Sulphur-ligand–Metal Complexes. Part 8.[1] Bis(diphenylphosphinothioyl)methane Complexes of Copper(I)

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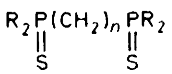
Crystals of $[(CuClL^2)_22(CuClL^2)]$ [L^2 = bis(diphenylphosphinothioyl)methane] † are triclinic, space group $P\bar{1}$, with a = 11.345(2), b = 16.569(3), c = 14.512(2) Å, α = 81.05(1), β = 78.76(1), γ = 109.09(1)°, and Z = 2. The structure was solved by direct methods and refined to R = 0.098 full-matrix least squares for 4 267 diffractometer data. It shows $[(CuClL^2)_22(CuClL^2)]$ to be a structurally mixed complex with three-co-ordinate monomers and tetrahedral sulphur-bridged dimers, co-existing in the same crystal. The formation of $[(CuClL^2)_22(CuClL^2)]$ from $[CuClL^2].Me_2CO$ (a three-co-ordinate monomer) has been followed by differential scanning calorimetry. The interaction of L^2, PMe_2PhS, and $P(NEt_2)_3S$ with copper(II) ions has allowed the identification of $Ph_2P(S)CH_2P(O)Ph_2$, PMe_2PhO, and $[(Et_2N)_3P{-}S{-}S{-}P(NEt_2)_3]^{2+}$ respectively, as oxidised ligand species.

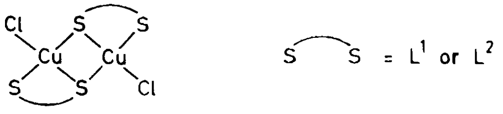
THE bidentate tertiary phosphine sulphide ligands, L^1—L^3, form an interesting series of 1 : 1 CuClL ($L = L^1$—L^3) complexes with copper(I) which exhibit a variety of structural types. Although single-crystal *X*-ray analyses on the L^1 and L^3 ligand complexes show them to be



$R_2P(CH_2)_nPR_2$ (P=S, P=S)

	R	*n*
L^1	Me	0
L^2	Ph	1
L^3	Ph	2

dimers with each copper in a distorted tetrahedral co-ordination sphere, the mode of co-ordination of the sulphide ligand is different in each case. In $[(CuClL^1)_2]$ each L^1 ligand chelates one copper and bridges two *via* one sulphur atom (1),[2] whereas in $[(CuClL^3)_2]$ dimerization is achieved by the ligand L^3 bridging two separate copper atoms (2).[3] With L^2 a different behaviour is observed however. In a previous report[4] we have shown that two distinct complexes, (A) and (B), could be prepared (depending on the solvent used) and that complex (A) could be converted into complex (B) by heating.



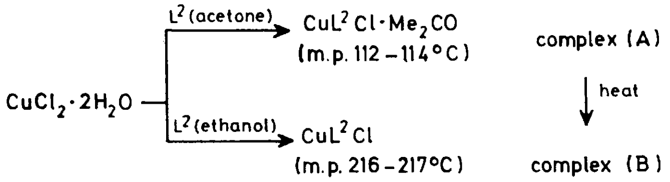
(1)

(2)

Complex (A) was shown to be not a dimer, but a three-co-ordinate monomer (3), with occluded acetone filling a void. From a physicochemical study, we suggested complex (B) was a dimer, but that in solution it existed in equilibrium with the monomeric species (3).

In this paper, we now report that complex (B) has been subject to a single-crystal *X*-ray analysis, and that in fact in the solid state (as in solution) it contains two distinct structural types, *i.e.* a three-co-ordinate monomer (3) and a tetrahedral dimer (1). Complex (B) should therefore be formulated as $[(CuClL^2)_22(CuClL^2)]$. This complex joins the small but unusual class where structurally different molecules exist as separate entities within the same crystalline substance.

Recently a preliminary report[5] indicated that the *NN*-di(isopropyl)dithiocarbamate complex $Hg(S_2CNPr^i{}_2)_2$ crystallizes in a form in which both monomers and dimers, were present. Nickel(II) gives other examples of structurally mixed complexes, but involving monomeric species only *viz.* $[Ni(CN)_5]^{3-}$ (square pyramidal and trigonal bipyramidal)[6] and $[NiBr_2L_2]$ (L = benzyldiphenylphosphine) (tetrahedral and square planar).[7] We also report the results of a study on the L^2 complexes using differential scanning calorimetry (d.s.c.). This is a technique which has been used to obtain enthalpies of decomposition processes for a variety of transition-metal complexes[8] but few studies appear to have been made on thermally induced structural changes such as the conversion of $[CuClL^2]{\cdot}Me_2CO$ into $[(CuClL^2)_22(CuClL^2)]$. Finally, in an attempt to gain further information on the nature of the oxidised products formed in redox reactions of the type outlined in the scheme above, we have included the results of a ^{31}P n.m.r. study on the products formed when L^2 and related unidentate tertiary phos-



(3)

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† Bis{μ-[bis(diphenylthiophosphoryl)methane-*S*,μ-*S'*]-chloro-copper(I)}—[bis(diphenylthiophosphoryl)methane-*S*,*S'*]chloro-copper(I) (1/2).

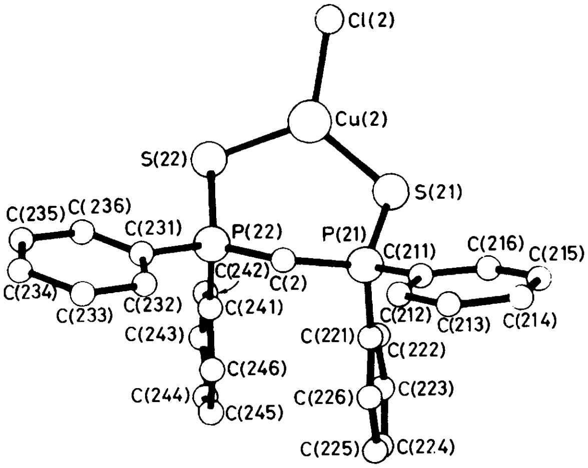

FIGURE 1 A view of the monomeric molecule CuClL^2 showing the numbering scheme

phine sulphide ligands, PMe$_2$PhS and P(NEt$_2$)$_3$S, interact with copper(II).

RESULTS AND DISCUSSION

Crystal Structure of $[(\mathrm{CuClL}^2)_2 2(\mathrm{CuClL}^2)]$.—The crystal structure consists of two distinct types of molecules. One (Figure 1) is a three-co-ordinate copper monomer resembling that previously described,[4] the second is a four-co-ordinate dimer (Figure 2) similar in bonding geometry to that of the L^1 ligand complex described by Cotton *et al.*[2]

The two CuClL^2 units of the *dimeric* molcule are related by a crystallographic centre of symmetry (Figure 2). Unlike $[(\mathrm{CuClL}^3)_2]$ which forms a chlorine-bridged complex,[3] (CuClL^2)$_2$ forms a sulphur-bridged dimer similar to $[(\mathrm{CuClL}^1)_2]$. The copper atom then adopts a distorted-tetrahedral co-ordination geometry. The three Cu–S bonds found in this dimer are all shorter than those in $[(\mathrm{CuClL}^1)_2]$. As the bite of the L^2 ligand is greater than the L^1 case [S(11)–Cu(1)–S(12) = 109.7°, *cf.* 103.5°], the strain in the ligand ring is less, and therefore the Cu–S bonds are a little stronger. This is reflected in the difference between the Cu(1)–S(12) and Cu(1)–S(12′) bond lengths (2.376 and 2.459 Å); these two bonds are more symmetric in the L^1 complex. The longer Cu–Cl distance (2.289 Å) for the L^2 complex, as compared to that in the L^1 complex (2.244 Å), is also consistent with the resultant increased electronic contribution from the more strongly bound L^2 ligand.

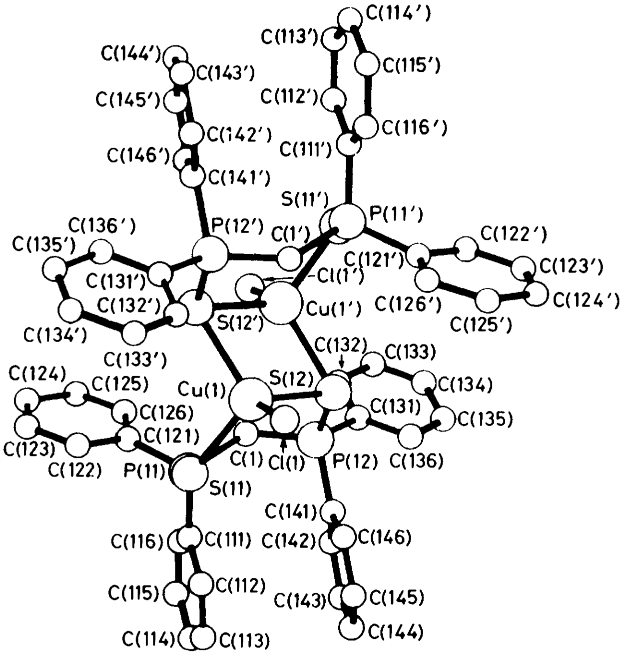

FIGURE 2 A view of the dimeric molecule (CuClL^2)$_2$ showing the numbering scheme

The two crystallographically related copper atoms are much closer (2.900 Å) than the L^1 case (3.406 Å), however, this is not in the range where any interactions can be expected. Differences in geometry of the copper coordination sphere between the L^2 and L^1 dimers follow from this change in the Cu–Cu distance. All other bond lengths in the L^2 dimer assume normal values. The conformation of the chelate ring and the disposition of the phenyl rings are similar to the monomer.

TABLE 1

Selected bond lengths (Å) and angles (°) for the crystal structure of $[(\mathrm{CuClL}^2)_2 2(\mathrm{CuClL}^2)]$ with estimated standard deviations in parentheses

(*a*) Bond lengths

Cu(1)–S(11)	2.287(4)	P(11)–C(1)	1.821(14)
Cu(1)–S(12)	2.376(4)	P(12)–C(1)	1.814(14)
Cu(1)–S(12′)	2.459(4)	P(11)–C(111)	1.798(8)
Cu(1)–Cl(1)	2.289(4)	P(11)–C(121)	1.795(10)
P(11)–S(11)	1.976(5)	P(12)–C(131)	1.782(8)
P(12)–S(12)	1.991(5)	P(12)–C(141)	1.794(7)
Cu(2)–S(21)	2.250(5)	P(22)–C(2)	1.793(16)
Cu(2)–S(22)	2.231(5)	P(21)–C(211)	1.806(8)
Cu(2)–Cl(2)	2.180(5)	P(21)–C(221)	1.784(9)
P(21)–S(21)	1.977(5)	P(22)–C(231)	1.799(10)
P(22)–S(22)	1.975(5)	P(22)–C(241)	1.795(8)
P(21)–C(2)	1.820(16)		

(*b*) Bond angles

S(11)–Cu(1)–S(12)	109.7(1)	S(11)–P(11)–C(121)	111.8(5)
S(11)–Cu(1)–S(12′)	108.8(1)	C(1)–P(11)–C(111)	106.3(6)
S(12)–Cu(1)–S(12′)	106.3(1)	C(1)–P(11)–C(121)	104.7(6)
S(11)–Cu(1)–Cl(1)	109.5(2)	C(111)–P(11)–C(121)	106.1(5)
S(12)–Cu(1)–Cl(1)	107.3(2)	S(12)–P(12)–C(1)	112.8(5)
S(12′)–Cu(1)–Cl(1)	115.1(2)	S(12)–P(12)–C(131)	110.3(4)
Cu(1)–S(11)–P(11)	110.1(2)	S(12)–P(12)–C(141)	114.4(3)
Cu(1)–S(12)–P(12)	106.8(2)	C(1)–P(12)–C(131)	106.4(6)
Cu(1)–S(12)–Cu(1′)	73.7(1)	C(1)–P(12)–C(141)	107.1(6)
S(11)–P(11)–C(1)	117.1(5)	C(131)–P(12)–C(141)	105.2(4)
S(11)–P(11)–C(111)	110.1(4)	P(12)–C(1)–P(11)	118.6(8)
S(21)–Cu(2)–S(22)	118.4(2)	C(2)–P(21)–C(221)	108.3(7)
S(21)–Cu(2)–Cl(2)	120.4(2)	C(211)–P(21)–C(221)	105.2(5)
S(22)–Cu(2)–Cl(2)	121.2(2)	S(22)–P(22)–C(2)	115.7(6)
Cu(2)–S(21)–P(21)	107.5(2)	S(22)–P(22)–C(231)	109.6(5)
Cu(2)–S(22)–P(22)	106.7(2)	S(22)–P(22)–C(241)	114.5(4)
S(21)–P(21)–C(2)	116.3(6)	C(2)–P(22)–C(231)	103.9(7)
S(21)–P(21)–C(211)	110.9(4)	C(2)–P(22)–C(241)	105.7(7)
S(21)–P(21)–C(221)	111.7(4)	C(231)–P(22)–C(241)	106.6(5)
C(2)–P(21)–C(211)	103.7(6)	P(22)–C(2)–P(21)	122.5(9)

The geometry of the copper co-ordination in the *monomeric* molcule is approximately trigonal planar. The distortion from perfect three-fold symmetry is considerably less than that found in the [CuClL^2]·Me$_2$CO complex.[4] The two Cu–S bond lengths are almost equal in length (Table 1) unlike those of the [CuClL^2]·Me$_2$CO complex which were markedly different. The two values are typical for non-bridging Cu–S bond lengths found in three-co-ordinate copper(I) complexes (2.23—2.26 Å).[4,9–11] All other bond lengths in the monomeric molecule are within the expected ranges. The two Cu(2)–S–P angles are close to tetrahedral (106 and 107°) as is usual for co-ordinated tertiary phosphine sulphide ligands,[4] but are substantially different to those in the [$CuClL^2$]·Me_2CO case (91.5° and 95.7°) reflecting the difference in conformation of the six-membered ligand ring. In the present structure, the chelate ring [atoms Cu(2), S(21), P(21), C(2), P(22), and S(22)] assumes a boat conformation, while the equivalent atoms in the [$CuClL^2$]·Me_2CO case are bonded in a twist-boat conformation. The boat conformation requires that two of the benzene rings are relatively close to one another, and these in fact lie almost parallel (Figure 1). This, together with the boat conformation, require the P–C–P angle to be greater in this case (122°) than in the twist conformation (117°) where the crowding of the phenyl groups is considerably eased.

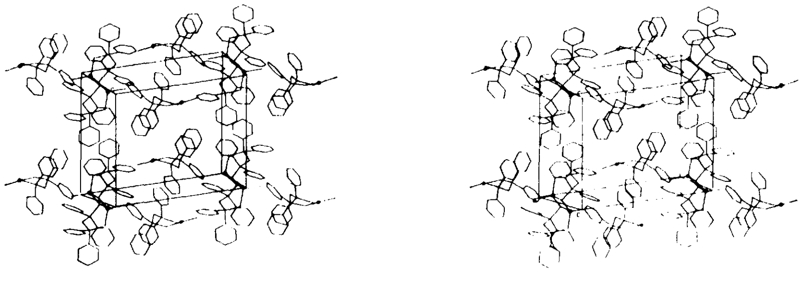

FIGURE 3 A stereoscopic view of the unit cell

The crystal structure consists of sheets of the monomeric molecule alternated with sheets of the dimeric molecule, both parallel to the *ac* plane (Figure 3). These sheets are bound loosely by weak Van der Waals forces, the shortest contacts are Cl (monomer)–H(phenyl dimer) = 2.91 Å and Cl(dimer)–H(phenyl monomer) = 2.87 Å.

The principal difference between the three-co-ordinate [$CuClL^2$] moieties in the present and the [$CuClL^2$]·Me_2CO crystal structures is in the conformation of the ligand ring. In the [$CuClL^2$]·Me_2CO case, the ligand ring shows a large amount of strain exemplified by the Cu–S–P angles of 91.5 and 95.7°. It is probable that this strained conformation is somewhat stabilised by the close contact of the oxygen, to the hydrogen atoms of the methylene group ($O \cdots H = 2.27$ Å).

Differential Scanning Calorimetry.—The technique of differential scanning calorimetry (d.s.c.) has been reviewed elsewhere.[8] Figure 4 shows typical d.s.c. thermograms for the two complexes [$CuClL^2$]·Me_2CO and [$(CuClL^2)_2 2(CuClL^2)$]. The curve for [$CuClL^2$]·Me_2CO shows a broad endotherm centred at 117 °C (ΔH = 67.0 J g^{-1}) corresponding to compound melting and loss of acetone. This is immediately followed by an exotherm, which has a minimum at 125 °C and a shoulder discernible at *ca.* 140 °C (ΔH = −28.6 J g^{-1}) representing structural rearrangement and solidification. The melting and solidification processes were confirmed visually using a hot-stage microscope. Acetone vaporization was apparent from the observation of bubbling during melting and the disappearance of the acetone bands from the i.r. spectrum of the sample. The endothermic and exothermic peaks overlap, thus making accurate ΔH determinations difficult. Also the values obtained depend very much on the history of the samples. Values reported are for samples held at 50 °C to establish thermal equilibrium before scanning commenced. However, if the sample was held at 100 °C for 5 min and then cooled to 50 °C before scanning, ΔH for the 117 °C endotherm was reduced to 38 J g^{-1} and that of the exotherm to −23.2 J g^{-1}. Heating a sample at 100 °C for 30 min showed the complete disappearance of both

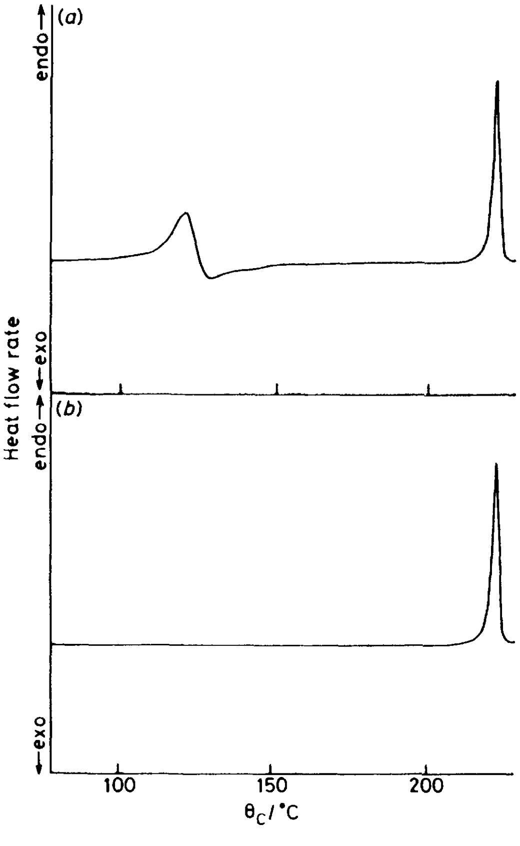

FIGURE 4 D.s.c. curves for (*a*) [$CuClL^2$]·Me_2CO, (*b*) [$(CuClL^2)_2 2(CuClL^2)$]

peaks. Finally a sharp second endothermic peak is seen at 218 °C ($\Delta H = 61.6$ J g^{-1}, a value independent of the history of the sample). That this corresponds to the melting of the complex [(CuClL^2)$_2$2(CuClL^2)] is seen by comparison of the curve with the d.s.c. thermogram for the pure [(CuClL^2)$_2$2(CuClL^2)] complex prepared from ethanol ($\Delta H = 61.5$ J g^{-1}). Moreover the far-i.r. spectrum of the complex [(CuClL^2)$_2$2(CuClL^2)] is identical to the spectrum of a sample prepared by heating [CuClL^2]·Me$_2$CO at 100 °C. A strong band at 228 cm^{-1}, since it is not present in the spectrum of [CuClL^2]·Me$_2$CO, is assigned to a ν(Cu–Cl) vibration for the terminal copper–chlorine bond in the tetrahedral dimer and a band at 292 cm^{-1} to ν(Cu–Cl) [presumably coupled with ν(Cu–S) which also would be expected to occur in this region] for the three-co-ordinate monomer. In the case of [CuClL^2]·Me$_2$CO, two strong bands are seen at 274 and 291 cm^{-1}, assignable to ν(Cu–Cl) and ν(Cu–S), but it is not possible to distinguish which is which.

From the results on the [CuClL^2]·Me$_2$CO complex it appears that the solvated acetone is important in stabilising this form of the compound and that this is a metastable form. Attempts to remove the acetone *in vacuo* without structural rearrangement were unsuccessful. A temperature of *ca.* 100 °C is required to cause acetone loss but conversion to [(CuClL^2)$_2$2(CuClL^2)] also occurs without the complex visually melting.

Interaction of Tertiary Phosphine Sulphide Ligands with Copper(II).—Previously we have reported that the interaction of tertiary phosphine sulphides with copper(II) salts in acetone affords unstable orange solutions which on the basis of electronic and e.s.r. spectral evidence appear to contain copper(II) species co-ordinated to the sulphide ligands.[4] In the case of L^1 and L^2 solid complexes with a pseudo-tetrahedral geometry have been isolated.[4,12] On standing, colourless copper(I) complexes are formed but the reducing agent is unknown. In the case of tris(dimethylamino)phosphine sulphide, P(NMe$_2$)$_3$S, with copper(II), stable species postulated to contain the cation L^4 have been isolated by Slinkard and Meek.[13]

$$[(R_2N)_3P\text{–}S\text{–}S\text{–}P(NR_2)_3]^{2+}$$
$$L^4{:}R = Me$$
$$L^5{:}R = Et$$

In the present work the disulphide ligand was allowed to react with copper(II) perchlorate in ethanol (details are given in the Experimental section). After isolation of the known[4] copper(I) complex [CuL$^2_2$][ClO$_4$], a ^{31}P n.m.r. on the CHCl$_3$ soluble residue showed a number of phosphorus species to be present. Subsequent chromatography on silica allowed the identification of Ph$_2$P(S)CH$_2$P(O)Ph$_2$ as one of the products. A similar reaction with the unidentate PMe$_2$PhS ligand showed the only phosphorus species present in solution, after the removal of [Cu(PMe$_2$PhS)$_3$][ClO$_4$] to be the oxide PMe$_2$PhO. It appears therefore that stable dications of the type L^4 are not formed in these reactions unless the substituents on the phosphorus atoms are dialkylamino-groups which allow delocalization of the positive charge.[14] However, the identification of oxide products in the case of L^2 and PMe$_2$PhS, does implicate these phosphine sulphides in the redox process.

Also included in Table 2 are ^{31}P n.m.r. data for the copper(I) complexes of these ligands. The co-ordination chemical shifts are only a few p.p.m., in contrast to the larger downfield shifts (*ca.* 20 p.p.m.) observed for the thiophosphoryl phosphorus in Ph$_2$P(S)CH$_2$PR$_2$ chelate complexes of the Group 6 metal carbonyls.[15] The compounds [CuClL^2]·Me$_2$CO and [(CuClL^2)$_2$2(CuClL^2)] have identical spectra each showing only one resonance at 32.8 p.p.m. indicative of an exchange process occurring in solution.

TABLE 2

Phosphorus-31 n.m.r. spectral data

Compound	δ [a]/p.p.m.	Solvent
L^2	35.5 [b]	CDCl$_3$
[CuL$^2_2$][ClO$_4$]	33.1	
[CuClL^2]·Me$_2$CO	32.8	
[(CuClL^2)$_2$2(CuClL^2)]	32.8	
PMe$_2$PhS	32.6	
PMe$_2$PhO	34.1	
[Cu(PMe$_2$PhS)$_3$][ClO$_4$]	36.6	
P(NEt$_2$)$_3$S	78.0 [c]	MeCN
[L^5][ClO$_4$]$_2$	58.5	
[(Et$_2$N)$_3$P–S–CH$_2$Ph][BF$_4$]	61.9 [d]	C$_6$H$_6$
[(Et$_2$N)$_3$P–S–C$_6$H$_4$Me](SO$_2$C$_6$H$_4$Me)	61.6 [d]	
PPh$_3$S	42.6 [e]	CH$_2$Cl$_2$
[Ph$_3$P–S–Me][SbCl$_6$]	46.6 [e]	
(MeO)$_2$P(S)SSP(S)(OMe)$_2$	89.5	CDCl$_3$
(MeO)$_2$P(S)SSP(S)(OMe)$_2$ + I$_2$ (in excess)	89.5	

[a] Reported downfield from 85% H$_3$PO$_4$. [b] Ref. 15 reports 34.6 p.p.m. (CH$_2$Cl$_2$). [c] Ref. 16 reports 78.5 p.p.m. (C$_6$H$_6$). [d] From ref. 16. [e] From ref. 17.

To gain further information on the dicationic species of the type L^4 we have prepared the diethylamino-derivative L^5 with the counter anion [ClO$_4$]$^-$ in order to record its ^{31}P n.m.r. spectrum. The ^{31}P chemical shift is listed in Table 2 and shows an upfield shift of *ca.* 20 p.p.m. from the value of the neutral ligand (δ = 78.0 p.p.m.). Moreover, the δ values are in the same range as those reported[16] for the cations [(Et$_2$N)$_3$P–S–R]$^+$ (where R = CH$_2$Ph or C$_6$H$_4$Me) implying that the nature of the P–S and N–P bonds, and the angles around the phosphorus must be similar and so supporting the dicationic formulation of the species L^4 and L^5. Schmidpeter and Brecht[17] have shown (Table 2) that on methylation the ^{31}P resonance in PPh$_3$S undergoes a slight downfield shift (4 p.p.m.) in line with the expected weakening of the P–S bond with the introduction of the positive charge. Therefore the upfield shift observed for the cationic species L^5 relative to P(NEt$_2$)$_3$S does give credence to the suggestion that such cations are stabilized by electron delocalization from the nitrogen atoms as it acts as a π donor to the phosphorus.

In an attempt to determine whether methoxy substituents on the phosphorus would have a similar effect the tetramethyl ester of thioperoxydiphosphoric acid (MeO)$_2$P(S)SSP(S)(OMe)$_2$ was interacted with I$_2$ [no reaction occurring with copper(II)[18]], however ^{31}P data suggested no oxidation but simply the formation of a charge-transfer complex, there being no change in the ^{31}P resonance. For the case of L^5 with the counter ion $[Cu_2Cl_6]^{2-}$ spectroscopic data in the solid state and solution support a dimeric formulation of the anion with the copper(II) in a distorted tetrahedral environment. In the electronic spectrum [in acetone: Cl→Cu charge transfer 20 830 cm^{-1} ($\varepsilon = 1\,620$), *d–d* 11 110 cm^{-1} ($\varepsilon = 198$), 9 090 (sh) cm^{-1} ($\varepsilon = 104$); reflectance: 20 830, 11 360 cm^{-1}] the Cl→Cu charge-transfer band near 21 000 cm^{-1} points to a non-planar dimer structure since planar dimers are characterized by a band at lower wavenumbers.[19] In the e.s.r. spectrum (nitromethane at 77 K: $g_1 = 2.272$, $A = 148 \times 10^{-4}$ cm^{-1}, $g_2 = 2.100$, $g_3 = 2.024$) the value of A in the $g_{\|}$ region is also consistent with the proposed structure and in the i.r. bands attributable to ν(Cu–Cl) vibrations are seen at 316 cm^{-1} (terminal) and 251 cm^{-1} (bridging), in the region expected for such an anion.[19]

EXPERIMENTAL

Infrared spectra were recorded by use of a Beckman IR 20 spectrometer (250—4 000 cm^{-1}) and a Grubb-Parsons Cube Mark II Interferometer. Phosphorus-31 n.m.r. spectra were obtained on a JEOL FX60 Fourier-transform pulsed spectrometer. Electronic spectra were recorded on a Shimadzu MPS 5000 instrument and e.s.r. spectra on a Varian E104A spectrometer. Conductivity measurements were made at room temperature on a Philips PR 9500 conductivity meter and PW 9510 cell. Differential scanning calorimetry measurements were made on a Perkin-Elmer DSC-2 machine, calibrated with indium metal. Samples (*ca.* 3—5 mg) were encapsulated in aluminium pans with lids crimped in position. ΔH values were calculated in the usual manner.[8] Microanalyses are by Professor A. D. Campbell, University of Otago.

The tertiary phosphine sulphides L^2, PMe_2PhS, and $P(NEt_2)_3S$ were prepared according to literature methods [20] as were the complexes [4] $[CuClL^2]\cdot Me_2CO$ and $[(CuClL^2)_2\text{-}2(CuClL^2)]$.

Reaction of L^2 *with* $Cu[ClO_4]_2\cdot 6H_2O$.—To a stirred solution of $Cu[ClO_4]_2\cdot 6H_2O$ (0.368 g, 1.0 mmol) dissolved in ethanol (10 cm^3) was slowly added the ligand L^2 (1.113 g, 2.5 mmol) in a 1 : 1 mixture of ethanol and dichloromethane (25 cm^3). A red-brown colour appeared which faded and a white precipitate formed. After filtration the solid was shown to be $[CuL^2_2][ClO_4]$ from a comparison of its i.r. spectrum with that of an authentic sample.[4] Yield 1.052 g (100%). The filtrate was evaporated to dryness *in vacuo*, dissolved in $CHCl_3$, and treated with anhydrous $K_2[CO_3]$. A ^{31}P n.m.r. spectrum on this solution showed peaks at 31.4(d), 32.7(d), 33.8, 37.3, 45.6, and 65.4(d) p.p.m. Chromatography of the $CHCl_3$ solution on silica gel with $CHCl_3$ as eluant allowed the identification (from its mass spectrum, *m/e* 432) of the previously reported [21] compound $Ph_2P(S)CH_2P(O)Ph_2$ as a major component.

Reaction of PMe_2PhS *with* $Cu[ClO_4]_2\cdot 6H_2O$.—In a manner similar to that described above PMe_2PhS (0.677 g, 4.0 mmol) dissolved in ethanol was reacted with $Cu[ClO_4]_2\cdot 6H_2O$ (0.369 g, 1.0 mmol) in the same solvent. After the isolation of the known [22] complex $[Cu(PMe_2PhS)_3][ClO_4]$ the ^{31}P n.m.r. showed only one resonance at 34.1 p.p.m. identical to that of the tertiary phosphine oxide PMe_2PhO.

Preparation of $[L^5][ClO_4]_2$ *and* $[L^5][Cu_2Cl_6]$.—These were prepared from the interaction of $P(NEt_2)_3S$ and the appropriate copper(II) salt in a manner similar to that reported by Slinkard and Meek [13] for the dimethylamino-derivatives. For $[L^5][ClO_4]_2$ m.p. was 131—133 °C (Found: C, 38.0; H. 7.95; N, 11.0. $C_{24}H_{60}Cl_2N_6O_8P_2S_2$ requires C, 38.0; H, 8.0; N, 11.1%), Λ (in nitrobenzene) 46 S cm^2 mol^{-1}. For $[L^5][Cu_2Cl_6]$ m.p. 139—141 °C (Found: C, 31.4; H, 6.8; Cl, 23.2. $C_{24}H_{60}Cl_6N_6P_2S_2$ requires C, 32.1; H, 6.7; Cl, 23.7%), Λ (in nitrobenzene) 52 S cm^2 mol^{-1}.

Attempts to prepare an analytically pure sample of $[L^5][Br_3]_2$ from the interaction of bromine with $P(NEt_2)_3S$ in acetonitrile solution were unsuccessful although the i.r. spectrum of the product showed the disappearance of bands characteristic of $P(NEt_2)_3S$ in the 500—700 cm^{-1} range and was similar to the spectra of $[L^5][ClO_4]_2$ and $[L^5][Cu_2Cl_6]$.

Crystal Structure of $[(CuClL^2)_2 2(CuClL^2)]$.—*Crystal data.* $C_{50}H_{44}Cl_2Cu_2P_4S_4$, $M = 1\,095.04$, $C_{25}H_{22}ClCuP_2S_2$, $M = 547.52$, $F(000) = 1\,120$, $a = 11.345(2)$, $b = 16.569(3)$, $c = 14.512(2)$ Å, $\alpha = 81.05(1)$, $\beta = 78.76(1)$, $\gamma = 109.09(1)$°, $U = 2\,476.8$ Å^3, D_m(flotation) $= 1.47(2)$, $Z = 2$, $D_c = 1.48$ g cm^{-3}. Mo-K_α radiation (Zr filtered), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) $= 13.3$ cm^{-1}. Space group $P\bar{1}$.

Data collection. The crystals were elongated thick plates. Approximate cell dimensions were determined from precession photographs, and no systematic absences were observed. Unit-cell dimensions were refined by a least-squares treatment [23] of the setting angles of 12 reflections centred automatically on a Hilger and Watts automated diffractometer.

The crystal used for data collection was of maximum dimensions 0.5 × 0.4 × 0.15 mm. The intensities were measured by the θ—2θ scan technique with 50 steps of 0.01° s^{-1}. The local background was measured for 12.5 s at each end of the step scan by the stationary-counter-stationary crystal method. The intensities of three reflections measured periodically throughout the data collection showed only random fluctuations of ±2% in their mean values. All independent reflections in the $\pm h \pm kl$ hemisphere for which $\theta < 28°$ were measured. The integrated intensities and their deviations were derived as described by Corfield *et al.*[24] with an uncertainty factor of 0.05. Of the 5 932 reflections measured, 4 267 with $I > 3\sigma(I)$ were used in the subsequent analysis. The data were corrected for absorption effects by the analytical method of De Meulenaer and Tompa,[25] absorption coefficients ranging from 1.059 to 1.239.

Solution and refinement. The structure was solved by direct methods [26] and refined by a full-matrix least squares * analysis, the function minimised being $\Sigma w(|F_o| - |F_c|)^2$ where $w = [1/\sigma(F)]^2$. Scattering factors for hydrogen atoms are those of Stewart *et al.*[27] all others are from standard sources.[28] The copper, sulphur, chlorine, and phosphorus atoms were refined with anisotropic temperature factors. In order to reduce the rather large number of parameters in each refinement cycle, all phenyl rings were treated as rigid groups with C–C and C–H bond lengths of 1.395 and 1.08 Å respectively and C–C–C bond angles of 120°. Individual isotropic temperature factors for the benzene carbon atoms were allowed to refine, but the temperature factors for all hydrogen atoms were fixed at $U_H = 0.09$ Å^2. The hydrogen atoms for the methylene groups were placed in their idealised positions and their positional parameters refined. With these conditions,

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* Local programs for data reduction, otherwise the 'SHELX' system, G. M. Sheldrick, University of Cambridge, 1976.

refinement converged at $R = 0.098$ and $R' = 0.097$. Further refinement, for example with anisotropic thermal parameters for the benzene rings, was not considered necessary, as the essential features of the structure had been adequately defined. In the final cycle, all parameter shifts were less than 0.6 of their estimated standard deviation. A final difference-Fourier synthesis showed a number of peaks of the order of 0.9 e $Å^{-3}$. These peaks were all associated with carbon atoms of the phenyl groups which had greater than average isotropic temperature factors, and may be due to anisotropic thermal motion of these atoms. Final observed and calculated structure factors are listed, together with thermal parameters for the non-hydrogen atoms, in Supplementary Publication No. SUP 22740 (26 pp.).* The refined atom co-ordinates are listed in Table 3.

TABLE 3

Postional co-ordinates (× 10^4) for the crystal structure of $[(CuClL^2)_2 2(CuClL^2)]$ with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Cu(1)	5 149(2)	9 383(1)	752(1)
S(11)	5 413(4)	9 668(3)	2 206(3)
S(12)	3 150(3)	9 448(2)	552(2)
P(11)	4 882(3)	10 659(3)	2 431(3)
P(12)	2 514(3)	9 994(2)	1 575(2)
Cl(1)	5 066(4)	7 987(2)	730(3)
C(1)	3 793(13)	10 903(9)	1 758(11)
C(111)	4 092(9)	10 471(7)	3 689(6)
C(112)	3 714	7 648	4 312
C(113)	3 071	9 503	5 280
C(114)	2 806	10 182	5 626
C(115)	3 184	11 006	5 002
C(116)	3 827	11 151	4 034
C(121)	6 245(10)	11 673(7)	2 145(8)
C(122)	7 389	11 618	2 312
C(123)	8 453	12 384	2 197
C(124)	8 372	13 204	1 914
C(125)	7 228	13 259	1 747
C(126)	6 164	12 494	1 863
C(131)	1 367(8)	10 427(6)	1 249(7)
C(132)	1 721	11 302	770
C(133)	801	11 595	477
C(134)	−473	11 013	664
C(135)	−826	10 138	1 143
C(136)	94	9 844	1 436
C(141)	1 689(8)	9 245(5)	2 734(5)
C(142)	1 001	9 518	3 447
C(143)	364	8 953	4 358
C(144)	416	8 116	4 556
C(145)	1 104	7 843	3 842
C(146)	1 741	8 408	2 931
Cu(2)	2 565(2)	3 429(1)	3 172(1)
S(21)	4 714(4)	4 144(3)	2 855(3)
S(22)	1 274(4)	4 169(3)	3 513(4)
P(21)	5 111(3)	5 375(2)	2 193(3)
P(22)	2 326(4)	5 425(2)	2 935(3)
Cl(2)	1 781(5)	2 057(3)	3 101(3)
C(2)	3 745(16)	5 651(12)	1 984(12)
C(211)	6 175(9)	5 650(7)	994(6)
C(212)	6 036	6 167	198
C(213)	6 920	6 386	−701
C(214)	7 943	6 087	−805
C(215)	8 082	5 570	−8
C(216)	7 198	5 351	891
C(221)	5 960(9)	6 132(6)	2 806(7)
C(222)	6 032	5 836	3 739
C(223)	6 744	6 424	4 199
C(224)	7 385	7 309	3 725
C(225)	7 313	7 606	2 791
C(226)	6 601	7 017	2 332
C(231)	1 392(12)	5 939(8)	2 369(9)
C(232)	1 899	6 540	1 472
C(233)	1 129	6 933	1 088
C(234)	−147	6 726	1 601
C(235)	−655	6 126	2 498
C(236)	115	5 732	2 882
C(241)	2 865(9)	6 045(6)	3 783(7)
C(242)	2 496	5 622	4 761
C(243)	2 908	6 089	5 434
C(244)	3 688	6 797	5 129
C(245)	4 057	7 403	4 152
C(246)	3 646	6 936	3 479

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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