Sulphur-ligand–Metal Complexes. Part IV.[1] Copper Complexes with Bidentate Tertiary-phosphine Sulphide and Selenide Ligands and the Crystal Structure of a Three-co-ordinate Copper(I) Complex

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The preparation of the following compounds is described: $[CuL_2][ClO_4]$ [L = bis(diphenylphosphinothioyl)-methane (bdtm), bis(diphenylphosphinothioyl)ethane (bdte), or bis(diphenylphosphinoselenoyl)methane (bdsm)], $[CuLX]_n$ [L = bdtm, bdte, bdtm, or tetramethyldiphosphine disulphide (tmdpds); n = 1 or 2], and $[Cu(bdtm)Cl_2]$ (where spectroscopic evidence suggests a distorted tetrahedral arrangement of ligands). Similar species $[CuL_2Cl_2]$ (L = Me_2PhPS or $MePh_2PS$, L_2 = bdte or tmdpds) are detected in solution and have the same tetrahedral stereochemistry. Related complexes of Ag^I, Hg^{II}, Zn^{II}, Pt^{II}, and Pd^{II} are reported. Crystals of $[Cu(bdtm)Cl]\cdot Me_2CO$ are orthorhombic, space group $Pna2_1$ with a = 17.185(2), b = 13.640(3), c = 12.058(1) Å, Z = 4. The structure was determined by the heavy-atom method and refined by least-squares methods to R 0.052 for 2 876 reflections measured by diffractometer. The molecule is a three-co-ordinate monomer with the occluded acetone filling a void.

EVEN though a large number of metal complexes of unidentate phosphine sulphide and selenide ligands with 'class B' metals[2-5] and more recently with cobalt(II) and nickel(II)[6-8] have been reported, comparatively less is known about similar complexes containing the bidentate phosphine sulphides and selenides $R_2P(X)\cdot[CH_2]_n\cdot P(X)R_2$ (n = 0—2; X = S or Se); some are reported in refs. 9—11. Recently we have reported[12] sulphide complexes of iridium(I) and rhodium(I) in which the ligand was bidentate, and chromium(0) and tungsten(0) carbonyl derivatives[13] where it was shown to be unidentate. Current interest in copper complexes with sulphur ligands has prompted this report on the interaction of these ligands with this metal as well as with silver(I), mercury(II), zinc(II), platinum(II), and palladium(II). Structures are suggested where possible from physico-chemical studies and a spectral study of unidentate phosphine sulphide complexes of copper(II) is presented, as well as a single-crystal X-ray analysis on the three-co-ordinate bis(diphenylphosphinothioyl)-methane complex $[Cu(bdtm)Cl]\cdot Me_2CO$. A preliminary account of some of this work has appeared.[14]

RESULTS AND DISCUSSION

Preparation of Copper Complexes.—The copper(I) complexes were generally prepared from copper(II) salts by use of hypophosphorous acid as a reducing agent; the isolation of copper(II) complexes was favoured by use of acetone as solvent. When acetone solutions of copper(II) chloride dihydrate and bdtm (I) were mixed an orange solution resulted from which $[Cu(bdtm)Cl_2]$ was isolated.

$$R_2P(\colon X)\cdot[CH_2]_n\cdot P(\colon X)R_2$$

		R	X	n
(I)	bdtm	Ph	S	1
(II)	bdte	Ph	S	2
(III)	bdsm	Ph	Se	1
(IV)	bdse	Ph	Se	2
(V)	tmdpds	Me	S	0

However, in ethanol solution the major product was the colourless copper(I) derivative $[Cu(bdtm)Cl]_n$ (m.p. 216—217 °C) with a small amount of $[Cu(bdtm)Cl_2]$. The same copper(I) complex could also be isolated after heating under reflux an ethanol solution of copper(I) chloride and bdtm. Another bdtm copper(I) complex $[Cu(bdtm)Cl]\cdot Me_2CO$ (m.p. 112—114 °C) was isolated by reducing the orange copper(II)–bdtm acetone solution with hypophosphorous acid. With bdte (II) the product in acetone was a mixture of $[Cu(bdte)Cl_2]$ with some $[Cu(bdte)Cl]_n$† the concentration of the latter increasing with time, while in alcohol it was exclusively $[Cu(bdte)Cl]_n$. For the selenide ligands bdsm (III) and bdse (IV) reduction was instantaneous in both solvents, accompanied by the precipitation of some selenium. Only with the former ligand was a pure complex isolated. With tmdpds (V) in acetone solution a brown precipitate

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† A single-crystal X-ray analysis has just been completed on $[Cu(bdte)Cl]_2$. This is a dimeric molecule containing bridging chlorines and bridging bdte groups, giving a distorted tetrahedral arrangement of ligands about the copper. The structure is different from that of the bdtm analogue.

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TABLE 1

Analytical (%), conductivity, and i.r. data for the complexes

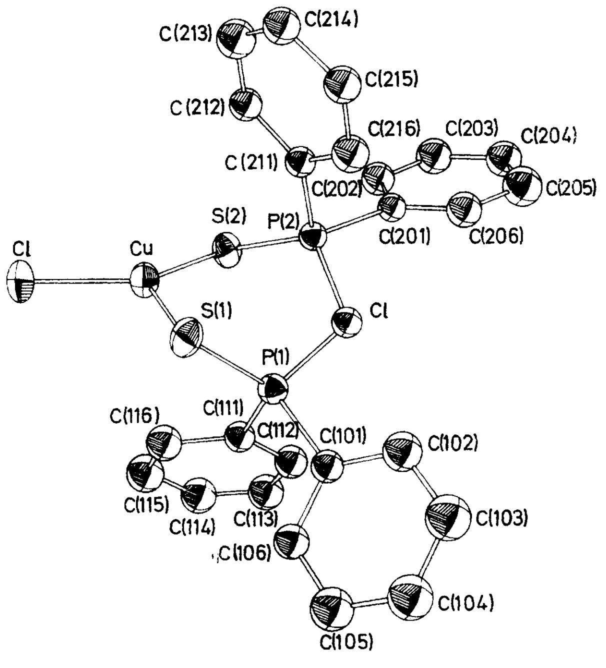
Compound	Found (calc.)				
	C	H	X	Λ^c/S cm^2	ν(P:X) [k]/cm^{-1}
[Cu(bdtm)Cl$_2$]	52.2 (51.5)	3.8 (3.8)	9.9 (10.9) [a]	44 [d]	575
[Cu(bdtm)Cl]·Me$_2$CO	55.3 (55.2)	5.0 (5.3)	9.4 (10.5) [a]	*e*	598, 580
[Cu(bdtm)Cl]$_2$	54.9 (54.8)	4.2 (4.1)	6.6 (6.3) [b]	8 [f]	570
[Cu(bdtm)Br$_2$]$_n$	50.8 (50.4)	3.8 (4.4)	10.8 (10.8) [a]	5 [f]	577sh, 573
[Cu(bdte)Cl]$_n$	55.4 (56.6)	4.4 (4.4)	11.3 (11.6) [a]	8 [f]	589
[Cu(bdte)Br]$_n$	50.7 (51.2)	4.3 (4.6)	10.2 (10.5) [a]	5 [f]	589
[Cu(tmdpds)Cl]$_2$	16.7 (16.8)	4.5 (4.4)		15 [g]	595, 557
[Cu(tmdpds)Br]$_n$	15.2 (14.6)	4.2 (3.7)		10 [g]	592, 553
[Cu(bdtm)$_2$][ClO$_4$]	56.5 (56.6)	4.5 (4.2)	12.4 (12.1) [a]	28 [f]	606, 580
[Cu(bdsm)$_2$][ClO$_4$]	47.3 (48.1)	3.9 (3.5)	3.5 (2.9) [b]	75 [h]	520
[Cu(tmdpds)$_2$][BF$_4$]	18.8 (18.4)	5.1 (4.6)	23.1 (24.5) [a]	27 [f]	595, 561
[Ag(bdtm)$_2$][ClO$_4$]	50.4 (54.4)	4.1 (4.0)	11.8 (11.6) [a]	28 [f]	567
[Ag(bdsm)$_2$][ClO$_4$]	46.1 (46.3)	3.7 (3.4)		28	519
[Ag(bdse)$_2$][ClO$_4$]	44.7 (46.6)	3.8 (3.6)		90 [h]	524
[Ag(bdtm)NO$_3$]·2H$_2$O	45.7 (45.8)	3.7 (3.7)	6.6 (6.4) [a]	32 [h]	568
[Hg(bdtm)Cl$_2$]	41.8 (41.7)	3.2 (3.1)	10.0 (10.0) [b]	12 [h]	582, 564
[Hg(bdte)Cl$_2$]	42.3 (42.5)	3.8 (3.0)		2 [f]	580
[Hg(bdsm)Cl$_2$]	38.7 (37.5)	2.9 (2.8)	8.4 (8.7) [b]	*i*	528
[Hg(bdse)Cl$_2$]	36.0 (37.3)	3.4 (2.9)		6 [h]	522
[Hg(bdsm)Br$_2$]	38.6 (37.1)	3.7 (2.8)		*j*	529
[Hg(bdtm)$_2$][ClO$_4$]$_2$	45.0 (46.3)	3.8 (3.4)	9.8 (9.9) [a]	160 [h]	587, 568
[Zn(bdtm)$_2$][ClO$_4$]$_2$	50.3 (51.7)	4.3 (4.3)	10.3 (11.0) [a]	160 [h]	586, 569
[Pd(bdtm)Cl$_2$]	47.6 (47.9)	3.6 (3.6)	10.7 (10.2) [a]	12 [g]	573
[Pd(bdsm)Cl$_2$]·2H$_2$O	39.5 (39.7)	3.3 (3.4)	8.8 (9.4) [b]	*i*	532
[Pt(bdsm)Cl$_2$]	35.5 (35.5)	3.3 (3.1)		10 [g]	533

bdtm = Bis(diphenylphosphinothioyl)methane, bdte = bis(diphenylphosphinothioyl)ethane, bdsm = bis(diphenylphosphinoselenoyl)methane, bdse = bis(diphenylphosphinoselenoyl)ethane, tmdpds = tetramethyldiphosphine disulphide.

[a] S. [b] Cl. [c] For 10^{-3} M-solutions. [d] Acetone. [e] Not measured. [f] Nitrobenzene. [g] Dimethyl sulphoxide. [h] Nitromethane. [i] Decomposed on dissolving. [j] Insoluble. [k] As Nujol mulls; X = S or Se; ν(P:S) for bdtm: 628, 616, 596; bdte: 614, 610; tmdpds: 568; ν(P:Se) for bdsm: 531; bdse: 530 cm^{-1}.

initially formed which has been identified as [Cu(tmdpds)Cl$_2$]$_n$;[15] however, we found this compound was quickly reduced to a copper(I) complex, and this was hastened by i.r. radiation. It appears that the previously reported i.r. spectra of [Cu(tmdpds)X$_2$]$_n$ (X = Cl or Br) are those for impure copper(I) compounds. In alcohol only the copper(I) derivative [Cu(tmdpds)Cl]$_2$ could be isolated. For all the foregoing cases the use of copper(II) bromide in either solvent resulted in the isolation of the copper(I) complex.

The interaction of the chelating sulphide and selenide ligands with copper(II) perchlorate hexahydrate in either solvent resulted in the precipitation of colourless copper(I) complexes [CuL$_2$][ClO$_4$] (L = bdtm, bdte, bdsm, and tmdpds). As yet the oxidised product has not been identified. An initial reddish-brown colour was apparent upon the addition of the ligand to the copper(II) acetone solutions and this may have been indicative of the formation of [CuL$_2$][ClO$_4$]$_2$ which was quickly reduced. When tmdpds was added to copper tetrafluoroborate hexahydrate a brown product, presumably [Cu(tmdpds)$_2$][BF$_4$]$_2$, precipitated and this was reduced to [Cu(tmdpds)$_2$][BF$_4$] on attempted isolation. The similar complex [Cu(tmdpds)$_2$][ClO$_4$]$_2$ was explosive. The non-isolation of the intermediate copper(II) species was probably a reflection of the reducing ability of the ligands and the fact that four sulphur or selenium atoms attached to a copper(II) ion may be arranged in a distorted tetrahedral array hence facilitating an easy pathway for reduction. Analytical data for the complexes are listed in Table 1.



A view of the [Cu(bdtm)Cl] molecule showing the atom numbering scheme; thermal ellipsoids are scaled to enclose 50% of the electron density

Crystal Structure of [Cu(bdtm)Cl]·Me$_2$CO.—The crystal structure consists of discrete molecules of [Cu(bdtm)Cl] (Figure), with one occluded acetone molecule per asym-

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metric unit. Bond lengths and angles are given in Table 2 together with their estimated standard deviations. The geometry around the copper atom is distorted trigonal planar with the copper atom out of the plane of the chlorine and sulphur atoms by 0.08 Å. The distortion from trigonal-planar geometry is larger than that usually found for mononuclear three-co-ordinate copper(I) complexes, the angles subtended at the copper atom being 119, 113, and 117°. There is a significant (15σ) difference in the Cu–S bond lengths. Cu–S(2) [2.259(2)Å] is within the range expected (*ca.* 2.23—2.26 Å) for simple three-co-ordinate copper–sulphur complexes, *e.g.* [Cu(Me$_3$PS)$_3$]$^+$ [2.253(5)—2.264(5) Å] [16] and [Cu(2-thiouracil)$_2$Cl] [2.226(1) Å],[17] while the Cu–S(1) distance [2.321(2) Å] is longer than expected, but typical for a 'tetrahedral' Cu–S bond [$\geqslant$2.3 Å (ref. 18)]. The Cu–Cl bond length [2.207(2) Å] is similar to those found in [Cu(Me$_3$PS)Cl]$_3$ [19] [2.209(2) and 2.220(1) Å] but significantly shorter than those in other three-co-ordinate copper(I) complexes which, however, with one exception,[17] involve bridging chlorine atoms.[20-22] The short Cu–Cl distance in [Cu(bdtm)Cl], as compared to that in [Cu(2-thiouracil)$_2$Cl],[17] is presumably a reflection of the lower total electronic contribution from the more weakly bound phosphine-sulphide ligand.

TABLE 2

Selected bond lengths and angles

(*a*) Bonds (Å)

Cu–S(1)	2.321(2)	C(115)–C(116)	1.38(1)
Cu–S(2)	2.259(2)	C(116)–C(111)	1.39(1)
Cu–Cl	2.207(2)	P(2)–C(201)	1.811(6)
S(1)–P(1)	1.970(2)	C(201)–C(202)	1.37(1)
S(2)–P(2)	1.974(3)	C(202)–C(203)	1.40(1)
P(1)–C(1)	1.815(6)	C(203)–C(204)	1.38(1)
P(2)–C(1)	1.818(6)	C(204)–C(205)	1.39(1)
C(1)–C(101)	1.800(6)	C(205)–C(206)	1.39(1)
C(101)–C(102)	1.37(1)	C(206)–C(201)	1.39(1)
C(102)–C(103)	1.37(1)	P(2)–C(211)	1.800(7)
C(103)–C(104)	1.36(1)	C(211)–C(212)	1.40(1)
C(104)–C(105)	1.35(1)	C(212)–C(213)	1.37(1)
C(105)–C(106)	1.41(1)	C(213)–C(214)	1.33(1)
C(106)–C(101)	1.38(1)	C(214)–C(215)	1.37(1)
P(1)–C(111)	1.802(7)	C(215)–C(216)	1.37(1)
C(111)–C(112)	1.38(1)	C(216)–C(211)	1.36(1)
C(112)–C(113)	1.38(1)	C(2)–C(3)	1.44(1)
C(113)–C(114)	1.34(1)	C(2)–C(4)	1.45(1)
C(114)–C(115)	1.37(1)	C(2)–O	1.24(1)

(*b*) Angles (°)

S(1)–Cu–S(2)	119.23(6)	S(2)–P(2)–C(211)	113.5(2)
S(1)–Cu–Cl	113.11(7)	C(1)–P(2)–C(201)	103.6(3)
S(2)–Cu–Cl	123.32(8)	C(1)–P(2)–C(211)	107.9(3)
Cu–S(1)–P(1)	91.52(8)	C(201)–P(2)–C(211)	104.5(3)
Cu–S(2)–P(2)	95.68(8)	P(1)–C(1)–P(2)	117.2(3)
S(1)–P(1)–C(1)	113.8(2)	P(1)–C(101)–C(102)	123.1(5)
S(1)–P(2)–C(101)	112.4(2)	P(1)–C(101)–C(106)	118.1(5)
S(1)–P(1)–C(111)	113.5(2)	P(1)–C(111)–C(112)	119.4(5)
C(1)–P(1)–C(101)	104.6(4)	P(1)–C(111)–C(116)	120.8(5)
C(1)–P(1)–C(111)	106.0(3)	P(2)–C(201)–C(202)	119.3(5)
C(101)–P(1)–C(111)	105.9(3)	P(2)–C(201)–C(206)	120.2(5)
S(2)–P(2)–C(1)	114.3(2)	P(2)–C(211)–C(212)	118.7(5)
S(2)–P(2)–C(201)	112.1(2)	P(2)–C(211)–C(162)	123.1(5)

Mean Ph ring C–C distances: Ring 100 1.377(4), Ring 110 1.376(4), Ring 200 1.387(4), Ring 210 1.368(4)

The chelate ring, which adopts a very distorted boat conformation, shows some interesting features. The P–S distances are equal and do not reflect the differences in Cu–S lengths. However the Cu–S–P angles [91.52(8) and 95.68(8)°] are significantly smaller than expected (>100°).[19] From a number of structures involving co-ordinated tertiary-phosphine sulphide and related ligands it is evident that the sulphur atom exhibits a definite tendency to be tetrahedral and that the bonding may be regarded as simple σ donation from filled *sp*^{3} hybrid orbitals on the sulphur to the metal atom.[19] However the previously published structures all involve unidentate ligands {[Cr(CO)$_5$(Me$_3$PS)] (ref. 23), [Cu(Me$_3$PS)$_3$]$^+$ (ref. 16), [Cu(Me$_3$PS)Cl]$_3$ (ref. 19), and [MoOCl$_3$(Ph$_3$PS)] (ref. 24)}, a bridging bidentate ligand {[Cu(tmdpds)$_2$Cl$_2$]$_n$ (ref. 25)}, or chelating ligands bound to 'tetrahedral' metals {[Cu(tmdpds)$_2$Cl] (ref. 26) and [M{Me$_2$P(S)-NP(S)Me$_2$}$_2$] (ref. 27) (M = Fe and Ni)}. From a molecular model it is apparent that the formation of a six-membered chelate ring involving a three-co-ordinate trigonal copper(I) centre would be highly strained if all other angles were to remain approximately tetrahedral. The phosphorus and carbon atoms within the ring have relatively rigid steric requirements. Although the angles about the phosphorus atoms are approximately tetrahedral [103.6(3)—114.3(2)°] and lie within the range found for other co-ordinated phosphine-sulphide ligands [16,19,26] it is relevant that the largest angles are those involved in the chelate ring, *i.e.* S–P–Cl [113.8(2) and 114.3(2)°]. The P(1)–C(1)–P(2) angle [117.2(3)°] is also somewhat greater than tetrahedral. From the model it is apparent that a decrease in the Cu–S–P angles from the expected tetrahedral values will minimise strain in the chelate ring and possibly an increase in a Cu–S distance is also desirable. All other bond lengths and angles show no discrepancies from expected values. The acetone molecule simply fills a void and shows only non-bonding contacts with the complex.

During the progress of this work the crystal structure of a tetramethyldiphosphine disulphide complex [26] which has the same metal–ligand stoicheiometry as [Cu(bdtm)Cl]·Me$_2$CO was reported. In contrast, however,

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this complex [Cu(tmdpds)Cl]$_2$ forms a dimer which has a distorted tetrahedral geometry around the copper atom and involves bridging sulphide ligands. The preference for tetrahedral geometry probably results from the smaller 'bite' available in this ligand, and the fact that the methyl groups of the ligand would tend to make the sulphur atoms more basic than in bdtm and therefore more liable to form a bridged sulphur complex.

The structures of two other compounds discussed in this present paper have also recently been completed by other workers. [Cu(tmdpds)Cl$_2$]$_n$ has a polymeric structure [25] with approximately tetrahedral copper(II) atoms linked by bidentate tmdpds ligands and [Cu(tmdpds)$_2$][ClO$_4$] has a tetrahedral arrangement [28] of sulphur atoms about the copper(I) atom.

TABLE 3

I.r. spectral data (700—1 400 cm^{-1}) for tmdpds complexes [a]

Assignment [b]	tmdpds	[Cu(tmdpds)Cl]$_2$	[Cu(tmdpds)Br]$_n$	[Cu(tmdpds)$_2$][BF$_4$]	[Ag(tmdpds)$_2$][ClO$_4$]
P–CH$_3$ asymmetric stretch	733vs	722msh	720msh	722msh	727msh
		732s	728s	727s	730s
	747s	762m	755m	761m	760m
CH$_3$ rock and wag	824w	846w	838w	838w	838w
			854w		850w
	862vs	870w	863w	849w	860w
	883vs	906s	898s	893s	870w
		935s	925s	927s	895vs
	943vs	955s	945sbr	949s	930s
		960sh		961s	950s
C–H symmetric stretch	1 280	1 294m	1 290w	1 290s	1 290s
		1 304w	1 300w	1 310s	1 310m
		1 317w	1 310w		

[a] As Nujol mulls. [b] According to refs. 15 and 31. s = Strong, m = medium, w = weak, v = very, sh = shoulder.

Physicochemical Study of Copper(II) *and Copper*(I) *Complexes.*—I.r. spectra are reported in Table 1. For complexes containing bdtm ν(P:S) is lowered from 628 cm^{-1} in the free ligand by *ca.* 30—45 cm^{-1} in the complexes, indicating metal–sulphur bonding. For [Cu(bdtm)Cl]·Me$_2$CO a doublet at 573 and 598 cm^{-1} for ν(P:S) is reduced to a single band at 570 cm^{-1} on removal of the acetone by heating. For complexes containing bdte a lowering of *ca.* 20 cm^{-1} is observed, while for complexes of tmdpds two bands at *ca.* 595 and 557 cm^{-1} (instead of one at 568 cm^{-1} as in the free ligand) confirm the *cis* nature of the ligand in the complexes rather than the *trans* as found in the free form.[15] As expected this change in symmetry is reflected in the shifts and splittings in the methyl rocking frequencies (Table 3).

A band at 304 cm^{-1} in the far-i.r. spectrum of [Cu(bdtm)Cl$_2$] can be assigned to ν(Cu–Cl) and upon reduction to [Cu(bdtm)Cl]·Me$_2$CO this band moved to 274 cm^{-1}. This is consistent with a terminal Cu–Cl bond as found from the *X*-ray structure. Other three-co-ordinated derivatives of the type [CuLCl]$_3$ (L = Me$_3$PS or Me$_3$AsS) with terminal chlorines also have similar Cu–Cl stretching frequencies.[29] However for [Cu(bdtm)Cl]$_n$ a band at 230 cm^{-1} (at liquid-nitrogen temperature) assignable to ν(Cu–Cl) is indicative of bridging chlorine atoms. Furthermore molecular weights in 1,2-dichloroethane for both the copper(I) complexes {710 ± 10; calc. for [Cu(bdtm)Cl] 547, calc. for [Cu(bdtm)Cl]$_2$ 1 094} suggest that the complex [Cu-bdtm)Cl]$_n$ should be formulated as the tetrahedral dimer [Cu(bdtm)Cl]$_2$ but in solution it exists in equilibrium with the three-co-ordinated monomeric species. In the solid state the conversion from one species into the other is also possible. On gentle heating (100 °C, *ca.* 5 min) i.r. evidence indicates that the solvated acetone is lost from [Cu(bdtm)Cl]·Me$_2$CO without major structural change. The three-co-ordinate complex melts at 112—114 °C; however on further heating it resolidifies at *ca.* 140 °C and then remelts at 216—217 °C, the m.p. of the halogen-bridged species, [Cu(bdtm)Cl]$_2$. This is an unusual example of two copper(I) complexes having the same stoicheiometry but different structures.

For [Cu(bdte)Cl]$_n$ a broad band centred at 227 cm^{-1} may be assigned to ν(Cu–Cl) indicating halogen bridging. A dimeric structure ($n = 2$) is possible, or a polymeric one involving bdte bridges as well.[30] The i.r. spectrum of [Cu(tmdpds)Cl]$_2$ shows a band at 257 cm^{-1} assignable to ν(Cu–Cl), consistent with a terminal chlorine bound to a tetrahedral copper atom as found from the *X*-ray analysis.[26]

A Raman-active band at 440 cm^{-1} in solid tmdpds has been assigned [31] to ν(P–P). This band is not i.r.-active. A Raman study on [Cu(tmdpds)Cl]$_2$, [Cu(tmdpds)Br]$_n$, and [Cu(tmdpds)$_2$][BF$_4$] confirms that bands at 434, 434, and 439 cm^{-1} respectively can be assigned to ν(P–P). It is thus shown that complex formation involving sulphur atoms did not appreciably alter this frequency which for the complexes becomes weakly allowed in the i.r. This is supported by the observation that on hydrolysis of the complexes the P–P bond did not break.[15]

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Conductivity measurements are reported in Table 1. The complexes [Cu(bdtm)$_2$][ClO$_4$], [Cu(bdsm)$_2$][ClO$_4$], and [Cu(tmdpds)$_2$][BF$_4$] are 1 : 1 electrolytes in nitrobenzene or nitromethane suggesting these compounds have a tetrahedron of sulphur or selenium atoms about copper, as found from the single-crystal *X*-ray structure performed on [Cu(tmdpds)$_2$][ClO$_4$].[28] The molar conductivity values for the species [CuLX] (L = bdte, bdtm, or tmdpds; X = Br or Cl) (see Table 1) show some dissociation of essentially non-electrolytes (the values were calculated on the formula weights).

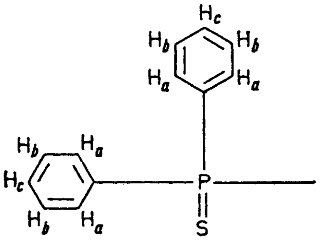
^{1}H N.m.r. spectra recorded for sufficiently soluble compounds are listed in Table 4. The expected deshielding of the methyl protons in [Cu(tmdpds)$_2$][BF$_4$] and [Cu(tmdpds)Cl]$_2$ is seen, again giving indication of bond formation between copper and sulphur and the reduction in electron density about the protons in the methyl groups. The methylene protons of [Cu(bdtm)-Cl]·Me$_2$CO are similarly affected but their shift (0.13 p.p.m.) is not as great as with the analogous phosphines (0.40 p.p.m.) where the methylene group is nearer to the directly co-ordinated phosphorus atom.[32] The phenyl protons are also deshielded in this complex. A multiplet is resolved into two groups of peaks which integrate in the ratio 2 : 3. The lower-field multiplet is assigned to the H$_a$ set of nuclei and the higher-field peaks to the H$_b$ and H$_c$ set.

TABLE 4

^{1}H N.m.r. spectral data; [a] τ values with *J*/Hz in parentheses

Compound	
tmdpds	8.12 (6.0) [b]
[Cu(tmdpds)$_2$][BF$_4$]	8.01 (6.0) [b]
[Cu(tmdpds)Cl]$_2$	7.96 (6.0) [b]
bdtm	6.09 (13.4),[c] 2.78, 2.41 [d]
[Cu(bdtm)Cl]·Me$_2$CO	5.96 (12.5),[c] 7.85,[e] 2.60, 2.22
[Cu(bdtm)$_2$][ClO$_4$]	5.94 (12.5,[c] 2.65), 2.32 [d]

[a] In (CD$_3$)$_2$CO for tmdpds compounds and in CDCl$_3$ for bdtm compounds. [b] CH$_3$, quartet, ^2J(P–H) + ^3J(P–H). [c] CH$_2$, triplet, *J*(P–H). [d] C$_6$H$_5$, multiplet. [e] CH$_3$.



The visible and near-i.r. absorption spectra are recorded in Table 5 for the copper(II) complexes. [Cu(bdtm)Cl$_2$], which was isolated in moderate purity, dissolved readily in acetone and the observation of broad *d–d* bands at 880 (ε ≈ 80) and 1 100 nm (shoulder, ε ≈ 40) are consistent with a distorted tetrahedral arrangement of ligands about copper(II). Furthermore, a molecular-weight measurement in acetone {found 544, calc. for [Cu(bdtm)Cl$_2$] 583} indicates the monomeric nature of the complex and also the chelating function of the ligand. The electronic spectrum is similar to that of those of other copper(II) complexes [33–35] to which the same stereochemistry has been assigned. As a molecular model shows no steric reasons for the distortion from a plane, presumably electronic factors are important.

TABLE 5

Electronic spectral data for the copper(II) complexes

	(λ$_{max.}$/nm) [a]	
Compound	S→Cu charge-transfer	*d–d*
[Cu(bdtm)Cl$_2$]	477 (340) [c]	880 (80),[c] 1 100sh (40 [c]
[Cu(bdte)Cl$_2$] [b]	477	890br
[Cu(tmdpds)Cl$_2$]	477	875, 1 100sh
[Cu(PhMe$_2$PS)$_2$Cl$_2$]	477	875, 1 100sh
[Cu(Ph$_2$MePS)$_2$Cl$_2$]	477 (260) [c]	880 (80),[c] 1 100sh (40) [c]

[a] Acetone solution. [b] Acetone–dichloromethane solution. [c] Extinction coefficient (ε/l cm^{-1} mol^{-1}) where this could be recorded.

The e.s.r. spectrum of [Cu(bdtm)Cl$_2$] was recorded in frozen acetone at 77 K and has $g_{\parallel}$ 2.348, $A_{\parallel}$ 137.6 G, and $g_{\perp}$ 2.051. We have also noticed another minor species with $A_{\parallel}$ 120 G and $g_{\parallel}$ 2.455. The e.s.r. spectra of pseudo-tetrahedral species have $A_{\parallel}$ values between 78 and 117 G.[36–38] The e.s.r. parameters are remarkably similar to those observed for copper(II) carboxypeptidase A for which a distorted tetrahedral structure has been suggested.[39]

Even though [Cu(bdte)Cl$_2$] was not isolated in a pure state, its *d–d* spectrum in acetone is similar to that of [Cu(bdtm)Cl$_2$] (Table 5) and hence a similar stereochemistry is assigned. Both solutions lose their orange colour and become colourless (*i.e.* reduction to the appropriate copper(I) derivatives) when set aside. In a similar way [Cu(tmdpds)Cl$_2$]$_n$ is assigned a pseudo-tetrahedral stereochemistry and this has been substantiated by a single-crystal *X*-ray analysis.[25]

These results prompted us to investigate the reactions of copper(II) chloride dihydrate with the bulky phosphine sulphides Me$_3$PS, PhMe$_2$PS, Ph$_2$MePS, and Ph$_3$PS when added (1 : 2 molar) in acetone. Other workers have tried similar reactions but by using alcohol as solvent only the reduced complexes were observed.[2] With Me$_3$PS reduction was instantaneous, whereas PhMe$_2$PS and Ph$_2$MePS both produced orange solutions which decolourized after 30 min, and whose visible spectra were similar to that of [Cu(bdtm)Cl$_2$] as were the e.s.r. spectra, but complications arose due to decomposition. Hence it appears that [Cu(PhMe$_2$PS)$_2$Cl$_2$] and

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$[Cu(Ph_2MePS)_2Cl_2]$ have been detected in solution, and furthermore that they have pseudotetrahedral structure as assigned for $[Cu(bdtm)Cl_2]$. Excess of ligand did not change the visible spectra. No reaction occurred with Ph_3PS. These unidentate phosphine sulphides quickly reduced acetone solutions containing $Cu[BF_4]_2\cdot6H_2O$. However for tris(2-methoxyphenyl)phosphine sulphide bands at 825 and 950sh nm were recorded before the copper(II) was reduced. Interestingly, Cotton and Goodgame[40] found that Ph_3PO reacted with copper(II) chloride dihydrate whereupon $[Cu(Ph_3PO)_2Cl_2]$ was isolated and this was considered to have a distorted tetrahedral structure. When solutions were set aside, reduction was completed and compounds of the type [CuLCl] were isolated.[28] For L = Me_3PS, this compound has been shown to be the trimer $[CuLCl]_3$ in which each copper(I) is three-co-ordinated.[19]

When $[Cu(bdtm)Cl]\cdot Me_2CO$ and Me_3PS (1 : 1 molar) were heated under reflux in alcohol the bidentate ligand bdtm was displaced and $[Cu(Me_3PS)Cl]_3$ isolated. The reaction of chlorine with the complexes produced a similar result. For example when chlorine gas was bubbled through an acetone suspension of $[Cu(bdtm)Cl]\cdot Me_2CO$ an orange solution resulted, which was essentially due to the pseudo-tetrahedral species $[CuCl_4]^{2-}$.[41] An i.r. spectrum of the resulting oil obtained showed attack by chlorine had also occurred at the P⁚S bond, since ν(P⁚S) was then absent. The nature of the other products was not determined.

Complexes of Silver, Mercury, Zinc, Platinum, and Palladium.—The complexes of silver are listed in Table 1. The disulphide ligands react readily with silver perchlorate to form $[AgL_2][ClO_4]$ (L = bdtm, tmdpds, bdsm, or bdse) which were 1 : 1 electrolytes and probably have tetrahedral structures. The i.r. spectra (Table 1) showed little change in ν(P⁚Se). This is similar to Meek's finding.[8]

Mercury(II) chloride reacted with L (L = bdtm, bdte, or bdsm) to form complexes $[HgLCl_2]$, which were nonelectrolytes (Table 1; far-i.r. spectra in the Experimental section). The ν(Hg–X) bands were consistent with the presence of terminal halogen. The molecular weight of $[Hg(bdtm)Cl_2]$ in acetone was found to be 526 (*cf.* calc. for monomer 720). $[Hg(bdtm)Br_2]$ has been prepared previously,[11] $[Hg(bdsm)Br_2]$ has been isolated in the present study, and $[Hg(tmdpds)X_2]$ (X = Cl, Br, or I) by Arshad *et al.*[15]

Platinum- and palladium-(II) chloride also formed nonelectrolyte complexes of the type $[PdLCl_2]\cdot nH_2O$ (L = bdtm, *n* = 0; L = bdsm, *n* = 2) (Table 1). No bischelated complexes could be obtained. Zinc and mercury perchlorate hexahydrate reacted with bdtm to form the 2 : 1 electrolytes $[Zn(bdtm)_2][ClO_4]_2$ and $[Hg(bdtm)_2][ClO_4]_2$ which are probably like the copper(I) derivatives and have a tetrahedral stereochemistry.

EXPERIMENTAL

I.r. spectra were recorded by use of a Beckman IR 20 spectrophotometer (4 000—250 cm^{-1}) and a Grubb–Parsons Cube Mk II Interferometer (300—40 cm^{-1}). N.m.r. spectra were measured on a JEOL JNM C 60 HL spectrometer and electronic spectra on a Shimadzu MPS 5000 spectrophotometer. Room-temperature conductivity measurements were made by use of Philips PR 9500 and PW 9510 conductivity meter and cell. Microanalyses were by Professor A. D. Campbell, University of Otago. Analytical data are summarised in Table 1.

Benzene was sodium dried. Other laboratory-grade solvents were used as purchased [bis(diphenylphosphino)-methane and -ethane were from Strem Chemicals Inc.].

Synthesis of Ligands.—The ligands bdtm and bdsm were synthesised following the method of Meek,[9] while bdte was obtained by the addition of a small excess of sulphur to bis(diphenylphosphino)ethane in warm benzene, and bdse by the addition of excess of KSeCN to the phosphine in acetonitrile following the method of Meek.[42] Yields and m.p.s were 71% and 227 °C, and 88% and 193 °C respectively; tmdpds was prepared by the method of ref. 43.

Preparation of the Complexes.—$[Cu(bdtm)Cl_2]$. To an acetone solution of $CuCl_2\cdot2H_2O$ (0.17 g, 1 mmol) was added an acetone solution of bdtm (0.448 g, 1 mmol). The volume of the resulting dark brown solution was rapidly reduced by use of a rotary evaporator. After the addition of diethyl ether to the cooled solution a brown solid (60%) was isolated, washed (diethyl ether), and dried *in vacuo*.

$[CuLCl]_n$ (L = bdtm, bdte, *or* tmdpds). In a typical preparation, to $CuCl_2\cdot2H_2O$ (2 mmol) dissolved in acetone was added the ligand (2 mmol) in acetone–dichloromethane. Reduction was enhanced by the addition of *ca.* 10 drops of hypophosphorous acid. For L = bdtm it was found that when the solution was set aside overnight $[Cu(bdtm)Cl]\cdot Me_2CO$ was isolated. Products (60—80%) were washed (diethyl ether) and dried *in vacuo*.

$[Cu(bdtm)Cl]_2$. To a suspension of CuCl (0.099 g, 1 mmol) in ethanol (40 cm^3) was added bdtm (0.448 g, 1 mmol) and the mixture heated under reflux (1 h). The volume of the filtered solution was then reduced to 20 cm^3, diethyl ether (10 cm^3) added, and the white product precipitated (0.27 g, 50%). The same complex was obtained from an ethanol solution of the ligand and $CuCl_2\cdot2H_2O$.

$[CuLBr]_n$ (L = bdtm, bdte, *or* tmdpds). These were obtained in a manner analogous to that for the chloro-derivatives. For bdtm, $[Cu(bdtm)Br]\cdot Me_2CO$ was first isolated, but readily lost acetone on gentle heating.

$[CuL_2][ClO_4]$ (L = bdtm *or* bdsm). In a typical preparation, to an ethanol solution of $Cu[ClO_4]_2\cdot6H_2O$ (0.5 mmol) was added an ethanol–dichloromethane (10 : 1) solution of the ligand (1 mmol). A crystalline product appeared when the solution was set aside overnight. For L = bdsm a small amount of selenium was filtered off and the solution reduced in volume causing precipitation of the product (*ca.* 60%).

Attempted preparation of $[Cu(tmdpds)_2][ClO_4]_2$. If acetone was used in the previous preparation for L = tmdpds, a brown precipitate, probably $[Cu(tmdpds)_2][ClO_4]_2$, appeared. However this compound was very shock-sensitive and no further characterisation was attempted.

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[Cu(tmdpds)$_2$][BF$_4$]. The ligand tmdpds (0.186 g, 1 mmol) in dichloromethane–acetone was added to Cu[BF$_4$]$_2$·6H$_2$O (0.172 g, 0.5 mmol) in acetone and *ca.* 10 drops hypophosphorous acid added. The white precipitate of the product (90%) was washed (ethanol) and dried *in vacuo*.

[AgL$_2$][ClO$_4$] (L = bdtm, bdsm, bdse, *or* tmdpds). In a typical preparation, to AgClO$_4$ (0.5 mmol) in ethanol was added the appropriate ligand (1 mmol) in dichloromethane–ethanol. If precipitation did not occur immediately the solution was reduced in volume. Diethyl ether was added and the resulting product washed (diethyl ether) and dried *in vacuo*. Yields were *ca.* 70%. **CAUTION** [Ag(tmdpds)$_2$][ClO$_4$] is sensitive to light and moisture, and *EXPLODES VIOLENTLY* on heating or with shock.

[Ag(bdtm)(NO$_3$)]·2H$_2$O. To AgNO$_3$ (0.17 g, 1 mmol) in ethanol–water (50 : 1) was added bdtm (0.44 g, 1 mmol) in acetone. The volume was reduced and precipitation effected by the addition of diethyl ether. The product (40%) was washed (diethyl ether), dried *in vacuo*, and stored in the dark.

[HgLX$_2$] (X = Cl, L = bdtm, bdte, bdsm, *or* bdse; X = Br, L = bdsm). In a typical preparation, to HgX$_2$ (0.5 mmol) in methanol or acetone was added the appropriate ligand (0.5 mmol) in dichloromethane–methanol. Generally a white precipitate appeared when the solution (30 cm^3) was set aside; otherwise the volume was reduced and diethyl ether added. Yields were 60—80%. I.r. data for [HgLCl$_2$] complexes, ν(Hg–Cl)/cm^{-1}: L = bdsm, 270s, 235vs; L = bdtm, 257s, 247sh; L = bdte, 271m, 255s; L = bdse, 245s, 235s. For [Hg(bdsm)Br$_2$], ν(Hg–Br)/cm^{-1}: 166s.

[Zn(bdtm)$_2$][ClO$_4$]$_2$. To Zn[ClO$_4$]$_2$·6H$_2$O (0.189 g, 0.5 mmol) dissolved in a minimum volume of hot ethanol containing ethyl orthoformate as dehydrating agent was added a hot ethanol solution of bdtm (0.448 g, 1 mmol). On cooling the free ligand crystallised first, followed by white crystals of the product.

[Hg(bdtm)$_2$][ClO$_4$]$_2$. The ligand bdtm (0.448 g, 1 mmol) dissolved in dichloromethane was added to Hg[ClO$_4$]$_2$·6H$_2$O (0.204 g, 0.5 mmol) dissolved in a minimum volume of acetone. The white product was washed (diethyl ether) and dried *in vacuo*.

[PdLCl$_2$]·nH$_2$O (L = bdtm, n = 0; L = bdsm, n = 2). In a typical preparation, to Na$_2$[PdCl$_4$]·3H$_2$O (0.5 mmol) in water–acetone (1 : 20) was added the ligand (0.5 mmol). Diethyl ether was added and the precipitated product (40%) washed thoroughly with water (to remove NaCl) and then diethyl ether. ν(Pd–Cl)/cm^{-1}: L = bdtm, 307, 287; L = bdsm, 310, 297.

[Pt(bdsm)Cl$_2$]. To [Pt(PhCN)$_2$Cl$_2$] (0.237 g, 0.5 mmol) in acetone was added bdsm (0.271 g, 0.5 mmol) in dichloromethane–acetone. A precipitate of the product (30%) appeared on warming.

Reaction of [Cu(bdtm)Cl]·Me$_2$CO *with* Me$_3$PS.—Me$_3$PS (0.054 g, 0.05 mmol) and the complex (0.275 g, 0.05 mmol) were suspended in ethanol and the solution heated under reflux for 30 min. After reducing the volume a white precipitate was isolated and identified as [Cu(Me$_3$PS)Cl]$_3$ from elemental analyses and a comparison of its i.r. spectrum with that of an authentic sample.[28, 29]

Reaction of the Complexes [CuLCl]$_n$ *with Chlorine.*—Chlorine was bubbled through an acetone suspension of [CuLCl]$_n$ until an orange solution resulted; this showed bands at 880 and 1 130 nm in its electronic absorption spectrum typical of [CuCl$_4$]$^{2-}$ species.[41] Although a solid compound could not be isolated from the oil obtained on reduction of the volume, the oil showed no band in its i.r. spectrum in the range expected for ν(P:S).

Crystal Structure of Cu(bdtm)Cl·Me$_2$CO.—*Crystal data.* C$_{28}$H$_{28}$ClCuP$_2$S$_2$O, M = 605.6, F(000) = 312, a = 17.185(2), b = 13.640(3), c = 12.058(1) Å, U = 2 826.436 Å^3, D_m (flotation) = 1.39, Z = 4, D_c = 1.42 g cm^{-3}. F(000) = 312. Mo-K_α X-radiation (Zr-filtered), λ = 0.710 7 Å; μ(Mo-K_α) = 11.7 cm^{-1}. Space group $Pna2_1$.

TABLE 6

Positional and thermal parameters for the crystal structure of [Cu(bdtm)Cl]·Me$_2$CO

	x/a	y/b	z/c	U/Å^2 ×10^2
Cu	0.212 57(5)	0.181 98(5)	0.000 00	*
S(1)	0.318 4(1)	0 233 8(1)	0.104 2(2)	*
S(2)	0.110 6(1)	0.284 3(1)	−0.023 6(2)	*
P(1)	0.305 61(8)	0.3697 (1)	0.052 0(2)	*
P(2)	0.130 11(8)	0.362 7(1)	0.111 1(1)	*
Cl	0.231 6(1)	0.038 8(1)	−0.080 8(2)	*
C(1)	0.220 9(3)	0.431 2(4)	0.108 9(5)	3.38(12)
C(101)	0.386 3)3)	0.446 7(4)	0.090 4(5)	3.83(14)
C(102)	0.385 2(4)	0.507 4(5)	0.180 9(6)	5.32(17)
C(103)	0.449 8(5)	0.561 7(6)	0.207 6(8)	7.69(24)
C(104)	0.516 5(5)	0.556 6(6)	0.147 7(7)	6.82(21)
C(105)	0.520 2(5)	0.495 2(6)	0.059 8(7)	6.42(20)
C(106)	0.454 5(4)	0.438 5(4)	0.030 1(5)	4.55(16)
C(111)	0.297 1(3)	0.379 9(5)	−0.096 5(5)	3.80(14)
C(112)	0.277 2(4)	0.469 1(5)	−0.143 1(6)	4.76(16)
C(113)	0.268 1(4)	0.475 9(6)	−0.256 9(7)	5.62(19)
C(114)	0.277 7(4)	0.396 5(6)	−0.321 5(7)	5.85(19)
C(115)	0.297 0(4)	0.307 5(6)	−0.276 8(7)	5.98(20)
C(116)	0.308 8(4)	0.299 0(5)	−0.164 2(7)	4.58(18)
C(201)	0.056 9(3)	0.456 6(4)	0.131 5(5)	3.75(13)
C(202)	−0.082 9(4)	0.449 0(5)	0.077 0(6)	4.66(16)
C(203)	−0.071 2(4)	0.519 1(5)	0.095 1(7)	6.07(19)
C(204)	−0.057 6(5)	0.595 0(6)	0.168 8(7)	6.29(19)
C(205)	0.013 5(5)	0.603 4(6)	0.223 3(7)	6.55(21)
C(206)	0.070 3(4)	0.533 0(5)	0.205 0(6)	5.00(17)
C(211)	0.127 9(3)	0.291 7(4)	0.236 9(5)	3.42(13)
C(212)	0.086 1(4)	0.203 9(5)	0.238 0(6)	4.77(16)
C(213)	0.079 2(4)	0.151 4(6)	0.334 3(7)	5.78(18)
C(214)	0.110 8(4)	0.183 4(5)	0.428 6(6)	5.25(17)
C(215)	0.151 9(4)	4.269 1(5)	0.429 2(7)	5.47(18)
C(216)	0.158 6(4)	0.323 9(5)	0.334 7(6)	5.09(17)
C(2)	0.370 4(4)	0.179 6(5)	0.434 1(6)	4.86(16)
C(3)	0.418 0(5)	0.112 7(7)	0.370 6(8)	7.84(25)
C(4)	0.380 6(5)	0.284 2(6)	0.416 9(8)	7.15(23)
O	0.320 7(3)	0.147 4(4)	0.498 6(5)	6.96(14)

* Anisotropic thermal parameters: the form of the thermal ellipsoids is given by exp $[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$, with parameters:

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	6.11(5)	3.91(4)	5.08(5)	0.07(4)	0.79(4)	0.48(4)
S(1)	5.04(9)	3.43(8)	5.41(9)	0.62(7)	−0.61(9)	0.70(8)
S(2)	4.52(9)	5.14(9)	4.14(10)	0.09(7)	−0.50(7)	−0.93(7)
P(1)	2.93(7)	3.39(8)	3.65(8)	0.23(6)	0.17(6)	0.40(7)
P(2)	2.90(7)	3.37(7)	3.65(7)	−0.06(6)	0.15(7)	0.05(7)
Cl	7.47(12)	4.30(9)	5.80(11)	0.98(8)	−0.77(9)	−1.49(9)

Data collection. The crystals were close to octahedral in habit. Approximate cell dimensions and space-group absences were determined from Weissenberg and precession photographs. The absences ($0kl$, $k + 1 = 2n + 1$; $h0l$, $h = 2n + 1$) are consistent with space groups $Pna2_1$ and re-oriented $Pnma$. Subsequent structure solution and refinement showed $Pna2_1$ to be the correct choice. The observed density indicated that one molecule of acetone per ligand was present, which was substantiated by an integrated n.m.r. spectrum. Unit-cell dimensions were refined[44] by a least-squares treatment of the setting angles of

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[44] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1967, **22**, 457.

12 reflections centred automatically on a Hilger and Watts Y 290 diffractometer controlled by a PDP 81 computer.

The crystal employed for data collection was of maximum dimensions 0.45 × 0.6 × 0.6 mm, and was oriented to make an angle of *ca.* 8° between the *b* axis and ϕ axis of the diffractometer in order to minimise multiple-diffraction effects. The intensities were measured by the θ–2θ scan technique, with 60 steps of 1 s^{-1}. The local background was measured for 15 s at each end of the step scan by the stationary-counter–stationary-crystal technique. The intensities of 3 reflections well separated in reciprocal space measured periodically throughout data collection showed only random fluctuations of up to $\pm 2\%$ in their mean values.

All independent reflections in the *hkl* octant with $\theta < 32°$ were measured. The integrated intensities and their standard deviations were derived as described by Corfield *et al.*[45] with an 'uncertainty' factor *p* of 0.05. Of the 4 330 reflections collected, 2 876 with $I > 3\sigma(I)$ were used in the subsequent analysis. Data were corrected for absorption effects by the Gaussian quadrature method,[46] absorption co-efficients ranging from 1.596 to 1.439.

Solution and refinement. A Patterson function was calculated and the copper atom was located in the *xy* plane. The structure was solved by the normal combination of least-squares refinements and Fourier syntheses.[47] The quantity minimised in the least-squares refinements was $\Sigma w(|F_o| - |F_c|)^2$ where the weight w is $[2F_o/\sigma(F_o)]^2$. Scattering factors for copper were taken from ref. 48, for hydrogen atoms from ref. 49 and for all other atoms from ref. 50. Anomalous dispersion corrections for Cu, Cl, S, and P atoms were included.[51]

After all non-hydrogen atoms in the asymmetric unit had been located, refinement was carried to convergence, the copper, phosphorus, sulphur, and chlorine atoms having anisotropic temperature factors, the remaining atoms being refined isotropically. Hydrogen atoms were then placed in their idealised positions, assuming C–H 0.95 Å.[52] Two further cycles of least-squares refinement carried out with the hydrogen atoms included in the structure-factor calculation with an isotropic temperature factor of 6.0 Å^2 gave R 0.052 and the weighted factor, R', 0.064 where $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}$. Parameter changes in this final cycle were all $< 0.20\sigma$. A final difference-Fourier synthesis gave no peaks > 0.12 of that expected for a carbon atom, and a weighting analysis showed no dependence of $\Sigma w||F_o| - |F_c||^2$ on either $\sin\theta/\lambda$ or $|F_o|$. When the polarity of the molecule was checked by refining the enantiomorph to convergence, no significant difference could be detected. Final observed and calculated structure factors are listed together with hydrogen-atom positions in Supplementary Publication SUP 21739 (20 pp., 1 microfiche).* The refined atom co-ordinates and thermal parameters are listed in Table 6.

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* See Notice in Authors No. 7, in *J.C.S. Dalton* 1975, Index issue.

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