The Crystal Structures of Di-μ-chloro-bis{[*N*-(2-aminoethyl)thiophen-2-aldimine]chlorocopper(II)} and Bis[*N*-(2-aminoethyl)thiophen-2-aldimine]diperchloratocopper(II)

By **P. Gerard Beckingsale, Anthony T. Morcom, Clifton E. F. Rickard,*** and **T. Neil Waters,** Department of Chemistry, University of Auckland, New Zealand

The structures of the title complexes have been investigated by single-crystal *X*-ray crystallography. In both the complexes the ligands are co-ordinated through nitrogen only, the thiophen sulphur atoms remaining unattached. The chloro-complex is dimeric with chloride bridges and has a distorted square-pyrimidal co-ordination polyhedron. The perchlorato-complex is monomeric with an octahedral co-ordination geometry which includes the perchlorate groups.

RECENT reports of complexes formed between copper(II) and the ligand *NN'*-ethylenebis(thiophen-2-aldimine) (L^1) have posed several problems. For example, it is not clear whether the ligand co-ordinates in a bidentate or quadridentate manner, one report [1] suggesting co-ordination through nitrogen only whereas a second [2] indicates co-ordination through both nitrogen and sulphur. Hydrolysis of the co-ordinated ligand leading to the loss of one or both thiophen-2-aldehyde moieties has been noted [3] as has the importance of anion effects. Thus complexes with 1 : 1 metal : ligand stoicheiometries are formed with most anions but $CuL^1_2(ClO_4)_2$ results when perchlorate is used.[1-3] The hydrolysis reactions have variously been ascribed to electronic [4] or steric [5] effects and, indeed, models indicate that steric strain is likely to be present if the sulphur atoms are co-ordinated.

In view of these uncertainties we have undertaken an *X*-ray structural investigation to determine the role of thiophen sulphur atoms and to investigate the anion effects. Unfortunately, all the attempts to obtain single crystals of complexes of L^1 were fruitless, presumably due to the ready occurrence of solvolysis reactions leading to the loss of one thiophen-2-aldehyde moiety during crystallisation. Consequently we present here the structures of two complexes based on the ligand *N*-(2-aminoethyl)thiophen-2-aldimine (L^2) with chloride and perchlorate as anions.

EXPERIMENTAL AND RESULTS

The complexes CuL^1Cl_2 and $CuL^1_2(ClO_4)_2$ were prepared as previously described [3] and recrystallisation from ethanol–diethyl ether yielded blue needles of $[\{CuL^2Cl_2\}_2]$ and purple needles of $[CuL^2_2(ClO_4)_2]$.

Preliminary cell parameters were obtained from rotation and Weissenberg photographs, and final parameters and standard deviations by a least-squares procedure [6] from the four-circle diffractometer (Hilger and Watts Y290) co-ordinates of 12 reflections. Intensity data were measured with zirconium-filtered Mo-K_α radiation (λ 0.710 7 Å) using an ω—2θ scan. Each reflection was counted for 60 s at a scan rate of 0.01° s^{-1} with background counts of 15 s being made at the start and finish of measurement. The intensities of three standard reflections were monitored at intervals as a check on crystal movement or decomposition but no evidence of either was found. Standard deviations were estimated from the relation $\sigma^2 = [T + tB + (T_cP)^2]$, T being the total integrated intensity, t the ratio of scan-to-background count times, B the background count, T_c the intensity corrected for background, and P a correction factor taken as 0.05. The standard Lorentz and polarisation corrections were applied and reflections with intensities less than three times the standard deviation were rejected as unobserved. Totals of 712 and 787 reflections were thereby recorded for CuL^2Cl_2 and $CuL^2_2(ClO_4)_2$ respectively. No absorption corrections were applied.

Crystallographic Data for Di-μ-chloro-bis{[N-(2-*amino-ethyl*)*thiophen*-2-*aldimine*]*chlorocopper*(II)}.— $C_{14}H_{20}Cl_4Cu_2N_4S_2$, $M = 577.0$, Monoclinic, $a = 9.777(2)$, $b = 11.922(3)$, $c = 9.247(4)$ Å, $\beta = 101.98(3)°$, $U = 1\,054$ Å^3, $D_m = 1.83$, $Z = 2$, $D_c = 1.82$ g cm^{-3}; $\mu = 26$ cm^{-1} for Mo-K_α *X*-rays (λ 0.710 7 Å), space group = $P2_1/c$.

The structure was solved by conventional heavy-atom techniques and refined by full-matrix least-squares methods to a final residual, R, of 0.064, it being not known that the molecule was dimeric until the chlorine atoms were located. Atomic-scattering factors were taken from ref. 7 for neutral atoms but with copper values adjusted for the real part of the dispersion correction. Atomic co-ordinates are given in Table 1. Tables of thermal parameters and observed and calculated structure factors are listed as Supplementary Publication No. SUP 22105 (11 pp.).†

The complex molecule is dimeric and centrosymmetric with chlorine bridges between copper centres (Figure 1). Each metal is five-co-ordinate with a distorted square-pyramidal bond geometry involving two nitrogen and three chlorine atoms. The Cu–Cl distances in the bridge [2.288 (equatorial) and 2.767 Å (axial)] and the equatorial terminal distance (2.278 Å) are all in accord with expected values. Distances to the nitrogen donors [2.01(1) (amine) and 2.03(1) Å (imine)] do not differ significantly even though the imine bond is found to be shorter in many

---

† For details, see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[1] R. K. Y. Ho and S. E. Livingstone, *Austral. J. Chem.*, 1965, **18**, 659.

[2] M. P. Coakley, L. H. Young, and R. A. Gallagher, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1449.

[3] A. C. Braithwaite, C. E. F. Rickard, and T. N. Waters, *J.C.S. Dalton*, 1975, 2149.

[4] G. L. Eichhorn and I. M. Trachtenberg, *J. Amer. Chem. Soc.*, 1954, **76**, 5183.

[5] D. H. Busch and J. C. Bailar, *J. Amer. Chem. Soc.*, 1956, **78**, 1137.

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

[7] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3.

complexes.[8,9] The distance of a sulphur atom from the nearest copper is 5.65 Å confirming that there is no bonding interaction with this potential donor. Interatomic distances are given in Table 2 and the corresponding angles in Table 3, all being within the expected range. The unit-cell contents are shown in Figure 3.

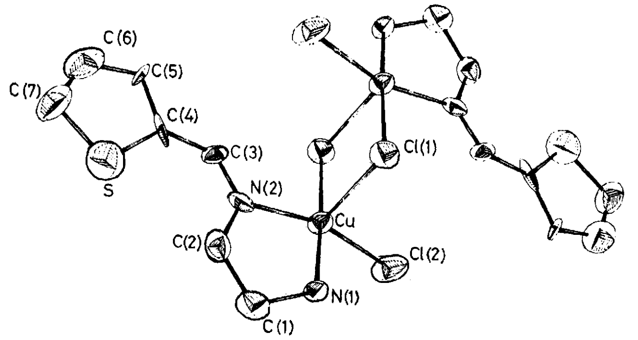

FIGURE 1 ORTEP diagram and atom-numbering scheme for [{CuL^{2}Cl$_2$}$_2$]

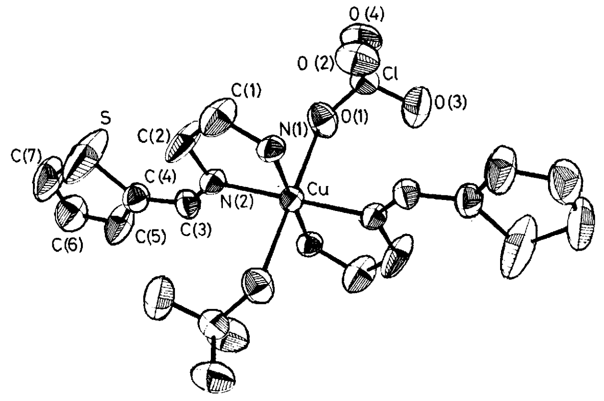

FIGURE 2 ORTEP diagram and atom-numbering scheme for [CuL$^2_2$(ClO$_4$)$_2$]

Examination of the equatorial donors around the copper atom shows a considerable deviation from the ideal planar arrangement. The mean plane through the donor set is $0.723x + 0.523y - 0.451z + 1.279 = 0$ (referred to orthogonal axes) and it is found that N(1) and N(2) deviate from this plane by -0.22 and 0.24 Å respectively. A χ^2 test (χ^2 669) confirms the deviation. The copper atom is situated 0.15 Å above the plane in the direction of the axial chlorine atom. Consideration of the bond angles around copper shows that three of the donors, N(1), N(2), and Cl(1), are approximately at right angles to the axial chlorine atom but that the remaining chlorine donor makes an angle of 101.9°. Thus the polyhedron can be thought of as being very slightly distorted towards a trigonal-bipyramidal geometry.

The carbon atoms of the ethylene group are displaced by -0.61 and -0.08 Å below the plane defined by N(1), N(2), and Cu, giving a distorted *gauche* conformation to the ring which differs from the usual unsymmetrical arrangement in having both carbon atoms displaced to the same side of the co-ordination plane.

The thiophen group is planar. The mean plane through all the ring atoms is $0.620x + 0.643y - 0.449z + 1.389 = 0$ and no atom deviates from it by >0.02 Å. The value of χ^2 is 2.9. The imine double bond also lies in the plane of the ring so that there is maximum delocalisation of the π electrons. The sulphur atom lies 2.5 Å from one of the ethylene hydrogen atoms which is within the distance given by Hamilton and Ibers[10] for a hydrogen bond. However, since the angles around the sulphur are C(4)–S–H(2,1) 81° and C(7)–S–H(2,1) 166°, so that the interaction is not directed towards the sulphur lone pair, the interaction is likely to be very weak.

TABLE 1

Atom co-ordinates for [{CuL^{2}Cl$_2$}$_2$]

	x/*a*	*y*/*b*	*z*/*c*
Cu	0.068 6(3)	−0.012 8(2)	0.335 0(3)
Cl(1)	0.077 8(5)	0.135 7(4)	0.493 4(5)
Cl(2)	−0.107 3(5)	0.063 5(4)	0.162 7(6)
S	0.557 3(6)	−0.196 7(5)	0.620 2(6)
N(1)	0.070 3(13)	−0.144 3(11)	0.200 1(13)
N(2)	0.257 0(13)	−0.075 2(12)	0.437 1(15)
C(1)	0.212 4(18)	−0.173 5(14)	0.201 7(19)
C(2)	0.298 0(16)	−0.172 8(14)	0.360 0(19)
C(3)	0.328 1(17)	−0.044 7(14)	0.564 0(18)
C(4)	0.451 8(17)	−0.086 0(13)	0.656 3(21)
C(5)	0.513 5(16)	−0.041 1(13)	0.799 7(17)
C(6)	0.637 7(22)	−0.095 4(19)	0.857 6(22)
C(7)	0.681 4(20)	−0.184 8(18)	0.779 9(22)
H(1,1) *	0.284	−0.123	0.148
H(1,2)	0.211	−0.255	0.140
H(2,1)	0.409	−0.174	0.370
H(2,2)	0.271	−0.250	0.418
H(3)	0.298	0.016	0.626
H(5)	0.466	0.028	0.847
H(6)	0.724	−0.104	0.954
H(7)	0.787	−0.233	0.793
H(N1,1)	0.007	−0.206	0.242
H(N1,2)	0.027	−0.132	0.084

* Hydrogen atoms are numbered according to the atoms to which they are bound.

TABLE 2

Bond lengths (Å) in [{CuL^{2}Cl$_2$}$_2$]

Cu–Cl(1)	2.288(5)	S–C(4)	1.75(2)
Cu–Cl(1′)	2.767(5)	S–C(7)	1.71(2)
Cu–Cl(2)	2.278(5)	C(1)–C(2)	1.53(2)
Cu–N(1)	2.006(12)	C(3)–C(4)	1.42(2)
Cu–N(2)	2.029(13)	C(4)–C(5)	1.44(2)
N(1)–C(1)	1.43(2)	C(5)–C(6)	1.38(3)
N(2)–C(2)	1.46(2)	C(6)–C(7)	1.40(3)
N(2)–C(3)	1.29(2)		

TABLE 3

Bond angles (°) in [{CuL^{2}Cl$_2$}$_2$]

Cu–Cl(1)–Cu′	90.1(2)	C(2)–N(2)–C(3)	121(1)
Cl(1)–Cu–Cl(1′)	90.0(2)	C(4)–S–C(7)	96.5(9)
Cl(1)–Cu–Cl(2)	93.6(2)	N(1)–C(1)–C(2)	110(1)
Cl(1)–Cu–N(2)	94.3(4)	N(2)–C(2)–C(1)	109(1)
Cl(1′)–Cu–Cl(2)	102.0(2)	N(2)–C(3)–C(4)	133(1)
Cl(1′)–Cu–N(1)	90.9(4)	S–C(4)–C(3)	128(1)
Cl(1′)–Cu–N(2)	93.8(4)	S–C(4)–C(5)	108(1)
Cl(2)–Cu–N(1)	88.8(4)	C(3)–C(4)–C(5)	125(1)
N(1)–Cu–N(2)	83.0(5)	C(4)–C(5)–C(6)	110(1)
Cu–N(1)–C(1)	108.5(9)	C(5)–C(6)–C(7)	120(2)
Cu–N(2)–C(2)	112.3(9)	S–C(7)–C(6)	106(1)
Cu–N(2)–C(3)	126(1)		

Crystallographic Data for Bis-[N-(2-*aminoethyl*)*thiophen-2-aldimine*]*diperchloratocopper*(II).— $C_{14}H_{20}Cl_2CuN_4O_8S_2$,

---

[8] B. F. Hoskins and F. D. Whillans, *J. Chem. Soc.* (*A*), 1970, 123.

[9] D. W. Martin and T. N. Waters, *J.C.S. Dalton*, 1973, 2440.

[10] W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' Benjamin, New York, 1968.

$M = 570.9$, Monoclinic, $a = 11.562(3)$, $b = 9.282(2)$, $c = 10.028(3)$ Å, $\beta = 94.20\ (1)^\circ$, $U = 1\,073$ Å^3, $D_m = 1.79$, $Z = 2$, $D_c = 1.77$ g cm^{-3}, $\mu = 13.5$ cm^{-1} for Mo-K_α X-rays (λ 0.710 7 Å), space group $P2_1/c$.

Since the copper atom is constrained by the space group to lie on a centre of symmetry an electron-density synthesis was calculated using those data which were phased by the heavy atom. It was possible to obtain consistent positions for chlorine and sulphur atoms in spite of the false symmetry imposed and a subsequent map phased by copper, chlorine, and sulphur allowed the remaining non-hydrogen atoms to be placed. Refinement was again by the full-matrix least-squares method, hydrogen atoms being included in their calculated positions but not refined. The process converged to a residual of 0.044. Final atomic co-ordinates are given in Table 4 and Tables of observed and calculated structure factors and thermal parameters are listed in the Supplementary publication.

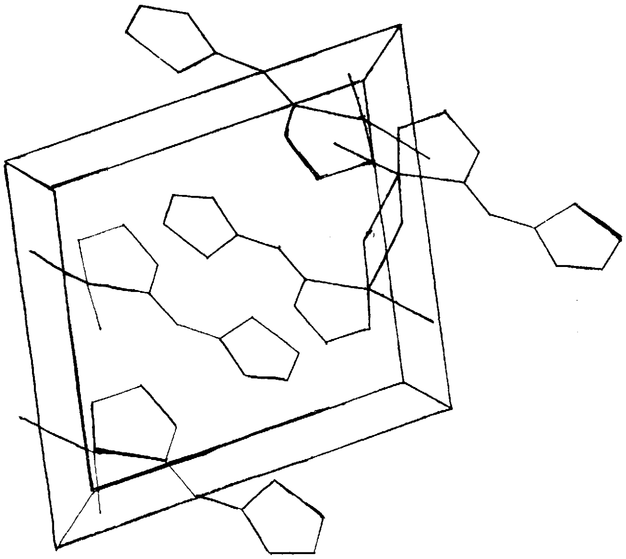

FIGURE 3 Unit-cell contents for [{CuL^{2}Cl$_2$}$_2$]. The axes are conventionally placed at the upper left-hand corner with *b* vertical

The copper atom is co-ordinated to four nitrogen atoms in a *trans* square-planar arrangement (Figure 2). The metal-to-donor distances [Cu–N(1) 1.997(8) and Cu–N(2) 2.018(7) Å] are very similar to those found for [{CuL^{2}Cl$_2$}$_2$]. In addition there is an axial interaction between copper and perchlorate oxygen atoms [Cu–O(1) 2.571 Å] similar to that found in the perchlorate and tetrafluoroborate salts of bis(ethylenediamine)copper(II).[11,12]

TABLE 4

Atom co-ordinates for [CuL^2$_2$(ClO$_4$)$_2$]

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu	0	0	0
Cl	0.155 0(2)	−0.333 8(3)	0.007 4(3)
S	0.447 6(4)	0.163 2(9)	0.095 3(6)
O(1)	0.062 4(6)	−0.255 4(9)	−0.063 4(7)
O(2)	0.150 8(8)	−0.479 4(9)	−0.034 6(9)
O(3)	0.143 0(8)	−0.323 5(9)	0.147 4(7)
O(4)	0.262 6(6)	−0.271(1)	−0.019 8(9)
N(1)	0.026 9(7)	0.059 0(9)	−0.186 7(8)
N(2)	0.166 6(7)	0.062 1(8)	0.035 9(6)
C(1)	0.131 4(8)	0.144(1)	−0.188 1(9)
C(2)	0.212 4(9)	0.128(1)	−0.078(1)
C(3)	0.231 3(7)	0.042 2(9)	0.143 5(8)
C(4)	0.350 1(8)	0.075(1)	0.181 4(8)
C(5)	0.405 1(8)	0.043(1)	0.300 1(9)
C(6)	0.519 1(9)	0.083(1)	0.319(1)
C(7)	0.554 2(8)	0.150(1)	0.219(1)
H(1,1) *	0.106	0.256	−0.194
H(1,2)	0.174	0.116	−0.277
H(2,1)	0.245	0.234	−0.049
H(2,2)	0.283	0.063	−0.109
H(3)	0.187	−0.010	0.222
H(5)	0.361	−0.012	0.377
H(6)	0.573	0.060	0.409
H(7)	0.641	0.193	0.213
H(N1,1)	−0.046	0.122	−0.228
H(N1,2)	0.035	−0.036	−0.247

* Hydrogen atoms are numbered according to the atoms to which they are bound.

TABLE 5

Bond lengths (Å) in [CuL^2$_2$(ClO$_4$)$_2$]

Cu–O(1)	2.571(8)	C(3)–C(4)	1.43(1)
Cu–N(1)	1.997(8)	C(4)–C(5)	1.34(1)
Cu–N(2)	2.018(7)	C(4)–S	1.68(1)
N(1)–C(1)	1.45(1)	C(5)–C(6)	1.37(1)
C(1)–C(2)	1.40(1)	C(6)–C(7)	1.28(1)
N(2)–C(2)	1.44(1)	C(7)–S	1.69(1)
N(2)–C(3)	1.28(1)		
Cl–O(1)	1.438(8)	Cl–O(3)	1.424(9)
Cl–O(2)	1.415(9)	Cl–O(4)	1.419(9)

TABLE 6

Bond angles (°) in [CuL^2$_2$(ClO$_4$)$_2$]

Cu–N(1)–C(1)	110.4(6)	N(2)–C(3)–C(4)	133.1(8)
Cu–N(2)–C(2)	112.5(6)	C(3)–C(4)–C(5)	124.8(9)
Cu–N(2)–C(3)	120.5(8)	C(3)–C(4)–S	129.4(7)
Cu–O(1)–Cl	123.8(4)	C(4)–C(5)–C(6)	117.0(9)
N(1)–Cu–N(2)	82.9(3)	C(4)–S–C(7)	94.1(6)
N(1)–C(1)–C(2)	116.5(9)	C(5)–C(4)–S	105.8(8)
C(1)–C(2)–N(2)	114.1(9)	C(5)–C(6)–C(7)	112.3(9)
C(2)–N(2)–C(3)	120.5(8)	C(6)–C(7)–S	110.9(9)
O(1)–Cl–O(2)	109.2(5)	O(2)–Cl–O(3)	110.7(5)
O(1)–Cl–O(3)	109.3(5)	O(2)–Cl–O(4)	110.3(5)
O(1)–Cl–O(4)	109.1(5)	O(3)–Cl–O(4)	108.2(5)

Interatomic distances and angles are given in Tables 5 and 6 respectively. With the exception of the carbon–carbon bond in the ethylene bridge these all agree with expected values. At 1.40(1) Å, the C(1)–C(2) bond is much shorter than the expected value but there seems no obvious reason to dismiss the measurement as erroneous. It is, however, unlikely that it is indicative of a true double bond since regions of positive electron density occur in the positions predicted for hydrogen atoms assuming an sp^3-hybridised carbon and, conversely, no positive density could be found in the predicted position for sp^2 hybridisation. The interpretation is made difficult by the relatively large thermal vibrations of the bridging atoms. As can be seen from Figure 2, the long axes of their ellipsoids are more or less perpendicular to the chelate plane and some correction to the bond length can be expected. It is not possible to calculate what this is since the relative motions of the atoms are unknown, but we note that the associated bonds to nitrogen [1.45(1) and 1.44(1) Å] are also short by *ca.* 0.03 and 0.035 Å. We also note that in the thiophen

---

[11] A. Pajunen, *Suomen Kem.*, 1957, **B40**, 32.

[12] D. S. Brown, J. D. Lee, and B. G. A. Melsom, *Acta Cryst.*, 1968, **B24**, 730.

moiety the sulphur atom has a large anisotropic motion perpendicular to the ring, with its associated bonds [1.68(1) and 1.69(1) Å] *ca.* 0.05 and 0.04 Å shorter than expected. (The sulphur atom has the largest degree of anisotropic motion, or apparent motion, in the structure and these discrepancies are correspondingly larger.) If it is assumed that the arcs of motion of atoms C(1) and C(2) are in planes which are perpendicular to the chelate ring and which bisect the N–C–C angles, in other words in the direction of least restraint from the bonds, then the contribution to the apparent shortening of the dimethylene link from each carbon will be about the same as that apparent in its link to nitrogen. The total shortening of C(1)–C(2) would thus be *ca.* 0.06—0.08 Å. It is suggested that the additional shortening is due to electron withdrawal through the nitrogen to the copper atom [13] assisted by the presence of electronegative perchlorate groups. The ethylene carbon atoms are situated below the plane of the chelate ring defined by Cu, N(1), and N(2) [C(1) −0.35 and C(2) −0.15 Å], a situation approaching an eclipsed conformation.

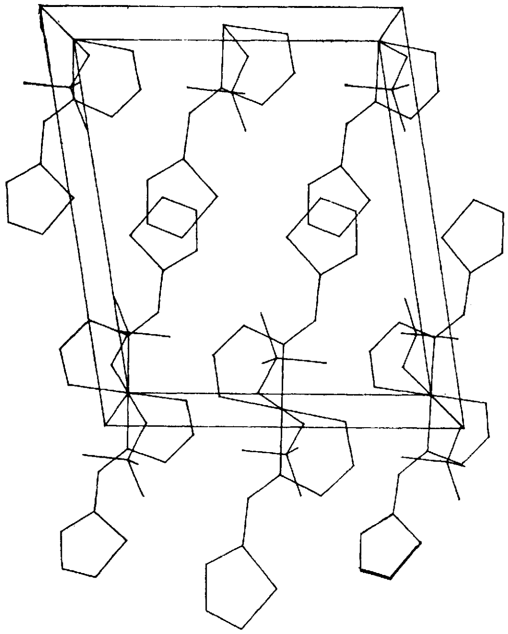

FIGURE 4 Unit-cell contents for $[CuL^2_2(ClO_4)_2]$. The axes are placed as in Figure 3

The equation of the plane through the thiophen ring is $0.313x - 0.863y - 0.373z + 0.060 = 0$ and $\chi^2 = 2.71$; the imine double bond lies in this plane allowing maximum delocalisation of the π-electron density. The sulphur atom again makes approaches (2.7 and 2.8 Å) to the hydrogen atoms of a carbon in the ethylene bridge but, in view of the distances and unfavourable disposition of the lone pair on the sulphur, significant hydrogen-bonding interactions must be regarded as unlikely.

The perchlorate group is involved in several intermolecular hydrogen bonds (Figure 4). Distances and angles are listed in Table 7. No such contacts are found in the chloro-complex.

TABLE 7

Some intra- and inter-molecular contacts for $[CuL^2_2(ClO_4)_2]$ [a]

Bond (Å)		Angle (°)	
O(1) · · · H(N1,1) (*i*) [b]	2.4	O(1) · · · H(N1,1)–N(1)	126.9
O(1) · · · N(1) (*i*)	3.15		
O(3) · · · H(N1,1) (*ii*)	2.4	O(3) · · · H(N1,1)–N(1)	132.6
O(3) · · · N(1) (*ii*)	3.19		
O(3) · · · H(N1,2) (*iii*)	2.1	O(3) · · · H(N1,2)–N(1)	149.1
O(3) · · · N(1) (*iii*)	3.11		

[a] There are no contacts for $[\{CuL^2Cl_2\}_2]$ which are significantly less than the sum of van der Waals radii. [b] Atoms at (*i*) $\bar{x}, y - \frac{1}{2}, \bar{z} - \frac{1}{2}$, (*ii*) $\bar{x}, \bar{y}, \bar{z}$, and (*iii*) $x, \bar{y} - \frac{1}{2}, \frac{1}{2} - z$.

DISCUSSION

In view of the structures found for the two complexes it seems that Cu^{II} has little affinity for the sulphur donor and a bidentate bonding mode with the parent ligand *NN′*-ethylenebis(thiophen-2-aldimine) is predicted. It is then apparent that the observed two-step hydrolysis of the parent ligand is not due to steric effects since the sulphur atoms, being unco-ordinated, allow all the interatomic distances and angles to retain their normal values. The most likely explanation for hydrolysis lies in the alternative electronic argument.[4]

The anion effects are much more subtle. In both complexes the copper ion achieves a co-ordination number greater than four, in one instance by use of bridging chlorine atoms and in the other by strong axial interactions with perchlorate groups. It is significant that only with perchlorate as anion is the 1 : 2 complex formed and it can be argued that this stoicheiometry results because of the weak bonding by perchlorate and its consequent unsuitability as a bridging group. In all the other complexes studied to date the anion is capable of bridging two metal centres and thus only a single ligand is necessary to achieve a co-ordination number greater than four.

[7/742 *Received, 3rd May,* 1977]

---

[13] H. S. Maslen and T. N. Waters, *Co-ordination Chem. Rev.*, 1975, **17**, 137.