Crystal and Molecular Structure of μ-Chloro-chlorobis[3,4-bis(2-aminoethylthio)toluene]dicopper(II) Diperchlorate

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Crystals of the title compound are monoclinic, a = 12.323(2), b = 10.426(3), c = 27.689(6) Å, β = 101.53(2)°, Z = 8, space group $P2_1/c$. The complex cation is binuclear with one bridging chloride ion. The stereochemistry at one copper centre is distorted octahedral and at the other distorted square pyramidal. The copper–nitrogen bonds occupy *trans*-equatorial positions and are similar in length (Cu–N 1.99, 2.02, and 1.98 Å at the two centres) whereas a sulphur donor occupies an axial site in each co-ordination sphere to give two long copper–sulphur bonds (2.61 and 2.57 Å). The remaining two equatorial bonds (Cu–S 2.45 and 2.43 Å) are also somewhat longer than usual. The structure was determined by a combination of Patterson and direct methods from 1 733 diffractometer intensities, and refined by full-matrix least-squares techniques to R 0.062.

REACTIONS between copper(II) ions and sulphur-containing ligands have received increasing attention in recent years [1-4] and the possibility of using complexes so prepared as models for cupro-enzymes has been considered.[5] Their redox capabilities are clearly one feature of interest in this connection but one which poses preparative problems. Thus thiol groups generally reduce copper(II) to copper(I) and only thioethers or particular unsaturated thiol ligands, such as 2-aminothiophenol or dithiocarbamates, provide the required stability. A further problem is raised by thioethers since it appears that they do not have a high affinity for copper(II).[6] In an attempt to prepare a stable copper(II) complex with sulphur donors the ligand 3,4-bis(2-aminoethylthio)-toluene was synthesised and allowed to react with simple copper salts. This brought a further difficulty to light in that the anions proved to be a factor in stabilising a crystalline product. In particular, it proved necessary to use chloride and perchlorate ions. An X-ray structural analysis of the product, characterised as having the stoicheiometry $CuLCl(ClO_4)$, was therefore undertaken to investigate the co-ordination arrangement of the ligand, the bonding ability of the thioether donors, and the specific roles of chloride and perchlorate (an anion dependence also observed in other systems [7-11]).

EXPERIMENTAL

Crystal Data.—$C_{11}H_{18}Cl_2CuN_2O_4S_2$, M = 440.5, Monoclinic, a = 12.323(2), b = 10.426(3), c = 27.689(6) Å, β = 101.53(2)° (from a least-squares fit to the diffractometer coordinates of 12 reflexions [12]), U = 3 486 Å,[3] D_m = 1.69 (by flotation), Z = 8, D_c = 1.68. Space group $P2_1/c$. Mo-K_α radiation, λ = 0.7107 Å; μ(Mo-K_α) = 18.2 cm^{-1}.

Intensity data were collected by four-circle diffractometry (Hilger–Watts computer-controlled Y 290) by use of a θ—ω step scan. A total of 1 733 intensity measurements with values $>2\sigma(I)$ were classed as observed. The crystal had dimensions 0.33 × 0.99 × 0.22 mm in the a, b, and c directions respectively. Absorption corrections [13] were applied by use of a 192 block Gaussian integration. Intensities were corrected to amplitudes with standard deviations, $\sigma(F^2)$, containing a p-factor [14] of 0.07. The weighting scheme for least-squares refinement, $w = 4F^2/\sigma^2(F^2)$, then down-weighted intense reflexions.

Structure solution proved unexpectedly difficult. A three-dimensional Patterson map gave a number of apparent solutions for the positions of the two copper atoms in the asymmetric unit but subsequent 'heavy-atom phased' electron-density maps could not be interpreted. Eventually recourse was had to 'direct' methods and the computer program *Multan*.[15] The normalised E values were in good agreement with the theoretical distribution but we found it impossible to define an origin which did not lead to a closed set of reflexions. A reappraisal of the Patterson map was then made, perhaps with fewer preconceptions about peak heights and features to be expected on initial electron-density maps. One solution (copper atoms at 0.31,0.03,0.18 and 0.11,0,0.29) finally proved productive and after tiresome, but conventional, problems with imposed symmetry all the expected non-hydrogen atoms were located properly. Refinement was by full-matrix least-squares methods checked by an electron-density map to aid the correct distribution of atoms relative to the imposed symmetry element and a 'difference' map to locate hydrogen atoms. This also revealed that one perchlorate group, containing Cl(4), would be better approximated by two half-weighted sets of oxygen atoms. All hydrogen atoms were placed at calculated positions after location and assumed to have an isotropic temperature factor of B 7.5 Å^2. Their parameters were not refined. With the exception of the disordered oxygen atoms all other non-hydrogen atoms were described anisotropically. A Hamilton statistical test [16] suggested that the progressive relaxing of constraints on the model produced drops in the conventional R factor which were significant at the 99.5% level. Refinement converged at R 0.062 with all shift-to-σ ratios <0.3.

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Atom co-ordinates, temperature parameters, bond lengths, and bond angles are listed in Tables 1—4. The atom numbering scheme is shown in Figure 1. Structure-factor data are listed in Supplementary Publication No. SUP 21338 (6 pp., 1 microfiche).*

TABLE 1

Atom co-ordinates, with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu(1)	0.11199(18)	−0.02181(26)	0.28765(9)
Cu(2)	0.30925(18)	0.03164(27)	0.17889(10)
Cl(1)	0.1348(5)	−0.1857(6)	0.2343(3)
Cl(2)	0.2594(4)	0.1450(6)	0.2425(2)
Cl(3)	−0.1083(4)	0.1065(6)	0.0940(2)
Cl(4)	0.5729(5)	−0.0177(7)	0.3579(3)
S(101)	−0.0451(4)	−0.0966(6)	0.3319(2)
S(102)	0.1186(4)	0.1651(6)	0.3415(2)
S(201)	0.2763(5)	−0.1170(6)	0.1098(2)
S(202)	0.5006(5)	0.0652(6)	0.1577(2)
O(101)	−0.1586(13)	0.0224(17)	0.0585(6)
O(102)	0.9802(11)	0.0487(18)	0.1273(5)
O(103)	−0.1820(13)	0.1540(17)	0.1223(7)
O(104)	0.9421(20)	0.2082(21)	0.0726(8)
O(201)	0.572(3)	0.001(4)	0.410(2)
O*(201)	0.531(4)	0.071(5)	0.389(2)
O(202)	0.625(5)	0.056(7)	0.326(2)
O*(202)	0.642(4)	0.094(5)	0.347(2)
O(203)	0.633(3)	−0.114(4)	0.388(2)
O*(203)	0.643(4)	−0.120(5)	0.347(2)
O(204)	0.476(3)	−0.091(4)	0.331(1)
O*(204)	0.468(2)	0.016(3)	0.327(1)
N(101)	−0.0105(12)	0.0526(14)	0.2377(5)
N(102)	0.2382(12)	−0.0928(17)	0.3387(6)
N(201)	0.2281(12)	0.1592(16)	0.1320(6)
N(202)	0.3847(11)	−0.1004(18)	0.2248(6)
C(101)	−0.1189(14)	−0.0239(24)	0.2358(7)
C(102)	−0.1504(15)	−0.0214(20)	0.2834(7)
C(103)	−0.0392(14)	0.0175(19)	0.3794(7)
C(104)	−0.1023(11)	−0.0029(21)	0.4169(6)
C(105)	−0.0990(18)	0.0848(28)	0.4524(8)
C(106)	−0.1738(17)	0.0564(25)	0.4919(8)
C(107)	−0.0289(18)	0.1895(22)	0.4574(8)
C(108)	0.0324(18)	0.2124(23)	0.4215(8)
C(109)	0.0292(16)	0.1274(21)	0.3843(7)
C(110)	0.2516(18)	0.1154(29)	0.3795(8)
C(111)	0.2599(19)	−0.0235(29)	0.3886(9)
C(201)	0.2247(17)	0.1271(25)	0.0779(7)
C(202)	0.1881(17)	−0.0076(25)	0.0677(9)
C(203)	0.4011(17)	−0.1091(24)	0.0859(8)
C(204)	0.4031(20)	−0.1872(24)	0.0438(9)
C(205)	0.4985(22)	−0.1886(25)	0.0234(8)
C(206)	0.4981(22)	−0.2782(28)	−0.0205(10)
C(207)	0.5883(17)	−0.1126(23)	0.0436(9)
C(208)	0.5814(16)	−0.0383(22)	0.0813(8)
C(209)	0.4931(15)	−0.0319(19)	0.1081(7)
C(210)	0.5637(15)	−0.0461(25)	0.2068(8)
C(211)	0.4862(20)	−0.1554(28)	0.2130(12)
HN(101)	−0.013	0.150	0.251
H′N(101)	0.000	0.048	0.200
HC(101)	−0.214	−0.044	0.226
H′C(101)	−0.095	−0.063	0.203
HC(102)	−0.230	−0.077	0.275
H′C(102)	−0.156	0.065	0.302
HC(110)	0.248	0.171	0.411
H′C(110)	0.319	0.123	0.363
HC(111)	0.187	−0.050	0.406
H′C(111)	0.331	−0.047	0.408
HN(102)	0.219	−0.184	0.352
H′N(102)	0.296	−0.083	0.317
HN(201)	0.267	0.247	0.140
H′N(201)	0.141	0.153	0.138
HC(201)	0.300	0.156	0.073
H′C(201)	0.159	0.183	0.051
HC(202)	0.095	−0.004	0.071
H′C(202)	0.183	−0.047	0.031
HC(210)	0.570	−0.050	0.242
H′C(210)	0.622	−0.032	0.183
HC(211)	0.448	0.232	0.187
H′C(211)	0.559	−0.211	0.234
HN(202)	0.320	−0.170	0.223
H′N(202)	0.425	−0.069	0.262
HC(104)	−0.147	−0.099	0.413
HC(107)	−0.040	0.246	0.486
HC(108)	0.089	0.303	0.428
HC(204)	0.339	−0.251	0.031
HC(207)	0.662	−0.120	0.032
HC(208)	0.641	0.025	0.094
HC(106)	−0.203	0.026	0.524
H′C(106)	−0.235	0.039	0.513
H″C(106)	−0.116	0.079	0.468
HC(206)	0.499	−0.340	−0.053
H′C(206)	0.419	−0.230	−0.027
H″C(206)	0.575	−0.331	−0.014

TABLE 2

Thermal parameters *, with estimated standard deviations in parentheses

(*a*) Anisotropic (× 10^3)

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cu(1)	4.7(2)	9.8(4)	1.3(1)	−0.1(2)	0.5(1)	0.1(1)
Cu(2)	4.3(2)	11.3(4)	1.7(1)	0.7(2)	0.6(1)	0.1(1)
Cl(1)	5.6(5)	8.2(8)	2.5(1)	−1.6(5)	0.9(2)	−1.1(3)
Cl(2)	7.2(5)	9.4(8)	1.5(1)	−1.4(5)	1.1(2)	−0.1(2)
Cl(3)	7.3(5)	11.4(8)	1.4(1)	0.8(5)	0.4(2)	0.2(3)
Cl(4)	7.4(5)	15.9(10)	2.1(1)	0.4(6)	0.4(2)	0.1(3)
S(101)	4.7(5)	8.5(7)	1.5(1)	−1.3(5)	0.8(2)	0.3(3)
S(102)	5.5(5)	8.6(8)	1.6(1)	−1.4(5)	0.4(2)	0.1(2)
S(201)	5.6(5)	1.1(9)	2.1(1)	−1.1(6)	0.9(2)	−0.5(3)
S(202)	5.6(2)	11.8(9)	2.1(1)	−2.2(5)	1.3(2)	−1.7(2)
O(101)	15(2)	23(3)	2.7(4)	−2(2)	−0.9(6)	−6.2(8)
O(102)	8.7(13)	32(4)	1.5(3)	6(2)	1.0(5)	1.1(8)
O(103)	10(2)	20(3)	4.4(5)	2(2)	2.8(7)	−5.4(10)
O(104)	23(3)	26(4)	3.9(5)	−5(3)	1.9(9)	5.0(11)
N(101)	6.1(14)	4(2)	1.5(3)	−1(1)	1.5(5)	0.2(6)
N(102)	4.5(14)	11(2)	1.7(3)	−2(1)	0.1(5)	1.3(8)
N(201)	7.2(15)	11(2)	1.2(3)	−3(2)	0.8(5)	0.4(7)
N(202)	3.5(13)	12(3)	2.2(4)	0(2)	−1.3(5)	0.4(8)
C(101)	45.0(17)	21(4)	0.8(4)	−2(2)	−0.2(6)	0.1(10)
C(102)	6.2(17)	7(3)	1.1(4)	0(2)	0.1(6)	−0.2(9)
C(103)	4.8(16)	5(3)	0.9(3)	2(2)	−1.5(6)	−1.3(8)
C(104)	1.0(13)	21(4)	0.8(3)	4(2)	−0.4(5)	1.6(9)
C(105)	7(2)	18(4)	0.9(4)	5(2)	−0.4(8)	−1.2(11)
C(106)	8(2)	26(5)	1.9(5)	2(3)	3.3(9)	−0.6(12)
C(107)	5(2)	6(3)	1.3(5)	1(2)	−2.1(8)	−0.2(9)
C(108)	9(2)	17(4)	0.6(4)	−6(2)	0.9(8)	0.5(10)
C(109)	9(2)	12(3)	0.7(4)	−3(2)	1.0(7)	0.2(9)
C(110)	8(2)	23(5)	0.8(4)	−2(3)	0.5(8)	0.6(12)
C(111)	8(2)	17(4)	1.9(5)	2(3)	−0.6(8)	0.4(13)
C(201)	6(2)	17(4)	0.8(4)	2(2)	−0.4(7)	−0.1(11)
C(202)	6(2)	12(4)	2.6(6)	2(2)	−1.0(8)	−2.5(11)
C(203)	6(2)	15(4)	1.5(4)	1(2)	0.5(7)	−0.4(12)
C(204)	9(2)	14(4)	1.5(5)	−4(3)	−0.3(9)	0.0(11)
C(205)	10(3)	16(4)	0.8(4)	2(3)	1.1(9)	−1.7(11)
C(206)	14(3)	26(5)	2.8(7)	−2(3)	2.6(12)	−6.0(16)
C(207)	5(2)	7(3)	2.7(6)	2(2)	1.3(9)	−1.5(12)
C(208)	5(2)	7(3)	2.4(5)	4(2)	1.7(8)	−1.1(11)
C(209)	9(2)	11(3)	0.9(4)	3(2)	0.4(6)	0.9(9)
C(210)	3(2)	26(4)	1.6(4)	1(2)	0.6(7)	1.9(11)
C(211)	4(2)	20(4)	2.6(10)	4(3)	−0.9(13)	−2.6(18)

* The scattering factor expression is given by $f = f_0 \exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)$.

(*b*) Isotropic

	B/Å²		*B*/Å²
O(201)	8.30	O(203)	7.85
O*(201)	13.65	O*(203)	13.06
O(202)	13.10	O(204)	5.71
O*(202)	10.17	O*(204)	6.64

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

TABLE 3

Bond lengths (Å)

Cu(1)–Cl(1)	2.312(6)	Cu(2)–Cl(2)	2.304(6)
Cu(1)–Cl(2)	2.966(6)		
Cu(1)–S(101)	2.609(6)	Cu(2)–S(201)	2.431(6)
Cu(1)–S(102)	2.445(6)	Cu(2)–S(202)	2.565(6)
Cu(1)–N(101)	1.991(14)	Cu(2)–N(201)	1.984(15)
Cu(1)–N(102)	2.021(16)	Cu(2)–N(202)	1.976(16)
S(101)–C(103)	1.76(2)	S(201)–C(203)	1.79(3)
S(102)–C(109)	1.82(2)	S(202)–C(209)	1.69(3)
S(101)–C(102)	1.85(2)	S(201)–C(202)	1.83(2)
S(102)–C(110)	1.84(3)	S(202)–C(210)	1.84(2)
N(101)–C(101)	1.55(2)	N(201)–C(201)	1.53(3)
N(102)–C(111)	1.54(4)	N(202)–C(211)	1.47(3)
C(101)–C(102)	1.45(3)	C(201)–C(202)	1.49(4)
C(110)–C(111)	1.47(4)	C(210)–C(211)	1.52(3)
C(103)–C(104)	1.43(3)	C(203)–C(204)	1.43(4)
C(104)–C(105)	1.34(3)	C(204)–C(205)	1.40(4)
C(105)–C(107)	1.38(3)	C(205)–C(207)	1.38(4)
C(107)–C(108)	1.39(3)	C(207)–C(208)	1.32(4)
C(108)–C(109)	1.35(3)	C(208)–C(209)	1.44(4)
C(109)–C(103)	1.41(3)	C(209)–C(203)	1.43(4)
C(105)–C(106)	1.59(3)	C(205)–C(206)	1.53(4)
Cl(3)–O(101)	1.37(2)	Cl(4)–O(201)	1.46(4)
		Cl(4)–O*(201)	1.43(5)
Cl(3)–O(102)	1.41(2)	Cl(4)–O(202)	1.41(7)
		Cl(4)–O*(202)	1.51(5)
Cl(3)–O(103)	1.41(2)	Cl(4)–O(203)	1.41(4)
		Cl(4)–O*(203)	1.45(5)
Cl(3)–O(104)	1.42(2)	Cl(4)–O(204)	1.49(3)
		Cl(4)–O*(204)	1.44(3)

TABLE 4

Bond angles (°)

Cl(1)–Cu(1)–N(101)	90.0(4)
Cl(1)–Cu(1)–N(102)	90.1(5)
N(101)–Cu(1)–S(102)	92.4(5)
N(102)–Cu(1)–S(102)	86.5(5)
S(101)–Cu(1)–Cl(1)	106.0(2)
S(101)–Cu(1)–N(101)	85.0(5)
S(101)–Cu(1)–N(102)	95.9(5)
S(101)–Cu(1)–S(102)	83.7(2)
Cl(2)–Cu(1)–Cl(1)	90.0(2)
Cl(2)–Cu(1)–N(101)	85.5(4)
Cl(2)–Cu(1)–N(102)	93.4(5)
Cl(2)–Cu(1)–S(102)	80.8(2)
Cu(1)–S(101)–C(102)	90.7(6)
Cu(1)–S(101)–C(103)	103.0(6)
Cu(1)–S(102)–C(110)	92.4(8)
Cu(1)–S(102)–C(109)	106.0(7)
Cu(1)–N(101)–C(101)	110.6(8)
Cu(1)–N(102)–C(111)	115.3(10)
N(101)–C(101)–C(102)	110.4(10)
N(102)–C(111)–C(110)	108.4(8)
S(101)–C(102)–C(101)	112.2(8)
S(102)–C(110)–C(111)	113.6(11)
S(101)–C(103)–C(109)	123.6(9)
S(102)–C(109)–C(103)	122.8(8)
C(102)–C(101)–C(103)	100.0(9)
C(110)–S(102)–C(109)	98.8(11)
S(101)–C(103)–C(104)	119.5(9)
S(102)–C(109)–C(108)	115.2(9)
C(104)–C(103)–C(109)	116.8(13)
C(103)–C(109)–C(108)	122.0(12)
C(103)–C(104)–C(105)	119.3(12)
C(104)–C(105)–C(107)	122.7(13)
C(105)–C(107)–C(108)	119.0(14)
C(107)–C(108)–C(109)	119.8(13)
C(104)–C(105)–C(106)	116.1(12)
C(106)–C(105)–C(107)	121.0(12)
O(101)–Cl(3)–O(102)	112.0(10)
O(101)–Cl(3)–O(103)	112.0(10)
O(101)–Cl(3)–O(104)	110.7(11)
O(102)–Cl(3)–O(103)	106.6(10)
O(102)–Cl(3)–O(104)	104.2(11)
O(103)–Cl(3)–O(104)	110.9(11)
Cl(2)–Cu(2)–N(201)	88.8(5)
Cl(2)–Cu(2)–N(202)	91.6(5)
N(201)–Cu(2)–S(201)	86.0(5)
N(202)–Cu(2)–S(201)	92.6(5)
S(202)–Cu(2)–Cl(2)	120.1(2)
S(202)–Cu(2)–N(201)	97.2(5)
S(202)–Cu(2)–N(202)	84.6(5)
S(202)–Cu(2)–S(201)	85.6(2)
Cu(2)–Cl(2)–Cu(1)	107.5(1)
Cu(2)–S(201)–C(202)	95.1(8)
Cu(2)–S(201)–C(203)	103.9(9)
Cu(2)–S(202)–C(210)	91.0(7)
Cu(2)–S(202)–C(209)	101.6(9)
Cu(2)–N(201)–C(201)	113.9(9)
Cu(2)–N(202)–C(211)	123.4(9)
N(201)–C(201)–C(202)	110.0(19)
N(202)–C(211)–C(210)	108.4(18)
S(201)–C(202)–C(201)	110.5(17)
S(202)–C(210)–C(211)	112.1(17)
S(201)–C(203)–C(209)	122.2(22)
S(202)–C(209)–C(203)	125.7(19)
C(202)–S(201)–C(203)	100.4(12)
C(210)–S(202)–C(209)	99.7(11)
S(201)–C(203)–C(204)	115.6(20)
S(202)–C(209)–C(208)	121.5(22)
C(204)–C(203)–C(209)	122.2(24)
C(203)–C(209)–C(208)	111.7(22)
C(203)–C(204)–C(205)	119.1(23)
C(204)–C(205)–C(207)	119.9(24)
C(205)–C(207)–C(208)	119.0(26)
C(207)–C(208)–C(209)	127.8(27)
C(204)–C(205)–C(206)	117.0(24)
C(206)–C(205)–C(207)	123.1(25)
O(201)–Cl(4)–O*(202)	101.8(24)
O*(201)–Cl(4)–O(202)	106.6(32)
O(201)–Cl(4)–O*(203)	115.4(28)
O*(201)–Cl(4)–O(203)	108.7(25)
O(201)–Cl(4)–O*(204)	112.1(20)
O*(201)–Cl(4)–O(204)	106.5(23)
O(202)–Cl(4)–O(203)	119.8(31)
O*(202)–Cl(4)–O*(203)	98.1(29)
O(202)–Cl(4)–O(204)	113.0(29)
O*(202)–Cl(4)–O*(204)	99.8(21)
O(203)–Cl(4)–O(204)	101.5(20)
O*(203)–Cl(4)–O*(204)	123.8(26)

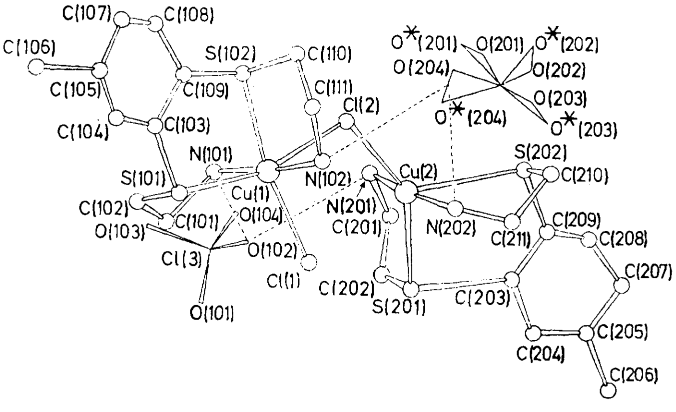

FIGURE 1 The dinuclear cation, showing the atom numbering scheme [hydrogen atoms are labelled according to the atoms to which they are attached; perchlorate groups are Cl(3), O(101)—O(104) and, half-weighted, Cl(4), O(201)—O(204); Cl(4), O*(201)—O*(204)]

DISCUSSION

The complex is found to be binuclear through the formation of one chlorine bridge between copper centres. A second chlorine is bonded to only one metal atom, its distance from the second being 3.66 Å. Each copper is also co-ordinated to two amine nitrogen and two thioether sulphur atoms, one centre, Cu(1), then having an octahedral donor array whereas the other, Cu(2), has a five-co-ordinate distorted-square-pyramidal stereochemistry. It is also possible to describe this latter geometry as distorted trigonal bipyramidal with the sulphur and chlorine atoms in the equatorial positions (see Figure 1) but for the reason outlined (see later) we prefer the square-pyramidal description. As is usually found for copper(II) complexes the octahedron is also distorted in the sense of having two longer axial bonds. This is demonstrated very clearly since the chemically equivalent thioether donors are 2.45 and 2.61 Å from Cu(1). The bridging chlorine, asymmetrically placed between the two centres, [Cu(1)–Cl(2) 2.97, Cu(2)–Cl(2) 2.30 Å] also reflects this axial bond increase. One bond at the five-co-ordinate copper, Cu(2), also to a thioether, is again long (2.57 *vs.* 2.43 Å) and is therefore readily described as the axial bond in the square-pyramidal stereochemistry. The alternative description, in which two unequal copper–sulphur bonds are in the trigonal plane, can thus be excluded. The amine nitrogen bonds, of equal length, are equatorially placed and mutually *trans* in both complex groupings. The two sets of equatorial donors are found to be considerably distorted from planarity as the deviations from the weighted planes of best fit [17] (Table 5) testify. A similar distortion from planarity has been observed in the basal planes of two recently published structures of copper(II) complexes containing 'soft' donors.[18,19]

The copper–sulphur bond lengths, already discussed, are rather long in comparison with several other types of sulphur donors where copper–sulphur lengths are in the range 2.17—2.32 Å.[20-22] This probably reflects the poor affinity of thioethers for copper(II) as does their positioning in axial co-ordination sites. Nevertheless a bond is clearly formed.

A common feature of the two co-ordination spheres is the *trans*-positions of the amine nitrogen atoms. The ethylene groups all have the expected *gauche* conformations (see Table 5). Both benzene rings are planar but there is a distinct 'fold' across the line through S(101) and S(102) so that the plane defined by Cu(1), S(101), S(102) makes a dihedral angle of 172.8° with that through C(103)—(105), C(107)—(109), S(101), and S(102). This bend is not evident at the other centre and a simple explanation for the difference is not obvious, unless it be merely a consequence of packing. The co-ordination geometry of the ligand with its *trans*-nitrogen atoms does not, itself, presuppose such a bend. Indeed, since the directions of the sulphur—methylene bonds become increasingly 'axial' and 'equatorial' (with respect to a plane through a copper and its two sulphur donors) as bending takes place, a geometry in which the nitrogens occupy *cis*-co-ordinating positions becomes more favourable. Notwithstanding the loss of equivalence in the sulphur bonding geometry, both dimethylene groups of the bent ligand maintain a *gauche* conformation (Table 5). Strain in both ligands is apparently accommodated in the bond angles at sulphur which are as small as 90.7°.

TABLE 5

Equations of planes of best fit in the form $lX + mY + nZ + p = 0$, where X, Y, and Z are orthogonal axes derived from the cell axes by the transformations $X = x + z\cos\beta$, $Y = y$, $Z = z\sin\beta$. Displacements (Å) of atoms from the planes are given in square brackets

Plane (I): N(101), N(102), S(102), Cl(1)

$$0.753X + 0.502Y - 0.426Z + 3.426 = 0$$

[Cu(1) −0.171, N(101) −0.133, N(102) −0.173, S(102) 0.022, Cl(1) 0.023]

Plane (II): N(201), N(202), S(201), Cl(2)

$$0.907X + 0.415Y - 0.074Z - 1.873 = 0$$

[Cu(2) 0.460, N(201) 0.435, N(202) 0.410, S(201) −0.064, Cl(2) −0.053]

Plane (III): Cu(1), N(101), S(101)

$$0.024X - 0.858Y - 0.513Z + 3.815 = 0$$

[C(101) 0.679, C(102) −0.022]

Plane (IV): Cu(1), N(102), S(102)

$$0.766X + 0.438Y - 0.470Z + 3.932 = 0$$

[C(110) 0.213, C(111) −0.327]

Plane (V): Cu(2), N(201), S(201)

$$0.928X + 0.282Y - 0.245Z - 1.521 = 0$$

[C(201) 0.504, C(202) −0.190]

Plane (VI): Cu(2), N(202), S(202)

$$-0.071X - 0.688Y - 0.722Z + 3.931 = 0$$

[C(210) −0.199, C(211) 0.533]

Plane (VII): C(103)—(105), C(107)—(109)

$$-0.654X + 0.521Y - 0.548Z + 3.867 = 0$$

[C(103) 0.006, C(104) −0.018, C(105) 0.032, C(107) −0.022, C(108) 0.013, C(109) −0.007, C(106) 0.036, S(101) −0.031, S(102) −0.038]

Plane (VIII): C(203)—(205), C(207)—(209)

$$-0.272X + 0.752Y - 0.601Z + 3.478 = 0$$

[C(203) 0.003, C(204) 0.016, C(205) −0.013, C(207) −0.018, C(208) 0.036, C(209) −0.025, C(206) −0.055, S(201) 0.011, S(202) −0.021]

Plane (IX): Cu(1), Cu(2), Cl(1), Cl(2)

$$-0.688X + 0.337Y - 0.643Z + 4.955 = 0$$

[Cu(1) 0.008, Cu(2) 0.007, Cl(1) −0.033, Cl(2) −0.039]

At first sight the behaviour of the two chlorine atoms seems equally inexplicable, especially since double

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chlorine bridges are well known.[23] The binuclear cation is ' planar ' in the sense that a least-squares fit to Cu(1), Cu(2), Cl(1), Cl(2) shows only small deviations (Table 5). A model then readily indicates that Cl(1) takes the position to be expected if the bridge angle at Cl(2) is to approximate to the tetrahedral value expected for maximum overlap of two lone pairs with metal orbitals. The reason for the ' detachment ' of Cl(1) and the consequent ' improvement ' in the angle at Cl(2) could lie in the presence of a strong hydrogen bond between Cl(1) and the HN(101′) group of an adjacent cation. The distance Cl(1) · · · N(101′) of 2.36 Å and the angles Cu(1)–Cl(1) · · · N(101′) of 105.3° and Cl(1) · · · HN(101′)–N(101′) of 143° confirm the character of this interaction.

TABLE 6

Hydrogen bonding interactions

(*a*) Bond lengths (Å)

O(102) · · · N(101)	3.04(2)	O(204) · · · H′N(202)	1.9
O(102) · · · N(201)	3.23(2)	O*(204) · · · H′N(202)	2.0
O(102) · · · H′N(101)	2.0	O(103) · · · N(102)	2.99(2)
O(102) · · · H′N(201)	2.2	O(203) · · · N(201)	3.11(4)
O(204) · · · N(102)	2.95(4)	O*(203) · · · N(201)	2.85(6)
O*(204) · · · N(102)	3.17(3)	O(103) · · · HN(102)	1.9
O(204) · · · N(202)	2.92(4)	O(203) · · · HN(201)	2.2
O*(204) · · · N(202)	3.08(3)	O*(203) · · · HN(201)	1.8
O(204) · · · H′N(201)	2.1	Cl(1) · · · N(101)	3.30(2)
O*(204) · · · H′N(102)	2.3	Cl(1) · · · HN(101)	2.4

(*b*) Bond angles (°)

Cl(3)–O(102) · · · H′N(101)	125
Cl(3)–O(102) · · · H′N(201)	116
O(102) · · · H′N(101)–N(101)	166
O(102) · · · H′N(201)–N(201)	148
Cl(4)–O(204) · · · H′N(102)	140
Cl(4)–O*(204) · · · H′N(102)	130
Cl(4)–O(204) · · · H′N(202)	120
Cl(4)–O*(204) · · · H′N(202)	120
O(204) · · · H′N(102)–N(102)	135
O*(204) · · · H′N(102)–N(102)	135
O(204) · · · H′N(202)–N(202)	155
O*(204) · · · H′N(202)–N(202)	167
Cl(3)–O(103) · · · HN(102)	137
Cl(4)–O(203) · · · HN(201)	119
Cl(4)–O*(203) · · · HN(201)	159
O(103) · · · HN(102)–N(102)	179
O(203) · · · HN(201)–N(201)	142
O*(203) · · · HN(201)–N(201)	164
Cu(1)–Cl(1) · · · HN(101)	105
Cl(1) · · · HN(101)–N(101)	143

The perchlorate groups have a space-filling and charge-balancing role and are not co-ordinated. They are also involved in hydrogen-bonding interactions (Table 6); in particular they both bind to two cations and presumably have an important role in stabilising the crystalline state. Figure 2 is a packing diagram showing these contacts.

The analysis thus reveals a binuclear complex cation with a somewhat unusual disparity in co-ordination numbers between metal centres. The copper atoms, clearly in the dipositive formal oxidation state, bind the thioether donors but equally clearly with little affinity. The lack of success in an attempted preparation of a crystalline 1 : 1 copper(II) complex with the aliphatic analogue, 1,8-diamino-4-methyl-3,6-dithiaoctane,[6] is readily understood if it be concluded that π-delocalisation is a necessary attribute in enhancing the bonding capacity of thioethers towards copper(II). In this situation other factors are also likely to determine the stability of a complex and the chances of obtaining a crystalline product. The necessity for chloride and perchlorate ions to complete at least five-fold co-ordination[24] and to increase intergroup cohesion is therefore also understood.

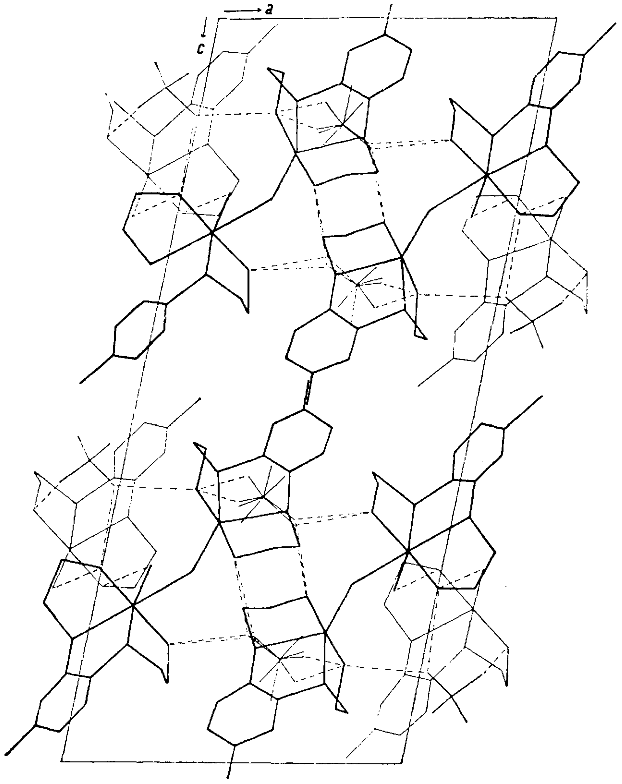

FIGURE 2 The unit cell contents projected down *b*

[4/2379 *Received*, 13*th November*, 1974]

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