Synthesis and Solid-state Crystal Structure of [2-(Diphenylphosphinoyl)-ethyl]diethylammonium Dichlorocuprate(I), containing a Discrete $CuCl_2^-$ Anion [1]

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[2-(Diphenylphosphino)ethyl]diethylamine, reacts with copper(II) chloride in ethanol or tetrahydrofuran to yield either [2-(diphenylphosphinoyl)ethyl]diethylammonium dichlorocuprate(I) (IV), or [2-(diphenylphosphino)ethyl]-diethylammonium dichlorocuprate(I) (III). Compound (IV) has been characterized by measurements of conductivity, magnetic susceptibility, and i.r. and u.v. spectra. Water in the solvents is apparently the source of both the proton and the oxygen atom required for formation of (IV). A three-dimensional *X*-ray structural analysis of (IV) was also undertaken. Crystals from either solvent are monoclinic, space group $P2_1/c$, $a = 12{\cdot}54(1)$, $b = 9{\cdot}119(8)$, $c = 21{\cdot}73(1)$ Å, $\beta = 123{\cdot}10\ (5)°$, and $Z = 4$. The structure was solved by a combination of the symbolic-addition and heavy-atom procedures and refined by least squares to R 11·0% for 2661 visually estimated observed reflections. The structure consists of discrete cations and $[CuCl_2^-]$ anions whose closest approach is Cu ··· O 3·74 Å; the anion is near-linear, Cu–Cl 2·090(5) Å, Cl–Cu–Cl 175·8(2)°.

THERE has been considerable interest in the co-ordinating ability of so-called ' mixed ' or ' hybrid ' Group V and VI multidentate ligands,[2] mostly in connection with factors dictating the stabilization of high- and/or low-spin five-co-ordinate complexes of the metal ions of the transition series. During our studies on the ligating properties of some simple ' mixed ' nitrogen–phosphorus bidentate ligands we investigated the reactions of $R_2N{\cdot}[CH_2]{\cdot}PPh_2$ (R = H, Me, or Et) with copper(II) halides, in order to ascertain whether or not the Cu^{2+} ion could be stabilized in the presence of a tertiary phosphine, even though it has been well documented that the reaction of tertiary phosphines with Cu^{II} halides invariably led to either Cu^{I}–tertiary phosphine complexes [3] or Cu^{II} complexes of the oxide of the parent phosphine.[4] Because of the presence of an amino-group in the ligand it was expected that this ' hard ' base would lend some additional stability to the resultant complex thereby preventing oxidation of the phosphine and/or reduction of the copper(II).

In fact, the reaction of copper(II) chloride with [2-(diphenylphosphino)ethyl]diethylamine (I) in ethanol or tetrahydrofuran does not yield a copper(II) complex of the parent ligand, but rather (IV) the dichlorocuprate(I) salt of the [2-(diphenylphosphinoyl)ethyl]diethylammonium cation, $\{Ph_2P(O){\cdot}[CH]_2{\cdot}N(H)Et_2\}^+CuCl_2^-$. In this unique reaction, simultaneous oxidation of the tertiary phosphine to the phosphine oxide, reduction of the Cu^{II} to Cu^{I}, and protonation of the tertiary amine takes place. Since there appears to be no precedent for this behaviour, we report the synthesis, and molecular and

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[3] W. E. Hatfield and R. Whyman, in 'Transition-Metal Chemistry,' ed. R. C. Carlin, Marcel Dekker, New York, 1969, vol. 5, pp. 47—179, and refs. therein.

[4] K. Issleib and H. Zimmermann, *Z. anorg. Chem.*, 1967, **353**, 197.

crystal structure of this compound. Preliminary reports have appeared.[5,6]

$Ph_2P\cdot[CH_2]_2\cdot NEt_2$ (I) $Ph_2P(O)\cdot[CH_2]_2\cdot NEt_2$ (II)

$\{Ph_2P\cdot[CH_2]_2\cdot N(H)Et_2\}[CuCl_2]$
(III)

$\{Ph_2P(O)\cdot[CH_2]_2\cdot N(H)Et_2\}[X]$
(IV; $X = CuCl_2$)
(V; $X = Cl$)

EXPERIMENTAL

Reagents and Chemicals.—Commercially available reagent-grade chemicals were used. Tetrahydrofuran was distilled from $LiAlH_4$ and stored over predried 5 Å molecular sieves. Spectral quality nitromethane and acetonitrile which had been stored over molecular sieves (5 Å) were used in conductivity studies. Reagent-grade absolute ethanol, for chemical investigations, was rigorously dried over preconditioned 3 Å molecular sieves according to the published procedure.[7] Extra-high-purity nitrogen and oxygen were used in all synthetic procedures. Copper(I) chloride was prepared by a standard method.[8] Copper(II) chloride was obtained by thermal dehydration of reagent-grade $CuCl_2,2H_2O$ *in vacuo*.

Carbon, hydrogen, and nitrogen analyses were determined on a Perkin-Elmer 240 elemental analyser, chloride and oxygen analyses were made commercially, and copper analysis used *X*-ray fluorescence techniques.[9]

Syntheses.—Compound (I) was prepared as described in refs. 10 and 11.

$Ph_2P(O)\cdot CH_2]_2\cdot NEt_2$, (II), was prepared by a modification of the procedure of ref. 10. Potassium iodide crystals were placed in a solution of (I) (5·2 g) in diethyl ether (20 ml), and the solution cooled in an ice bath while H_2O_2 (30% aqueous solution) was added dropwise until the iodine colour persisted. Solvent was removed by evaporation and the oily residue treated with aqueous 1M-NaOH when the reddish brown colour was dispelled and (II) separated as a viscous oil. It was washed several times with NaOH solution, extracted into dry ether, and subsequently dried (anhydrous Na_2SO_4). Ether was removed by distillation under reduced pressure to give (II) (4·4 g, 80%), which was used without further purification.

Compound (V) was prepared by dissolving crude (II) in ethanol and adding a stoicheiometric amount of anhydrous HCl. The product was isolated quantitatively as a pale yellow powder after complete removal of solvent; it was used without further purification.

Preparation of Compound (IV).—Compound (IV) was prepared by a number of different routes.

(i) A solution of $CuCl_2,2H_2O$ (1·71 g, 18 mmol) in tetrahydrofuran (30 ml) and (I) (1·43 g, 5 mmol) was heated under reflux for 5 min. During cooling for 4 h pale yellow needles of the product were deposited, and were washed with cold ethanol, and air dried [0·69 g, 31% based (I)], m.p. (decomp.) 170 °C [Found: C, 49·4; H, 5·7; Cl, 16·05; Cu, 14·55; N, 3·15; O, 3·45. $C_{18}H_{25}Cl_2CuNOP$ requires C, 49·6; H, 5·55; Cl, 16·25; Cu, 14·6; N, 3·2; O, 3·65%].

(ii) A hot solution of anhydrous $CuCl_2$ (1·23 g, 9 mmol) in absolute ethanol (15 ml) was added to a hot solution of (I) (0·80 g, 3 mmol) in ethanol (15 ml). Work-up as before yielded (IV) [38%, based on (I)].

(iii) The identical complex can also be prepared by oxidation of (III) (*vide infra*). (III) (1 g) was dissolved in methanol and oxygen bubbled through this solution for 90 min. The resultant greenish brown solution was filtered and concentrated under vacuum. The gummy yellow residue was dissolved in methyl ethyl ketone and a yellow powder obtained by reduction of solvent volume. The i.r. spectrum of this powder was identical in all respects with that of an authentic sample of (IV) prepared as in (i).

(iv) A slurry of CuCl (1·0 g, 10 mmol) in benzene (50 ml) was added to a solution of (V) (3·37 g, 10 mmol) in ethanol (50 ml). The mixture was heated and the clear solution obtained was filtered hot. Upon cooling a small quantity of (IV) was obtained, having an i.r. spectrum identical with that of an authentic sample.

Preparation of Compound (III).—When an excess of (I) was used the product obtained in (i)—(iv) did not contain oxygen. In a typical preparation (I) (2·85 g, 10 mmol) was dissolved in tetrahydrofuran (10 ml) and a solution of $CuCl_2$ (0·68 g, 10 mmol) in tetrahydrofuran (35 ml) was added. The mixture was heated under reflux. A white solid was precipitated when the colourless clear solution was cooled. The product was washed several times with tetrahydrofuran, and dried *in vacuo*; m.p. (decomp.) 176 °C (Found: C, 51·5; H, 3·50; N, 6·05; O, 0·00. $C_{18}H_{25}Cl_2CuNP$ requires C, 51·35; H, 3·35; N, 6·0%).

Experiments Designed to Determine the Source of Oxygen and Hydrogen in the Synthesis of (IV).—(*a*) Carefully dried $CuCl_2$ (1·24 g, 10 mmol) was dissolved in molecular sieve-dried ethanol (15 ml) doped with 1% by weight D_2O (99·5% D). A solution of (I) (0·80 g, 2·8 mmol) in dried ethanol (15 ml) was added and the mixture worked up as in (i). A solid-state (KBr pellet) i.r. spectrum indicated the product to be the deuteriated compound $\{Ph_2P(O)\cdot[CH_2]_2\cdot N(D)Et_2\}[CuCl_2]$ (see later).

(*b*) In a dry box, thoroughly flushed with extra-dry nitrogen, anhydrous $CuCl_2$ (1·23 g, 9·2 mmol) was dissolved in dry ethanol (30 ml) and (I) (0·80 g, 2·8 mmol) was added. After heating under reflux for 5 min the solution was allowed to cool and sealed before removal from the dry box. The olive-green coloured solution was set aside for 48 h, during which time a minute amount of white powder was deposited but the formation of (IV) was not observed. The seal was then broken and one drop of water added. Within 15 min a copious quantity of needles were deposited in the flask; the washed and dried crystals had i.r. spectrum identical with that of authentic (IV).

(*c*) In a separate experiment the dry box was flushed and then filled with extra-high-purity oxygen which had been previously scrubbed with concentrated sulphuric acid to remove residual traces of moisture. In this atmosphere anhydrous $CuCl_2$ (1·23 g, 9·2 mmol) was dissolved in molecular-sieve-dried ethanol (30 ml). (I) (0·80 g, 2·8 mmol) was added and the resultant solution heated under reflux for 5 min. After cooling, the flask was sealed and removed from the dry box. The olive-green solution

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(containing a minute amount of white powder) was set aside for 3 months during which time no crystal formation was detected. The seal was then broken, a drop of water added, and within 10 min pale yellow needles had separated. These had i.r. spectrum identical with that of (IV).

A subsequent analysis of the white powder obtained in these control experiments closely approximated to that required for CuCl.

Conductivity, Magnetic, and Spectral Data.—Conductance measurements were taken on a YSI 31 conductance bridge employing a conductivity cell with cell constant k 0·1792 cm^{-1}. Concentration-dependent conductivity measurements were carried out for (III) and (IV). (IV) Is a 1 : 1 electrolyte in acetonitrile and nitromethane, whereas (III) apparently decomposes in these solvents.

Magnetic susceptibility measurements were recorded for powdered samples using the Faraday method with $Hg[Co(SCN)_4]$ as calibrant.

I.r. spectra were initially recorded on a Perkin-Elmer 257 spectrophotometer. The ν(P=O) region was examined on a Perkin-Elmer 621 grating i.r. spectrophotometer, calibrated with polystyrene; far-i.r. spectra were obtained on a Beckman IR 11. U.v. and visible spectra were recorded on a Perkin-Elmer 202 spectrophotometer.

X-Ray Crystal Data for (IV).—$C_{18}H_{25}Cl_2CuNOP$, $M =$ 436·82, Monoclinic, $a =$ 12·54(1), $b =$ 9·119(8), $c =$ 21·73(1) Å, $\beta =$ 123·10(5)°, $U =$ 2081·62 Å^3, $D_m =$ 1·37, $Z = 4$, $D_c =$ 1·39. Space group $P2_1/c$ from systematic absences: $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$. Cu-K_α radiation, $\lambda =$ 1·5418 Å; μ(Cu-K_α) = 14·75 cm^{-1}.

Data Collection.—A single needle was selected from the batch which had been subjected to elemental analysis. It was trimmed along the axis of elongation to give a crystal *ca.* 0·15 × 0·15 × 0·90 mm, which was mounted in a sealed glass capillary. Preliminary precession film data recorded on a 60 mm radius Buerger precession camera with zirconium-filtered Mo-K_α ($\lambda =$ 0·7107 Å) radiation enabled determination of space group and unit-cell dimensions.[12]

Three-dimensional intensity data were recorded by the multiple film equi-inclination Weissenberg technique with nickel-filtered Cu-K_α radiation for the layers $h0$—$7l$. Diffraction maxima were estimated visually with the aid of a calibrated strip. The eight levels were correlated and corrected for Lorentz and polarization effects.[13] In all, 2661 unique non-zero reflections were recorded and used in the subsequent refinement. No absorption corrections were applied.

Structure Determination.—Initial attempts to locate the copper atom from the three-dimensional Patterson map [14] were unsuccessful. The symbolic-addition method for centrosymmetric space groups was then applied.[15] Program FAME [16] was employed to compute normalized structure factors (E values). Experimental and theoretical values for the functions of E did not definitively indicate a centric space group, however, systematic absences uniquely determined the space group as $P2_1/c$. A Σ_2 list was calculated and symbols assigned to six of the largest E values having the greatest number of Σ_2 interactions; these were used as the basis set. Reflections for which $|E| >$ 1·50 were arranged in descending order of magnitude in order to apply the Σ_2 formula.[15] The ordering was computed by use of the program MAGIC.[16] Starting with the six known signs, MAGIC calculated signs for 14 new reflections in the first iteration with a probability >0·9900. After fifteen iterations a total of 308 reflections with known signs were obtained, and from the E map calculated from these, the linear dichlorocuprate anion was readily discernible, as was the phosphorus atom of the organic cation. At this stage it was impossible to separate most of the carbon, nitrogen, and oxygen atomic positions from the spurious peaks in the initial E map. The structural analysis then followed the heavy-atom procedure.[17]

A structure-factor calculation [18] using the copper, two chlorines, and the phosphorus atomic positions obtained from the E map yielded an R 0·449. The resulting Fourier synthesis [14] calculated from the previous structure factors showed the atomic positions for all but four carbon atoms of the remaining non-hydrogen atoms. A structure-factor calculation based on these positions yielded R 0·329. A subsequent Fourier synthesis revealed all non-hydrogen atomic positions. The structure-factor calculation of these unrefined atomic co-ordinates gave R 0·278. Variation of all atomic positional parameters and isotropic temperature factors in a five-cycle full-matrix least-squares refinement,[19] all reflections being given equal weight, reduced R to 0·144. Finally, a five-cycle full-matrix least-squares refinement of all atomic positional parameters, anisotropic temperature factors for copper, chlorine, and phosphorus, and isotropic temperature factors for oxygen, nitrogen, and all carbon atoms yielded R 0·110 for the 2661 unique non-zero reflections.* Final positional and thermal parameters of all non-hydrogen atoms are given in Table 1. Atomic scattering curves were taken from ref. 20.

RESULTS AND DISCUSSION

Both (III) and (IV) have been characterized by conductivity measurements, magnetic susceptibility studies, and i.r. and u.v. spectral data. Data obtained from the concentration-dependent conductivity studies for both nitromethane and acetonitrile solutions has been treated according to the method outlined in ref. 21 but non-linear plots were obtained for both compounds. This behaviour may be attributed to the rapid rate of decomposition for both compounds, especially (III), in these two co-ordinating solvents. However, measurements of freshly prepared solutions of (IV) (*ca.* 10^{-3}M) in both nitromethane and acetonitrile yield values which are consistent with its formulation as a 1 : 1 electrolyte

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* Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20867 (20 pp., 1 microfiche). See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[12] 'International Tables for *X*-Ray Crystallography, vol. 1, Kynoch Press, Birmingham, 1952, pp. 89, 99.

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[17] J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 1937, 219.

[18] Program STRFAC for structure-factor calculations, abstracted from the U.C.L.A. Least-squares Structure-factor Program, by I. E. Paul, University of Illinois, modified by M. G. Newton.

[19] Program LSSF from P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, modified by M. G. Newton.

[20] Ref. 12, vol. III, 1962, pp. 201—212.

[21] R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 1964, 4587.

(Λ_m 94 in $MeNO_2$ and 167 cm^2 ohm^{-1} mol^{-1} in MeCN; accepted values for 1 : 1 electrolytes in these solvents are 91 and 159 cm^2 ohm^{-1} mol^{-1}).[22] Values for the molar conductivities for (III) were inconclusive in both solvents.

TABLE 1

Positional and thermal parameters for (IV), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	$B/Å^2$
Cu	0·8073(2)	0·2222(2)	0·7963(1)	*b*
Cl(1)	0·7601(3)	0·3625(4)	0·7086(2)	*b*
Cl(2)	0·8608(4)	0·0954(5)	0·8888(2)	*b*
P	0·2170(2)	0·1545(3)	0·3376(1)	*b*
O	0·1600(7)	0·0118(8)	0·3341(4)	4·5(1)
N	−0·0510(7)	0·3017(9)	0·1314(4)	3·5(2)
C(1)	0·1048(8)	0·2770(11)	0·2669(5)	3·3(2)
C(2)	0·0356(9)	0·1971(12)	0·1926(5)	3·9(2)
C(3)	−0·1460(11)	0·2084(14)	0·0647(6)	5·1(2)
C(4)	0·0191(10)	0·4175(13)	0·1152(6)	4·8(2)
C(5)	0·3491(9)	0·1346(12)	0·3270(5)	3·5(2)
C(6)	0·3962(11)	0·2570(14)	0·3096(6)	5·0(2)
C(7)	0·5041(13)	0·2321(16)	0·3031(7)	6·3(3)
C(8)	0·5577(13)	0·0986(16)	0·3155(7)	6·4(3)
C(9)	0·5128(12)	0·9795(15)	0·3362(7)	5·9(3)
C(10)	0·4064(10)	0·9975(13)	0·3414(6)	4·4(2)
C(11)	0·2717(10)	0·2484(12)	0·4216(5)	4·1(2)
C(12)	0·4030(12)	0·2785(16)	0·4712(7)	6·0(3)
C(13)	0·4402(16)	0·3504(19)	0·5388(9)	8·1(4)
C(14)	0·3516(15)	0·3938(18)	0·5541(8)	7·3(4)
C(15)	0·2254(14)	0·3622(16)	0·5058(8)	6·5(3)
C(16)	0·1847(11)	0·2932(14)	0·4393(6)	4·9(2)
C(17)	−0·2494(14)	0·3086(18)	0·0052(8)	7·3(3)
C(18)	0·0976(14)	0·3494(17)	0·0878(8)	7·1(3)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	117(2)	183(3)	47·3(7)	12(4)	77(2)	2(2)
Cl(1)	129(4)	133(5)	44(1)	−47(7)	49(3)	1(4)
Cl(2)	178(5)	261(8)	46(1)	67(9)	124(4)	36(5)
P	63(2)	79(4)	25·0(8)	−5(4)	41(2)	10(3)

[a] Anisotropic temperature factors were employed for these atoms in the form: $\exp[-(\beta_{11}h_2 + \beta_{22}k_2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, with parameters (× 104) as follows.

As expected, magnetic susceptibility studies on powdered samples of both compounds confirm the presence of diamagnetic copper(I). If either compound is exposed to air for extended periods of time, a gradual change in colour from white to amber is observed. Subsequent susceptibility measurements on these air exposed samples exhibit small but definite paramagnetism. In fact, samples from the initial synthesis of both compounds showed slight paramagnetic behaviour. Presumably this paramagnetism results from the air oxidation of Cu^I to Cu^{II} on the surface of the powder.

The presence of the phosphoryl group in (IV) and its absence in (III) has been confirmed from examination of the u.v. spectra. Jaffe and Orchin [23] have demonstrated the usefulness of u.v. spectra in detecting the presence or absence of the phosphoryl group when the phosphorus atom is also bonded to at least one phenyl ring. In such cases, the presence of the unshared electron pair on the phosphorus(III) atom is responsible for considerable perturbation of the benzene spectrum. Thus the spectra of all phenyl derivatives of P^{III} show a single major absorption band which cannot be clearly assigned the ^1L_a or ^1L_b (Platt's notation) band of benzene. In accord with this fact, both (I) and (III) exhibit an absorption band at 250 nm, as well as a second, but much weaker, absorption at 218 nm (Figure 1). On the other hand, the u.v. spectra of phenyl derivatives of phosphoryl compounds are strikingly different from their P^{III} counterparts. The absence of the electron pair on the P^V atom produces very little change in the benzenoid spectrum. In fact, it is always possible to recognize the forbidden ^1L_b band by its characteristic vibrational fine structure. Furthermore, bathochromic shifts of both ^1L_a and ^1L_b are readily detected. Accordingly, the spectra of (IV), (II), and dichlorobis(triphenylphosphine oxide)copper(II) [24] clearly exhibit these effects (Figure 1). The molar extinction coefficients of the ^1L_a and ^1L_b bands in (IV) are 7500 and 2500 l mol^{-1} cm^{-1} respectively.

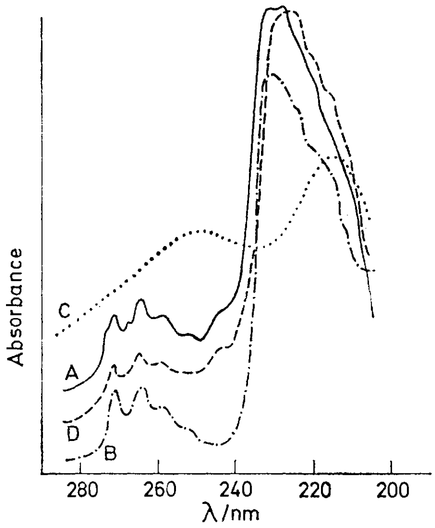

FIGURE 1 U.v. spectra for ethanol solutions of A, (IV); B, $[Ph_3P(O)]_2CuCl_2$; C, (I); and D, (II)

The solid-state i.r. spectrum (KBr pellet) of (IV) provides additional evidence for the presence of the phosphoryl group. An intense absorption occurs at 1165 cm^{-1} which is absent in that of the parent ligand (I), and in (III). This band has been assigned to the ν(P–O) stretching mode, and occurs at 1183 cm^{-1} in the i.r. spectrum of (V).

Evidence for the protonation of the amino-group in both dichlorocuprate(I) salts has been established by i.r. spectroscopy. In the non-protonated ligands (I) and (II), a strong broad absorption occurs at 2800 cm^{-1}, characteristic of tertiary amines.[25] Upon protonation of the tertiary amine the band at 2800 cm^{-1} disappears

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[22] W. G. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

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[24] D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 1961, 2298.

[25] P. Sanvageau and C. Sandorfy, *Canad. J. Chem.*, 1960, **38**, 1901 and refs. therein.

and a new broad absorption band emerges at lower-energy (2500—2750 cm^{-1}), assigned to a stretching mode of the $R_3\overset{+}{N}H$ group.[25] The other band of interest in the i.r. spectrum of (IV) is the antisymmetric ν(Cu–Cl) stretching mode of the linear dichlorocuprate(I) anion, assigned to an intense absorption at 408 cm^{-1}. This assignment is based on previous results of a far-i.r. study of tetrakis(diphenylmethylarsine oxide)copper(II) dichlorocuprate(I), $[(Ph_2MeAsO)_4Cu][CuCl_4]$,[26] where an intense absorption due to this same mode was observed at 410 cm^{-1}. All attempts to locate the totally symmetric Raman-active Cu–Cl stretching mode by use of a laser Raman spectrometer were unsuccessful because of rapid decomposition of the sample in the laser beam.

Several experiments were designed in an attempt to ascertain the source of oxygen and of the proton in the formation of (IV). There are three possible sources of oxygen: atmospheric, traces of moisture in solvents and reagents, and from the oxygenated solvents. We had shown previously that reaction of cobalt(II) halides with the same parent ligand, gave zwitterionic cobalt(II) complexes in which the amino-group was protonated.[27] Our subsequent studies [28] have shown conclusively that the source of protons in these reactions is from trace amounts of water in the ethanol solvent. These results strongly suggested that in the present case the most probable source of both oxygen and proton was again from trace quantities of moisture. Our results support, but do not conclusively prove, this hypothesis. (1) Addition of D_2O to the reaction mixture produces the deuteriated species $\{Ph_2P(O)\cdot[CH_2]_2\cdot N(D)Et_2\}$-$[CuCl_2^-]$, as shown by the replacement of the intense i.r. absorption at *ca.* 2700 cm^{-1}, which had been assigned to a stretching mode of the $R_3\overset{+}{N}H$ moiety, by an absorption at 2100 cm^{-1}, a shift in frequency which is expected upon replacing the proton by the deuteron. Deuteriation occurs in both ethanol and tetrahydrofuran, which would seem to negate the argument that the solvent is the proton source. Even though deuterium could rapidly exchange with the OH proton in ethanol, thereby preventing any definitive conclusion about the source of the proton in this solvent, the fact that the same results are obtained in tetrahydrofuran where deuterium–hydrogen exchange is diminishingly slow strongly suggests that trace amounts of water are the source of the proton also. (2) In experiments in which water was rigorously excluded, (IV) could not be obtained even in pure oxygen. Only subsequent addition of water enabled isolation of the complex.

The isolation of (III), which is formed only when the ligand is present in excess (see Experimental section), apparently also involves water as the proton source, but this system has not been investigated extensively.

In spite of the foregoing evidence the structure of (IV) was not definitely established, since simple dihalogenocuprate(I) salts may possess a variety of stereochemistries.[29] Furthermore, the relatively small decrease in ν(P–O) from (II) to (IV) ($\Delta\nu$ 18 cm^{-1}) did not establish whether or not the phosphoryl moiety was bonded to the Cu$^{\mathrm{I}}$ atom, and the *X*-ray diffraction study was therefore undertaken.

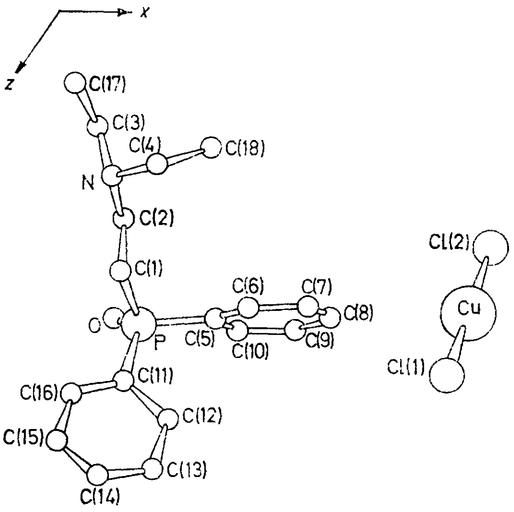

FIGURE 2 One formula unit of (IV)

TABLE 2

Bond lengths (Å) with estimated standard deviations in parentheses

Cu–Cl(1)	2·095(4)	C(5)–C(6)	1·41(2)
Cu–Cl(2)	2·086(5)	C(6)–C(7)	1·45(2)
P–O	1·466(8)	C(7)–C(8)	1·34(2)
P–C(1)	1·80(1)	C(8)–C(9)	1·41(2)
P–C(5)	1·80(1)	C(9)–C(10)	1·41(2)
P–C(11)	1·78(1)	C(10)–C(5)	1·39(2)
C(1)–C(2)	1·54(2)	C(11)–C(12)	1·42(2)
N–C(2)	1·51(1)	C(12)–C(13)	1·44(2)
N–C(3)	1·54(2)	C(13)–C(14)	1·38(3)
N–C(4)	1·53(2)	C(14)–C(15)	1·37(2)
C(3)–C(17)	1·54(2)	C(15)–C(16)	1·39(2)
C(4)–C(18)	1·53(2)	C(16)–C(11)	1·40(2)

Description of Crystal Structure (IV).—The molecular structure consists of an organic cation and the dichlorocuprate(I) anion and is shown in Figure 2 which also shows the atom numbering system used in the analysis. Interatomic bond distances and angles are given in Tables 2 and 3. The most important single feature of this structure is the linear and discrete dichlorocuprate(I) anion. Although this anion had been reported to exist in solution,[30] its solid-state structure had not been previously established until, simultaneously with our preliminary reports,[5,6] Trotter *et al.* reported [31] the structure of chloro[dodeca(dimethylamino)cyclohexaphosphazene-*NNNN*]copper(II) dichlorocuprate(I),

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[28] R. A. Kolodny, T. L. Morris, R. C. Taylor, *J.C.S. Dalton*, 1973, 328.

[29] R. Colton and J. H. Canterford, 'Halides of the Transition Elements, Halides of the First-row Transition Metals,' Wiley, London, 1969, ch. 9.

[30] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Interscience, New York, 1st edn., 1962, p. 750.

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$[N_6P_6(NMe_2)_{12}Cu^{II}Cl]^+[CuCl_2^-]$. They found Cu–Cl 2·11(1) Å, after correction for thermal libration, and a Cl–Cu–Cl 180·0° (the anion was located on a C_2 axis). In (IV) mean Cu–Cl is 2·090(5) Å, with Cl–Cu–Cl 175·8(2)°. These distances are somewhat shorter than that in CuCl itself (2·16 ± 0·015 Å), which has a trimeric structure with Cl–Cu–Cl *ca.* 150°. The sum of the covalent radii[32] of chlorine (0·99 Å) and of copper(I) (1·18 Å) is 2·17 Å, which is somewhat greater than that found either by us or by Trotter. This suggests some multiple-bond character between the copper(I) and chlorine atoms. The linear array of atoms would maximize this effect. The structures of related linear anions such as $AgCl_2^-$, $AuCl_2^-$, and $AuBr_2^-$ all exhibit this shortening of the M–X bond length relative to the sum of the covalent radii.[33,34]

TABLE 3

Bond angles (°), with estimated standard deviations in parentheses

Cl(1)–Cu–Cl(2)	175·8(2)	P–C(5)–C(10)	117(1)
O–P–C(1)	112·0(5)	C(10)–C(5)–C(6)	122(1)
O–P–C(5)	111·1(5)	C(5)–C(6)–C(7)	117(1)
O–P–C(11)	112·6(5)	C(6)–C(7)–C(8)	121(1)
C(1)–P–C(5)	107·4(5)	C(7)–C(8)–C(9)	121(1)
C(1)–P–C(11)	105·1(5)	C(8)–C(9)–C(10)	120(1)
C(5)–P–C(11)	108·2(5)	C(9)–C(10)–C(5)	119(1)
P–C(1)–C(2)	109·4(7)	P–C(11)–C(12)	121(1)
N–C(2)–C(1)	110·4(8)	P–C(11)–C(16)	120(1)
C(2)–N–C(3)	107·2(8)	C(16)–C(11)–C(12)	119(1)
C(2)–N–C(4)	114·3(9)	C(11)–C(12)–C(13)	117(1)
C(3)–N–C(4)	114·4(9)	C(12)–C(13)–C(14)	122(2)
N–C(3)–C(17)	109(1)	C(13)–C(14)–C(15)	120(2)
N–C(4)–C(18)	112(1)	C(14)–C(15)–C(16)	120(2)
P–C(5)–C(6)	120(1)	C(15)–C(16)–C(11)	121(1)

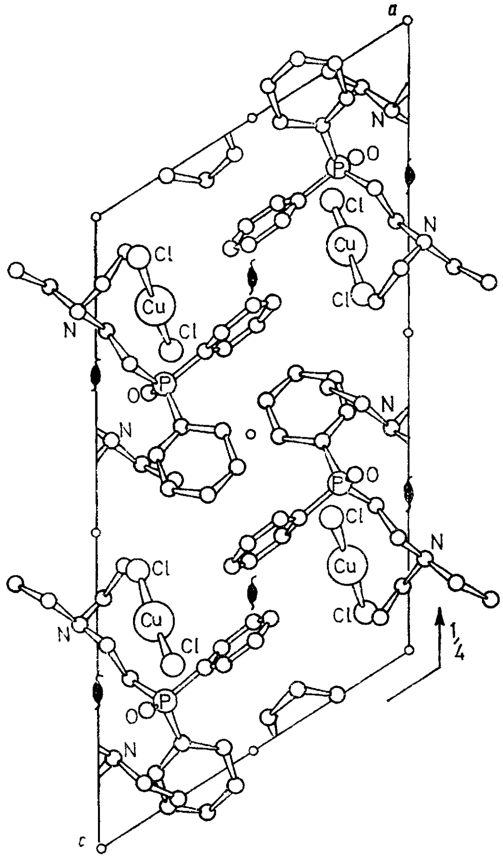

FIGURE 3 The packing of the unit cell in (IV), along the *ac* plane

As is evident from the structure of the unit cell (Figure 3), the diphenylphosphinoyl group is not co-ordinated to the anion. There appears to be nothing unusual about the structure of the cation. The P–O bond length [1·466(8) Å] is quite close to that found in trimethylphosphine oxide (1·48 Å).[35] Since no hydrogen atoms were located there is no direct evidence from the *X*-ray study for the protonation of the amine. The C–C bond distances in both phenyl rings range from 1·34(2) to 1·45(2) Å, however, the mean C–C distance [1·40(2) Å] is close to the commonly accepted value (1·39 Å). Distances of the phosphorus atom and the phenyl carbon atoms from the least-squares planes calculated[36] for each of the phenyl rings are shown in Table 4. The dihedral angles[37] for various segments of the cation are listed in Table 5. A nearly planar system with a dihedral angle of 169·5° has been found for the P–C(1)–C(2)–N grouping.

TABLE 4

Distances (Å) of atoms from least-squares planes. Equations of planes are in the form $PX + QY + RZ = S$, where X, Y, and Z are orthogonal co-ordinates in Å

Plane (I): C(5)–(10)

$$0{\cdot}1026X + 0{\cdot}2327Y + 0{\cdot}9671Z = 6{\cdot}111$$

C(5) − 0·017, C(6) 0·018, C(7) − 0·003, C(8) − 0·014, C(9) 0·015, C(10) 0·001, P 0·028

Plane (II): C(11)–(16)

$$0{\cdot}1575X + 0{\cdot}8836Y - 0{\cdot}4410Z = -1{\cdot}630$$

C(11) − 0·005, C(12) 0·006, C(13) − 0·011, C(14) 0·013, C(15) − 0·013, C(16) 0·009, P 0·038

TABLE 5

Dihedral angles (°)

O–P–C(1)–C(2)	40·2	C(3)–N–C(4)–C(18)	45·6
O–P–C(5)–C(6)	157·0	C(4)–N–C(3)–C(17)	63·6
O–P–C(11)–C(16)	29·3	C(1)–P–C(10)–C(6)	75·5
P–C(1)–C(2)–N	169·5	C(1)–P–C(16)–C(12)	130·8
C(1)–C(2)–N–C(3)	163·2	C(5)–P–C(1)–C(2)	105·0
C(1)–C(2)–N–C(4)	46·6	C(11)–P–C(1)–C(2)	167·3
C(2)–N–C(3)–C(17)	164·4	C(5)–P–C(11)–C(12)	3·7
C(2)–N–C(4)–C(18)	98·5	C(11)–P–C(5)–C(6)	61·0

The closest approach between the cation and anion is Cu · · · O 3·74 Å; the closest N · · · Cl approach is 4·49 Å.

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[36] Program PLANE for the calculation of best plane through *n* points, D. R. Harris and D. Harker.

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The exact parameters which enable dihalogenocuprate(I) salts to attain the linear X–Cu–X arrangement in the solid state are not known with any certainty. We suggest that the stabilization of the dichlorocuprate(I) cation in the solid state may be due to the presence of large bulky cations, but further structures must be determined before any definitive conclusions can be made.

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