-3}M in MeNO$_2$	Yellow	~350sh,	380 (640),	470 (720),		900 (160)b	
[Cu(Ph$_3$PO)$_2$Br$_2$]	Solid	Dark red	Very strong absorption below 550 mμ					>1100
	10^{-3}M in MeNO$_2$	Green	~350sh,	372 (1970),	430 (1115),	643 (575),	910 (340)	
[Cu(Ph$_3$AsO)$_2$Cl$_2$]	Solid	Yellow-brown	345,		417, 480,	675,	~940	>1100
[Cu(Ph$_3$AsO)$_2$Br$_2$]	Solid	Olive-green	~360b		~440sh,	680,	~900sh	
Cu(CH$_3$·CO$_2$)$_2$,Ph$_3$PO	Solid	Green	335,	~375sh,		750b		
	5 × 10^{-3}M in dioxan	Blue		374 (47),		659 (220)		
[Cu(Me$_3$PO)$_4$](ClO$_4$)$_2$	Solid	Pale blue				~600sh,	875b	
CuCl$_2$,4(HO·CH$_2$)$_3$PO	Solid	Pale blue-green	325,	~380sh,			~845b	

sh = shoulder; b = broad.

tetrachlorocuprate(II) ion was the first compound in which its occurrence was definitely proved,[14] and other salts of tetrahedral [CuCl$_4$]$^{2-}$ with the same characteristic yellow colour have subsequently been reported.[15,16] The *X*-ray study of cæsium tetrachlorocuprate(II) revealed a significant flattening of the tetrahedron, and in cæsium tetrabromocuprate(II) the flattening is even greater.[17] These distortions have often been attributed to the Jahn–Teller effect, but according to Liehr [18b] spin–orbit coupling should produce a ground state which is not susceptible to a Jahn–Teller distortion. The purple compound [Ph$_3$MeAs]$_2$[CuBr$_4$], has also been reported,[16] but no indication was given as to the configuration of the [CuBr$_4$]$^{2-}$ ion therein. Quite recently, Pappalardo [19] has studied the spectrum of copper(II) in the tetrahedral environment of the zinc oxide lattice.

Liehr [18] has published the complete theory (*i.e.*, including spin–orbit coupling) for the tetrahedrally co-ordinated copper(II) ion. As Pappalardo's paper [19] will show in detail, Liehr's results, together with the assumption that the Δ values in tetrahedral complexes will be ~4/9 of those (~11,000 cm.$^{-1}$) found in octahedral complexes, lead to the expectation that these complexes will have absorption bands in the region of 5000—7000 cm.$^{-1}$ but no absorption in the visible region due to *d–d* transitions. The reflectance spectrum of cæsium tetrachlorocuprate(II) [14] was indeed blank between 500 and 1000 mμ, the region where tetragonal and distorted octahedral copper(II) complexes normally absorb, and Pappalardo [19] has actually observed the absorption in ZnO:CuO at 5807 cm.$^{-1}$, in excellent agreement with theory. The yellow colour of the tetrachlorocuprate(II) ion is attributable to strong, presumably charge-transfer, absorption bands in the near ultraviolet region. Spectral data for solutions [14,16] of tetrachlorocuprate(II) and tetrabromocuprate(II) ions generally show some absorption in the red region, but this may be due to the instability of the tetrahedral configuration, leading to rearrangement or solvolytic decomposition in solution.

With regard to magnetic properties, Figgis [20] has shown that in a perfectly regular tetrahedral environment, copper(II) should have an effective moment of about 2·2 B.M.

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[14] Helmholtz and Kruh, *J. Amer. Chem. Soc.*, 1952, **74**, 1176.

[15] Stürzer, *Z. Naturforsch.*, 1960, **15**b, 544.

[16] Gill and Nyholm, *J.*, 1959, 3997.

[17] Morosin and Lingafelter, *Acta Cryst.*, 1960, **13**, 807.

[18] (*a*) Liehr, *J. Phys. Chem.*, 1960, **64**, 43; (*b*) specifically, footnote 65.

[19] Pappalardo, Symp. Molecular Structure and Spectroscopy, Ohio State Univ., Columbus, Ohio, June 1960; we thank Dr. Pappalardo for a copy of his manuscript.

[20] Figgis, *Nature*, 1958, **182**, 1568.

However, it is well established by measurements in three laboratories [16,21] that μ_{eff} of copper(II) in cæsium tetrachlorocuprate(II) is only 1·96—2·00 B.M., and Gill and Nyholm [16] report values of 1·91 B.M. for $[Ph_3MeAs]_2[CuCl_4]$ and 1·96 B.M. for $[Ph_3MeAs]_2[CuBr_4]$. It is assumed that the distortions of these ions from regular tetrahedral symmetry cause quenching of some of the orbital contribution to the moment.

The new compounds prepared and characterized in this work are listed in Tables 1 and 2. Their magnetic moments show that they contain copper(II); the significance of the exact values will be considered presently. We shall discuss first compounds 1—4 since these are the ones expected to have tetrahedral configurations, as indicated earlier. For compounds 1 and 2 this appears definitely to be the case. These compounds are yellow and red, and, as shown in Table 2, they show no absorption in the red part of the visible spectrum in accord with the earlier theoretical and experimental results summarized above. Their magnetic moments are relatively high (Table 1), although not as high as predicted by theory for truly tetrahedral compounds. However, the fact that the presence of different kinds of ligand atoms, as well as possible distortions, will cause a decrease in the moment means that we may take the observed values as being in satisfactory accord with the presumption of a tetrahedral configuration in these two solid compounds.

TABLE 3. *Molar conductances of the complexes.*

Compound	Solvent	Temp. (c)	Molar conductance (mho) for 10^{-3}M-solution
$[Cu(Ph_3PO)_2Cl_2]$	$MeNO_2$	25·4°	19·8
$[Cu(Ph_3PO)_2Br_2]$	$PhNO_2$	25·8	10·2 [a]
$[Cu(Me_3PO)_4](ClO_4)_2$	$MeNO_2$	23·1	201

[a] Colour of solid compound is dark red; colour of nitrobenzene solution is green.

Comparison of *X*-ray powder patterns of compounds 1 and 2 with those of their nickel(II), cobalt(II), and manganese(II) analogues, all of which seem definitely to be tetrahedral, has not provided any definite evidence concerning the configurations of the copper(II) compounds. Among the bromides, the nickel(II) and manganese(II) compounds are isomorphous, but the cobalt(II) and copper(II) compounds differ from the former two and from each other. Among the chlorides, the manganese(II) and cobalt(II) compounds are isomorphous and the pattern for the copper(II) compound is very similar but not quite identical. This may mean that the copper(II) compound is practically isomorphous but, as in other cases, slightly different because of a flattening of the tetrahedron. If this assumption is correct, then the *X*-ray data afford further evidence for the tetrahedral configuration in $[Cu(Ph_3PO)_2Cl_2]$ but provide no evidence either way in the case of $[Cu(Ph_3PO)_2Br_2]$.

Compounds 1 and 2 do not appear to be entirely stable in solution, even in the ionizing but relatively non-co-ordinating solvents, nitromethane and nitrobenzene. Their molar conductances in these solvents (Table 3) indicate that they are probably non-ionic as solids, as indicated by the manner in which we write their formulæ, but that some solvolytic dissociation does occur. In nitromethane and nitrobenzene, a true 1 : 1 electrolyte would have molar conductances in the ranges 80—100 and 20—30 ohm^{-1} respectively. $[Cu(Ph_3PO)_2Cl_2]$ gives a yellow solution in nitromethane with a spectrum that differs little from the reflectance spectrum of the solid, suggesting that the molecule retains its tetrahedral configuration in this solution. For $[Cu(Ph_3PO)_2Br_2]$ there is evidently considerable, if not total, loss of the tetrahedral configuration upon dissolution in nitromethane, since the red solid gives a green solution the spectrum of which shows prominent absorption bands at 643 and 910 mμ. For the chloride complex, yellow solutions were obtained in certain other solvents as well, *e.g.*, acetonitrile, acetone, ethyl acetate, benzene, toluene, and chlorobenzene, although alcohols gave green solutions. For the bromide complex, however, green solutions were obtained in all solvents used. Evidently the

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[21] Figgis and Harris, *J.*, 1955, 855; M. D. Meyers (M.I.T., 1957), unpublished results.

stability of the tetrahedral configuration in the bromide complex is very low, while for the chloride complex it is much higher.

For the arsine oxide complexes, $[Cu(Ph_3AsO)_2Cl_2]$ and $[Cu(Ph_3AsO)_2Br_2]$, the existence of the tetrahedral configuration is unlikely, especially for the latter. Both of these compounds show absorption in the red part of the spectrum in their reflectance spectra, and for the bromide complex the 680 mμ band appears to be quite strong. Both of these compounds were virtually insoluble in all common solvents tested, so that no investigations of their properties in solution were possible. The magnetic moment of $[Cu(Ph_3AsO)_2Cl_2]$, 1·92 B.M., would be equally consistent with a planar or a distorted tetrahedral configuration. The reason for the low moment, 1·56 B.M., of $[Cu(Ph_3AsO)_2Br_2]$ is not known. The measurement was repeated several times on a specimen giving a good analysis.

TABLE 4. *Infrared absorption spectra.*

	P–O stretching frequency (cm.$^{-1}$)	Shift (cm.$^{-1}$)
Ph_3PO [27]	1195	—
$[Cu(Ph_3PO)_2Cl_2]$	1142	−53
$[Cu(Ph_3PO)_2Br_2]$	1145, 1169	−38 (av)
$Cu(OAc)_2,Ph_3PO$	1168	−27
Me_3PO [27]	1174	—
$[Cu(Me_3PO)_4](ClO_4)_2$	$\leqslant$1125	$\geqslant$−49

	As–O stretching frequency (cm.$^{-1}$)	Shift (cm.$^{-1}$)
Ph_3AsO	880	—
$[Cu(Ph_3AsO)_2Cl_2]$	840	−40
$[Cu(Ph_3AsO)_2Br_2]$	842	−38

Data concerning anions:	Absorption maxima (cm.$^{-1}$)
$[Cu(Me_3PO)_4](ClO_4)_2$	1085 vs. (broad)
Ionic perchlorates [29]	1050—1150vs
$Cu(OAc)_2,Ph_3PO$	1630s, 1435s
$Cu(OAc)_2,H_2O$ [25]	1603 1418

With cupric acetate, triphenylphosphine oxide gives the 1 : 1 complex $Cu(OAc)_2,Ph_3PO$. The spectral data indicate the presence of octahedrally or tetragonally co-ordinated copper(II), and the low magnetic moment, 1·52 B.M., makes it likely that this compound is a dimer, closely related structurally to the previously known dimers of carboxylic acid salts of copper(II), in which the four $R{\cdot}CO_2$ groups form CuOC(R)OCu bridges, with a neutral ligand also co-ordinated to each copper ion.[22,23] Further support for this structure is provided by the appearance of an absorption band ~375 mμ; it appears that such a band is diagnostic for the carboxylate-bridged structure.[23,24] The infrared spectrum also supports the dimeric structure when the positions of the symmetric and the asymmetric carboxylate stretching frequencies (Table 4) are compared to the results of Nakamoto *et al.*[25] It has recently been shown that $[Cu(OAc)_2,C_5H_5N]_2$ has the carboxylate-bridged structure.[26] Evidently, a variety of neutral ligands may occur in this type of structure.

The green-blue complex, $CuCl_2,4(HO{\cdot}CH_2)_3PO$, appears definitely to contain tetragonally co-ordinated copper. Its magnetic moment is consistent with this, while the appearance of a broad asymmetric absorption band with a peak at ~845 mμ provides strong positive evidence. Its insolubility in suitable solvents prevented measurements of molecular weight or electrolytic conductance.

Tetrakis(trimethylphosphine oxide)copper(II) perchlorate was prepared for comparison with the triphenylphosphine oxide analogue previously reported [11] and shown to have an essentially planar CuO_4 grouping with non-linear Cu–O–P chains. In the methyl compound reported here, planarity of the CuO_4 grouping is possible even with little or no bending of the Cu–O–P chains, and the similarity of the spectral and magnetic properties of the copper(II) ions in the two compounds supports the belief that the copper(II) is tetragonally co-ordinated in both.

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[22] van Niekerk and Schoening, *Acta Cryst.*, 1953, **6**, 227.

[23] Martin and Whitley, *J.*, 1958, 1394.

[24] Tsuchida and Yamada, *Nature*, 1955, **176**, 1171; Tsuchida, Yamada, and Nakamura, *ibid.*, 1956, **178**, 1192.

[25] Nakamoto, Fujita, Tanaka, and Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904.

[26] Hanic, Štempelová, and Hanicová, Abs. Supplementary Papers, Fifth Internat. Congr. I.U.C., Cambridge, August, 1960.

Infrared spectra of all compounds were recorded in the rock-salt region and some of the more significant bands are listed in Table 4. It has previously been shown [27,28] that formation of a dative bond from the oxygen atom of an R_3PO or X_3PO molecule to a metal ion causes a significant lowering of the frequency of the infrared band due principally to P–O stretching. As Table 4 shows, the three triphenylphosphine oxide complexes reported here show this effect clearly. A similar effect would be expected for arsine oxide complexes and has been observed. By comparison of the spectra of triphenylarsine and triphenylarsine oxide, it seems evident that the As–O stretching frequency is 880 cm.$^{-1}$. In the two arsine oxide complexes reported here the position of this band is $\sim$40 cm.$^{-1}$ lower.

In $[Cu(Me_3PO)_4](ClO_4)_2$ the P–O band is difficult to identify because the heavy absorption by perchlorate ion obscures the region in which it is expected. We can thus only place an upper limit of $\sim$1125 cm.$^{-1}$ on its frequency. The infrared spectra of tris(hydroxymethyl)phosphine oxide and $CuCl_2,4(HO{\cdot}CH_2)_3PO$ are not easy to interpret with certainty, and the data are not therefore recorded in Table 4. It is not unlikely, however, that broad bands at 1137 cm.$^{-1}$ in tris(hydroxymethyl)phosphine oxide and at 1106 cm.$^{-1}$ in the complex are due to P–O stretching.

In summary, it may be said that the tendency of complexes of the type $[M(Ph_3PO)_2X_2]$, where X is a halogen, to be tetrahedral is observed when M = Cu(II) as well as when M = Ni(II),[6] Co(II),[30] and Mn(II),[8] but that on replacement of triphenylphosphine oxide with triphenylarsine oxide the tetrahedral configuration appears to be lost in the case of copper(II).

EXPERIMENTAL

Trimethylphosphine Oxide and Triphenylarsine Oxide.—These compounds were prepared by methods reported in the literature.[27,31]

Dichlorobis(triphenylphosphine Oxide)copper(II).—A solution of triphenylphosphine oxide (4·88 g., 0·0176 mole) and cupric chloride dihydrate (1·36 g., 0·008 mole) in absolute ethanol (29 ml.) was evaporated, in a partial vacuum over sulphuric acid, until clusters of pale yellow crystals were formed. These were filtered off, washed with a small quantity of cold absolute ethanol, and dried *in vacuo* over sulphuric acid (yield 85%) (Found: C, 62·4; H, 4·5; Cu, 9·2; P, 9·2. $C_{36}H_{30}Cl_2CuO_2P_2$ requires C, 62·6; H, 4·4; Cu, 9·2; P, 9·0%). The *compound* recrystallized from ethyl methyl ketone (3 g. in 17 ml.). It was soluble to form yellow solutions in nitromethane, acetonitrile, or acetone, and also in hot benzene, toluene, chlorobenzene, or ethyl acetate. Green solutions were formed with alcohols, suggesting dissociation and/or rearrangement of the complex. The complex was insoluble in chloroform, carbon tetrachloride, cyclohexane, and light petroleum. When the compound was moistened with absolute ethanol and exposed to the atmosphere it became green-blue on the exposed surface, presumably owing to hydration since the blue colour reverted to yellow in a desiccator. The compound melted at 176° to a dark red melt, which reverted to a yellow solid on cooling.

Dibromobis(triphenylphosphine Oxide)copper(II).—This compound was prepared by the procedure used for the corresponding chloro-complex. The crude, brown product was triturated with ether (2 × 25 ml.) and then recrystallized from ethyl acetate (5·2 g. in 225 ml.). Dark red needles were obtained which were washed first with ethyl acetate, then with dry ether, and dried *in vacuo* (yield 24%); they had m. p. 159·5° (Found: C, 55·4; H, 3·8; Cu, 8·2; P, 8·1. $C_{36}H_{30}Br_2CuO_2P_2$ requires C, 55·4; H, 3·9; Cu, 8·15; P, 7·9%). The *compound* was soluble to form green solutions in acetone, ethyl methyl ketone, acetonitrile, nitromethane, dimethylformamide, dioxan, or propan-2-ol, and in hot benzene and chlorobenzene. It was insoluble in carbon tetrachloride, cyclohexane, and light petroleum and decomposed in chloroform. The complex readily dissolved in alcohols to form yellow or brown solutions.

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[27] Cotton, Barnes, and Bannister, *J.*, 1960, 2199.
[28] Sheldon and Tyree, *J. Amer. Chem. Soc.*, 1958, **80**, 4775.
[29] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.
[30] Holm and Cotton, *J. Chem. Phys.*, 1960, **32**, 1168.
[31] Shriner and Wolf, *Org. Synth.*, 1950, **30**, 97.

Diacetato(triphenylphosphine Oxide)copper(II).—A solution of triphenylphosphine oxide (4·59 g., 0·0165 mole) and cupric acetate monohydrate (1·5 g., 0·0075 mole) in absolute ethanol (85 ml.) yielded green crystals in ~18 hr. The *product* was filtered off, washed with absolute ethanol, and dried *in vacuo* over phosphorus pentoxide (yield 77%), m. p. 238° (Found: C, 56·9; H, 4·7; Cu, 13·85; P, 6·9. $C_{22}H_{21}CuO_5P$ requires C, 57·45; H, 4·6; Cu, 13·8; P, 6·7%). The compound was initially soluble in methylene chloride and in chloroform giving blue solutions, but these rapidly became opalescent with decomposition of the complex. Green solutions were formed in the lower alcohols, but the compound was found to be little soluble in most organic solvents.

Tetrakis(trimethylphosphine Oxide)copper(II) *Perchlorate*.—A solution of trimethylphosphine oxide (2·46 g., 0·027 mole) in hot absolute ethanol (15 ml.) was added to one of cupric perchlorate (2·47 g., 0·0067 mole) also in hot absolute ethanol (10 ml.). The pale blue solid which immediately formed was collected and recrystallized from absolute ethanol (3·35 g. in 150 ml.). The pale blue *product* obtained was filtered off, washed with ethanol and dried, in a drying-pistol, *in vacuo* over phosphorus pentoxide at about 70° (yield 56%; m. p. 240° (Found: C, 22·7; H, 5·7; Cl, 11·0; Cu, 10·0; P, 19·4. $C_{12}H_{36}Cl_2CuO_{12}P_4$ requires C, 22·85; H, 5·75; Cl, 11·2; Cu, 10·1; P, 19·65%). The complex formed blue solutions in water, methanol, nitromethane, acetonitrile, and hot ethanol, but was insoluble in methylene chloride, chloroform, acetone, dioxan, and toluene.

Dichlorotetrakis(trishydroxymethylphosphine Oxide)copper(II).—On cooling a hot solution of trishydroxymethylphosphine oxide (4·2 g., 0·03 mole) and cupric chloride dihydrate (2·56 g., 0·015 mole) in n-butanol (90 ml.) long, very pale, green-blue needles were formed. These were filtered off, washed first with n-butanol, then absolute ethanol and dried *in vacuo* over phosphorus pentoxide (yield 74%, based on phosphine oxide; m. p. 126°) (Found: C, 21·5; H, 5·3; Cu, 9·1; P, 18·15. $C_{12}H_{36}Cl_2CuO_{16}P_4$ requires C, 20·7; H, 5·2; Cu, 9·1; P, 17·8%). The *compound* was soluble in water and somewhat soluble in the lower alcohols, but insoluble in all other common solvents tried.

Complex of Cupric Bromide with Trishydroxymethylphosphine Oxide.—A pale blue-green crystalline complex of trishydroxymethylphosphine oxide with cupric bromide was obtained by a method analogous to that used for the chloro-complex. However analyses were unsatisfactory and the compound decomposed in a few days after isolation.

Dichlorobis(triphenylarsine Oxide)copper(II).—A solution of triphenylarsine oxide (3·22 g., 0·01 mole) in absolute ethanol (14 ml.) was added to one of cupric chloride dihydrate (0·86 g., 0·005 mole) also in absolute ethanol (6 ml.). The yellow solid which was immediately formed was filtered off and recrystallized, first, from absolute ethanol and then from chlorobenzene. The yellow-brown product was washed with chlorobenzene, then benzene and dried *in vacuo* (yield 37%; m. p. 187°) (Found: C, 55·8; H, 3·9; As, 19·0. $C_{36}H_{30}As_2Cl_2CuO_2$ requires C, 55·5; H, 3·9; As, 19·2%). The *compound* was soluble to form greenish-yellow solutions in methylene chloride, chloroform, and dimethylformamide and in hot alcohols and chlorobenzene. It was insoluble in all other common solvents.

Dibromobis(triphenylarsine Oxide)copper(II).—This dark olive-green *complex* was prepared analogously to the chloro-complex in 73% yield, with m. p. 241° (Found: C, 50·6; H, 3·5; As, 17·45; Cu, 7·6. $C_{36}H_{30}As_2Br_2CuO_2$ requires C, 49·8; H, 3·5; As, 17·3; Cu, 7·3%). When first filtered from the ethanolic reaction mixture the compound was dark purple but changed to dark olive-green on drying. Attempts to obtain a dry, purple form of the compound were unsuccessful. The compound was soluble in hot alcohols, chlorobenzene, ethyl methyl ketone, and dimethylformamide, but insoluble in other organic solvents.

Electrolytic Conductance Measurements.—These were made with a Serfass bridge and a conventional cell, previously calibrated with aqueous potassium chloride. The results are shown in Table 3. The remaining complexes were too insoluble in, or were decomposed by, nitrobenzene and nitromethane.

Magnetic Measurements.—Magnetic-susceptibility measurements were made at room temperature by the Gouy method as previously described.[30] Mohr's salt and copper sulphate pentahydrate were used to calibrate the Gouy tube. Duplicate determinations were carried out for each compound, over a range of field strengths. The diamagnetic corrections were calculated by using Pascal's constants and previously reported values for the phosphine and arsine oxides.[11,32] The results are shown in Table 1.

[32] Foex, " Constants Selectionées Diamagnetisme et Paramagnetisme," Masson et Cie., Paris, 1957.

Infrared Absorption Spectra.—These were obtained with a Perkin-Elmer model 21 spectrophotometer, fitted with a rock-salt prism. Nujol mulls were used. The relevant data from the spectra are shown in Table 4, together with reference data from the literature.

Electronic Spectra.—The reflectance spectra of the solid compounds were measured by using a Beckman DU spectrophotometer with the standard Beckman reflectance accessory and magnesium carbonate as the reference sample. The solution spectra of the compounds $[Cu(Ph_3PO)_2Br_2]$ and $Cu(CH_3{\cdot}CO_2)_2,Ph_3PO$ were obtained with a Cary 11MS recording spectrophotometer; the solution spectrum of $[Cu(Ph_3PO)_2Cl_2]$ was obtained with a Beckman DU spectrophotometer. The results are shown in Table 2.

X-*Ray Powder Diagrams.*—These were obtained for us by Miss R. Babineau of Arthur D. Little Co., to whom we express our appreciation.

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