

Di- μ -chloro-bis[μ -1,2-bis(diphenylphosphinothioyl)ethane]-dicopper(I)

BY KEVIN L. BROWN

Chemistry Division, DSIR, Private Bag, Petone, New Zealand

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Abstract. $C_{52}H_{48}Cl_2Cu_2P_4S_4$, $Cu_2(C_{26}H_{24}P_2S_2)_2Cl_2$, $M_r = 1123.12$, monoclinic, $P2_1/n$, $a = 13.225$ (1), $b = 14.615$ (2), $c = 14.056$ (2) Å, $\beta = 105.99$ (1)° (Cu $K\alpha$, $\lambda = 1.5418$ Å); $Z = 2$, $D_m = 1.43$, $D_c = 1.43$ Mg m^{-3} , $R = 0.052$ for 2189 diffractometer data. The molecule exists as a dimer containing a crystallographic centre of symmetry. The Cu atoms are bonded to two S and two Cl atoms in a distorted tetrahedral geometry. Both the Cl atoms and the ligand act as bridges between the two Cu atoms.

Introduction. Phosphine sulphides of the type $R_2P(S)(CH_2)_n(S)PR_2$ form a series of bidentate metal complexes with transition metals. For bis(diphenylphosphinothioyl)methane (bdtm), $R = C_6H_5$, and $n = 1$, the complex $Cu^I(bdtm)Cl$ was isolated. An X-ray crystal analysis showed this complex to be a three-coordinated Cu monomer. The infrared spectrum of the equivalent ethane complex ($R = C_6H_5$, $n = 2$), $Cu(bdte)Cl$, suggested that it was not isostructural with $Cu(bdtm)Cl$, but instead had a chloro bridging structure (Ainscough, Bergen, Brodie & Brown, 1976). The present determination was undertaken to confirm this point.

The crystals were colourless octahedra. Intensities and cell dimensions were obtained from a crystal with maximum and minimum dimensions 0.25 and 0.11 mm. The systematic absences: $0k0$, $k \neq 2n$ and $h0l$, $h + l \neq 2n$, indicated space group $P2_1/n$. Cell dimensions were determined by least-squares refinement of the parameters of 12 reflections centred on a Hilger & Watts automated diffractometer. Data were collected to a maximum of $\theta = 53^\circ$ (Ni-filtered Cu $K\alpha$, $\theta - 2\theta$ scan, scan width = 0.70° , scan time = 105 s). Three standard reflections measured periodically showed only random fluctuations of $\pm 1.5\%$.

Intensity measurements were obtained for 3152 reflections, of which 2189 were considered observed ($I > 3\sigma_I$). Absorption corrections were applied (de Meulenaer & Tompa, 1965), the transmission coefficients ranging from 0.495 to 0.661. The structure was solved by direct methods and refined by a full-matrix least-squares procedure with experimental weights $w = 4F_o^2/\sigma_I^2$. The non-hydrogen atoms were refined with anisotropic thermal parameters and only the positional parameters of the H atoms were only

($U_H = 6.0$ Å²). At convergence (all shifts $< e.s.d.'s$), $R = 0.052$ and $R_w = 0.075$. A final difference synthesis showed no unusual features.

The atomic coordinates for the non-hydrogen atoms are given in Table 1, and a selection of bond lengths and angles in Table 2.* A general view of the molecule showing the numbering scheme is given in Fig. 1.

* Lists of anisotropic thermal parameters for the non-hydrogen atoms, hydrogen atom coordinates, bond lengths and angles and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34025 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ($\times 10^4$) for the non-hydrogen atoms (*e.s.d.'s* in parentheses)

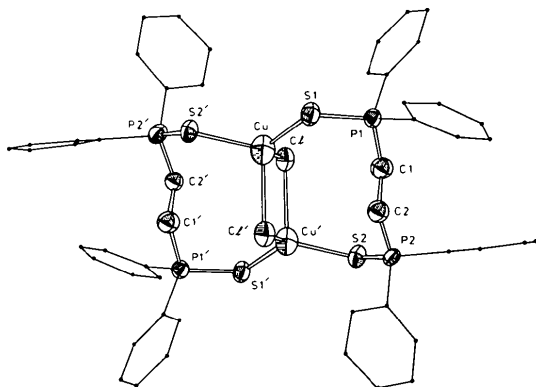
	<i>x</i>	<i>y</i>	<i>z</i>
Cu	4215 (1)	825 (1)	197 (1)
S(1)	2826 (2)	476 (1)	823 (1)
S(2)	6150 (2)	-2136 (1)	746 (1)
P(1)	3425 (2)	-194 (1)	2082 (1)
P(2)	4850 (1)	-2594 (1)	1031 (1)
Cl	4076 (2)	-520 (1)	-1086 (1)
C(1)	4405 (6)	-1023 (5)	1983 (6)
C(2)	3943 (6)	-1684 (5)	1138 (5)
C(101)	2437 (6)	-833 (5)	2465 (6)
C(102)	1397 (8)	-840 (7)	1942 (7)
C(103)	661 (8)	-1338 (9)	2266 (9)
C(104)	1024 (11)	-1863 (8)	3105 (9)
C(105)	2023 (10)	-1899 (8)	3626 (9)
C(106)	2741 (8)	-1378 (8)	3313 (7)
C(111)	4025 (7)	545 (5)	3111 (6)
C(112)	3449 (8)	875 (7)	3722 (8)
C(113)	3843 (11)	1472 (10)	4453 (9)
C(114)	4846 (12)	1774 (9)	4622 (8)
C(115)	5454 (10)	1477 (10)	3998 (10)
C(116)	5027 (9)	852 (8)	3253 (8)
C(201)	4069 (6)	-3356 (6)	104 (6)
C(202)	3969 (8)	-4280 (6)	281 (7)
C(203)	3389 (9)	-4843 (7)	448 (8)
C(204)	2864 (8)	-4482 (8)	-1343 (8)
C(205)	2963 (8)	-3563 (7)	-1541 (7)
C(206)	3553 (7)	-3013 (6)	-820 (6)
C(211)	5160 (6)	-3183 (5)	2205 (5)
C(212)	6157 (6)	-3528 (7)	2621 (7)
C(213)	6347 (8)	-3988 (8)	3528 (8)
C(214)	5612 (8)	-4058 (7)	4022 (7)
C(215)	4638 (8)	-3712 (7)	3608 (6)
C(216)	4388 (7)	-3290 (6)	2705 (6)

Table 2. Selected bond lengths (Å) and angles (°) (*e.s.d.*'s in parentheses)

Cu—Cl	2.305 (2)	Cl—Cu—Cl'	95.76 (10)
Cu—Cl'	2.639 (2)	Cl—Cu—S(1)	121.07 (10)
Cu—S(1)	2.303 (3)	Cl—Cu—S(2)	119.46 (10)
Cu—S(2)	2.305 (3)	S(1)—Cu—S(2)	109.92 (9)
S(1)—P(1)	1.986 (3)	S(1)—Cu—Cl'	100.62 (10)
S(2)—P(2)	1.985 (3)	S(2)—Cu—Cl'	105.19 (10)
P(1)—C(1)	1.807 (9)	Cu—S(1)—P(1)	106.57 (11)
C(1)—C(2)	1.523 (10)	S(1)—P(1)—C(1)	112.4 (3)
C(2)—P(2)	1.825 (8)	P(1)—C(1)—C(2)	110.1 (5)
P(1)—C(101)	1.806 (9)	C(1)—C(2)—P(2)	113.2 (5)
P(1)—C(111)	1.804 (8)	C(2)—P(2)—S(2)	113.4 (3)
P(2)—C(201)	1.807 (8)	P(2)—S(2)—Cu'	109.88 (10)
P(2)—C(211)	1.805 (7)		

Average phenyl C—C

Ring 10	1.37 (2)	Ring 20	1.37 (2)
Ring 11	1.37 (2)	Ring 21	1.38 (2)

Fig. 1. A view of the dimeric molecule [Cu(bdte)Cl]₂. Thermal ellipsoids (for the non-phenyl atoms) are drawn at the 50% probability level.

Discussion. The molecule exists as a dimer [Cu(bdte)Cl]₂ containing two bdte ligands related by the crystallographic centre of symmetry. The two Cu atoms are bridged both by the ligand and by the Cl atoms. The Cu atom adopts a distorted tetrahedral coordination sphere of two Cl and two S atoms. The Cl atoms are not bonded symmetrically to the two Cu atoms (Cu—Cl = 2.305, Cu—Cl' = 2.639 Å). The shorter Cu—Cl bond is longer than that in Cu(bdtm)Cl

(2.203 Å), but both are typical for bridging Cu^I—Cl—Cu^I (Albano, Bellon, Ciani & Manassero, 1972; Baenziger, Richards & Doyle, 1964). The two Cu—S bonds are intermediate in length between the two values obtained for Cu(bdtm)Cl, but in the normal range for non-bridging tetrahedral Cu—S bonds (Taylor, Weinger & Amma, 1974). The bond lengths within the chelate show no unusual features. The two Cu—S—P angles are considerably larger (109.9, 106.6°) than in Cu(bdtm)Cl (91.5, 95.7°), reflecting the tendency for the S atom to bond tetrahedrally when the ring strain is lowered (Tiethof, Stalick & Meek, 1973). There are no short intermolecular contacts.

Structural data are now available for the Cu^I-chloro complexes of R₂P(S)(CH₂)_n(S)PR₂ with *n* = 0, 1 and 2. As the electronic structure of the ligand is similar in each case, the differences in the Cu coordination geometry must depend on the steric requirements of the ligand. The bite of the *n* = 0 ligand is too small (S—Cu—S = 103°) to form a trigonal-planar complex, and the compound forms a S-shared dimer with a tetrahedral Cu coordination sphere (Cotton, Frenz, Hunter & Mester, 1974). The *n* = 1 complex has a larger bite (S—Cu—S = 119.2°) and can form either a trigonal planar monomer (Ainscough, Bergen, Brodie & Brown, 1976) or the S-shared tetrahedral dimer (Brown, 1978). The *n* = 2 complex (present study) is capable of a larger bite still, and prefers to bridge two Cu atoms with a shared Cl bridge.

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