

than  $90^\circ$  [ $94.6(1)^\circ$ ] while the interior Br(2)—Cu—Br(2a) angle is much smaller than  $90^\circ$  [ $82.9(1)^\circ$ ]. The *trans* Br—Cu—Br angles are  $173.9(9)$  and  $171.1(1)^\circ$ .

The anions and cations form stacks parallel to the short crystallographic (*a*) axis; the anions are shown in Fig. 3. The dimer stacks are characterized by the formation of semicoordinate Cu—Br bonds of  $3.243(2)$  and  $3.296(2)$  Å and are analogous to those in  $\text{KCuCl}_3$  and  $\text{NH}_4\text{CuCl}_3$  (Willett, Rundle, Dwiggens & Kruh, 1963), and is denoted a  $2(\frac{1}{2}, \frac{1}{2})$  stack in the notation recently introduced for the stacking of  $\text{Cu}_n\text{X}_{2n+2}^{2-}$  oligomers (Geiser, Willett, Lindbeck & Emerson, 1986).

Extensive hydrogen bonding gives rigidity to the lattices (Tables 2 and 4). In the copper(II) salt, the water molecule, *W*, forms donor hydrogen bonds to Br(1) and the amino N(2) atom of the pyridinium ion. It also accepts a hydrogen bond from the hydroxyl group. The pyridinium N(1) atom hydrogen bonds to Br(3), and the amino N(2) atom forms a normal hydrogen bond to Br(2) and a bifurcated hydrogen bond to Br(2) and Br(3). In the simple bromide salt, the hydroxyl proton forms a relatively short hydrogen bond to the lattice Br(1') ion while the pyridinium and amino

protons form longer bonds. Proton H(2B) actually appears to form a bifurcated hydrogen bond involving the Br(1') ion and lone pair on the adjacent O atom in the same cation.

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## Structures of Four Complexes of Copper with *N*-Methylimidazole and Chloro Ligands

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**Abstract.** (1): Tetrakis(*N*-methylimidazole-*N'*)-copper(II) trichlorocuprate(I) hydrate,  $[\text{Cu}(\text{C}_4\text{H}_6\text{N}_2)_4][\text{CuCl}_3] \cdot \text{H}_2\text{O}$ ,  $M_r = 579.9$ , triclinic, *P*1,  $a = 8.244(1)$ ,  $b = 9.440(1)$ ,  $c = 15.992(2)$  Å,  $\alpha = 96.00(1)$ ,  $\beta = 99.04(1)$ ,  $\gamma = 100.92(1)^\circ$ ,  $V = 1195.2$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.611$  Mg m<sup>-3</sup>,  $F(000) = 590$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 2.15$  mm<sup>-1</sup>,  $T = 291$  K,  $R = 0.044$  for 3607 reflections with  $F > 4\sigma(F)$ . (2): Hexachlorotetrakis(*N*-methylimidazole-*N'*)oxotetra-copper(II),  $[\text{Cu}_4\text{OCl}_6(\text{C}_4\text{H}_6\text{N}_2)_4]$ ,  $M_r = 811.3$  (ignoring acetonitrile solvent), orthorhombic, *Pbca*,  $a = 18.946(1)$ ,  $b = 19.043(1)$ ,  $c = 33.256(2)$  Å,  $V = 11998$  Å<sup>3</sup>,  $Z = 16$ ,  $D_x = 1.796$  Mg m<sup>-3</sup>,  $F(000) = 6432$ ,  $\mu(\text{Mo } K\alpha) = 3.37$  mm<sup>-1</sup>,  $T = 291$  K,  $R = 0.068$  for 4794 reflections. (3): Hexachlorotetrakis(*N*-methyl-

imidazole-*N'*)oxotetracopper(II) chlorotetrakis(*N*-methylimidazole-*N'*)copper(II) chloride,  $[\text{Cu}_4\text{OCl}_6(\text{C}_4\text{H}_6\text{N}_2)_4][\text{Cu}(\text{C}_4\text{H}_6\text{N}_2)_4\text{Cl}]\text{Cl}$ ,  $M_r = 1274.2$ , orthorhombic, *Pca*2<sub>1</sub>,  $a = 14.637(1)$ ,  $b = 13.233(1)$ ,  $c = 26.490(2)$  Å,  $V = 5130.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.649$  Mg m<sup>-3</sup>,  $F(000) = 2564$ ,  $\mu(\text{Mo } K\alpha) = 2.51$  mm<sup>-1</sup>,  $T = 291$  K,  $R = 0.052$  for 6999 reflections. (4): Diaquatetrakis(*N*-methylimidazole-*N'*)copper(II) chloride hydrate,  $[\text{Cu}(\text{C}_4\text{H}_6\text{N}_2)_4(\text{H}_2\text{O})_2] \cdot \text{Cl}_2 \cdot \text{H}_2\text{O}$ ,  $M_r = 516.9$ , triclinic, *P*1,  $a = 9.198(1)$ ,  $b = 9.338(1)$ ,  $c = 15.520(2)$  Å,  $\alpha = 99.41(1)$ ,  $\beta = 105.59(1)$ ,  $\gamma = 103.36(1)^\circ$ ,  $V = 1212.5$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.416$  Mg m<sup>-3</sup>,  $F(000) = 538$ ,  $\mu(\text{Mo } K\alpha) = 1.16$  mm<sup>-1</sup>,  $T = 291$  K,  $R = 0.036$  for 2959 reflections. The square-planar coordinated  $[\text{Cu}(\text{Meim})_4]^{2+}$

cations in the mixed-valence salt (1) are linked in chains *via* Cu...Cl axial contacts with the anions. The same cation in (4) achieves tetragonally distorted octahedral coordination by attachment of two water molecules, which, together with the additional water of crystallization, are extensively hydrogen bonded to the chloride anions. The discrete  $[\text{Cu}(\text{Meim})_4\text{Cl}]^+$  cation in (3) shows tetragonal pyramidal coordination. The molecule of (2) consists of a tetrahedral arrangement of Cu atoms about the central O, a  $\mu_2$ -Cl atom above each edge of this tetrahedron, and terminal Meim ligands; essentially the same structure is found for this species in (3).

**Introduction.** As a continuation of our studies of copper/imidazole complexes (Clegg, Acott & Garner, 1984*a,b*), we have carried out the reaction of  $\text{K}_2[\text{S}_2\text{-}o\text{-xyl}]$  ( $[\text{S}_2\text{-}o\text{-xyl}]^{2-} = \alpha, \alpha'\text{-xylenedithiolate}$ ) with  $[\text{Cu}(\text{Meim})_2\text{Cl}_2]$  (van Ooijen & Reedijk, 1978) in acetonitrile. This, and subsequent work-up and recrystallization procedures, produced several compounds, each of which involves coordination of copper by Meim and chloride ligands, but in no case was coordination by  $\text{S}_2\text{-}o\text{-xyl}$  observed. A previously reported reaction of copper(II) chloride with 4-methylthiazole (4-Metz) also yields a number of different products, the crystal structure of one of which,  $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}(4\text{-Metz})_4\text{Cl}_3]$ , was determined (Marsh, Hatfield & Hodgson, 1983). These reactions are important because of the very versatile coordination chemistry of copper encompassed by them; in addition, they demonstrate a facile redox chemistry of copper in the presence of imidazole and sulfur ligands, leading to mixed-valence compounds.

**Experimental.** Reactions were carried out under a dinitrogen atmosphere by standard Schlenk techniques. MeCN was freshly distilled from  $\text{CaH}_2$ ; anhydrous  $\text{Et}_2\text{O}$  was used as received. Electron spin resonance (ESR) measurements were performed at X-band frequency with equipment and methods described previously (Cooke, Collison, Mabbs & Earnshaw, 1985; Gahan & Mabbs, 1983).

### Synthesis

(1):  $[\text{Cu}(\text{Meim})_2\text{Cl}_2]$  (0.8 g, 2.7 mmol) was dissolved in freshly distilled MeCN (25 cm<sup>3</sup>), to give a deep-green solution, which was purged with dinitrogen gas. Solid  $\text{K}_2[\text{S}_2\text{-}o\text{-xyl}]$  (0.65 g, 2.7 mmol) was added, and the solution stirred for 30 min. Some white solid material (including unchanged  $\text{K}_2[\text{S}_2\text{-}o\text{-xyl}]$ ) was separated by filtration from the deep blue solution, to which freshly distilled  $\text{Et}_2\text{O}$  (*ca* 10 cm<sup>3</sup>) was carefully added. Cooling to 253 K overnight produced small deep-blue crystals of compound (1) in 18% yield (with respect to Cu). Observed analysis: C, 33.1; H, 4.4; N, 19.2; Cl, 18.5; Cu, 21.8%.  $\text{C}_{16}\text{H}_{26}\text{N}_8\text{Cl}_3\text{Cu}_2\text{O}$  re-

quires: C, 33.1; H, 4.5; N, 19.3; Cl, 18.3; Cu, 21.9%. ESR spectrum manifests resonances:  $g_1$  2.252 ( $a_1 = 180$  G),  $g_2 = g_3 = 2.056$ .  $\bar{g} = 2.122$  ( $\bar{a} = 66$  G).

(2): After separation of compound (1) by filtration, the volume of the filtrate was doubled by addition of further  $\text{Et}_2\text{O}$  and the mixture was allowed to stand at room temperature for several days. The solution became dark green and deposited a small quantity of blue crystals [compound (1)], together with larger amounts of yellow needle-shaped crystals of product (2). Observed analysis C, 24.5; H, 2.9; N, 13.8; Cl, 25.1; Cu, 29.8%.  $\text{C}_{16}\text{H}_{24}\text{N}_8\text{Cl}_6\text{Cu}_4\text{O}$  requires: C, 23.7; H, 3.0; N, 13.8; Cl, 26.2; Cu, 31.3%. Removal of the dark-green liquid by syringe and injection into a degassed Schlenk tube caused the precipitation of a yellow-green powder, which was separated by filtration and shown by analysis to be a further portion of the product (2). The combined yield of this product was 44% with respect to copper.

(3): The filtrate was left to stand at room temperature for several days. As well as further small amounts of product (2), some large dark-green crystals were also formed and separated by filtration as product (3), in a 4% yield. Observed analysis: C, 30.0; H, 3.7; N, 17.4; Cl, 23.0%.  $\text{C}_{32}\text{H}_{48}\text{N}_{16}\text{Cl}_8\text{Cu}_5\text{O}$  requires: C, 30.2; H, 3.8; N, 17.6; Cl, 22.3%.

(4): The resultant dark-green filtrate was concentrated by evaporation under reduced pressure, to a volume of *ca* 5 cm<sup>3</sup>, and cooled to 253 K, whence the solution became blue and deposited a blue product (4*a*). This material was washed with  $\text{Et}_2\text{O}$  and dried under vacuum, the yield being 14%. Observed analysis: C, 40.7; H, 5.2; N, 23.8; Cl, 17.6%.

The crystals of (1), (2) and (3), obtained as described above, proved to be suitable for X-ray crystallographic studies. However, the material (4*a*) showed surface discoloration and a greenish encrustation and was recrystallized from MeCN and  $\text{Et}_2\text{O}$  with no precaution taken to exclude moisture or air. Pale blue crystals of (4) were obtained, which proved to be of a suitable quality for X-ray crystallographic studies. Observed analysis: C, 36.6; H, 5.6; N, 20.2%.  $\text{C}_{16}\text{H}_{30}\text{N}_8\text{Cl}_2\text{CuO}_3$  requires C, 37.2; H, 5.8; N, 21.7%.

### Structure determination

Crystals were mounted on glass fibres and examined on a Stoe-Siemens AED diffractometer with graphite-monochromated  $\text{Mo K}\alpha$  radiation. Unit-cell parameters were refined from  $2\theta$  values (20–25°) of reflections measured on both sides of the direct beam. Intensities were collected in an  $\omega/\theta$  scan mode with variable scan width and time and on-line profile fitting (Clegg, 1981). No significant variation was observed for three standard reflections in each case. Semi-empirical absorption corrections were applied, based on sets of equivalent reflections measured at a range of azimuthal angles.

Structure refinement was by blocked-cascade refinement on  $F$ , with  $w^{-1} = \sigma^2(F) + gF^2$ ,  $g$  being optimized as part of the refinement. Anisotropic thermal parameters were refined for all non-H atoms. H atoms attached to the imidazole rings were constrained [ $C-H = 0.96 \text{ \AA}$  on external bisector of ring angle,  $U(H) = 1.2U_{eq}(C)$ ]; methyl H atoms, probably subject to torsional disorder, were not included: difference maps showed several small peaks around each methyl C atom. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The *SHELXTL* program system (Sheldrick, 1978) was used.

(1): Deep-blue crystal,  $0.17 \times 0.35 \times 0.38 \text{ mm}$ , 36 reflections for cell refinement, 5462 intensities measured with  $2\theta < 50^\circ$ ,  $h -9 \rightarrow 2$ ,  $k -11 \rightarrow 11$ ,  $l -19 \rightarrow 19$ , 4190 unique ( $R_{int} = 0.032$ ), 3607 with  $F > 4\sigma(F)$ , transmission 0.49–0.56. Reflections with  $k + l$  odd were rather broader than those with  $k + l$  even, and were of rather lower intensity on average (by a factor of ca 2), indicating a pseudo- $A$ -centred structure and some long-range disorder: the two sets of reflections were measured separately with different profile scan-width parameters. Structure solution by Patterson and difference syntheses, 281 parameters,  $R = 0.044$ ,  $wR = 0.064$ ,  $g = 0.00138$ , mean  $(\Delta/\sigma) = 0.007$ , max. = 0.027, max.  $(\Delta\rho) = 0.67$ , min. =  $-0.53 \text{ e \AA}^{-3}$ , slope of normal probability plot = 1.09.

(2): Yellow-green crystal,  $0.2 \times 0.3 \times 0.4 \text{ mm}$ , 52 reflections for cell refinement, 9203 intensities measured with  $2\theta < 45^\circ$ ,  $h 0 \rightarrow 20$ ,  $k 0 \rightarrow 20$ ,  $l 0 \rightarrow 35$  together with some equivalent reflections, 7804 unique ( $R_{int} = 0.042$ ), 4794 with  $F > 4\sigma(F)$ , transmission 0.18–0.26. Structure solution by direct methods. Residual electron density was attributed to MeCN solvent molecules, probably disordered or with partial occupancy. One such molecule per asymmetric unit (*i.e.* per two molecules of complex) was refined as a linear rigid group with C–C 1.47, C–N 1.15  $\text{\AA}$  and an overall isotropic thermal parameter. 638 parameters,  $R = 0.068$ ,  $wR = 0.046$ ,  $g = 0$ , mean  $(\Delta/\sigma) = 0.02$ , max. = 0.09, max.  $(\Delta\rho) = 0.94$ , min. =  $-0.67 \text{ e \AA}^{-3}$ , slope of normal probability plot = 1.49.

(3): Green crystal,  $0.4 \times 0.4 \times 0.35 \text{ mm}$ , 40 reflections for cell refinement, 11 845 intensities measured with  $2\theta < 50^\circ$ ,  $h 0 \rightarrow 15$ ,  $k 0 \rightarrow 17$ ,  $l 0 \rightarrow 31$  and  $h -15 \rightarrow 0$ ,  $k -17 \rightarrow 0$ ,  $l -31 \rightarrow 0$  together with some equivalent reflections, 9009 unique ( $R_{int} = 0.027$ ), 6999 with  $F > 4\sigma(F)$ , transmission 0.22–0.28. Structure solution by Patterson and difference syntheses, absolute structure determination by refinement of  $\eta = +0.89$  (4) (Rogers, 1981). 558 parameters,  $R = 0.052$ ,  $wR = 0.063$ ,  $g = 0.00083$ , mean  $(\Delta/\sigma) = 0.02$ , max. = 0.12, max.  $(\Delta\rho) = 1.13$ , min. =  $-0.98 \text{ e \AA}^{-3}$ , slope of normal probability plot = 1.14.

(4): Blue crystal  $0.5 \times 0.5 \times 0.7 \text{ mm}$ , 24 reflections for cell refinement, 3139 intensities measured with

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ ) for (1)

	$U_{eq} = \frac{1}{3}(\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$			
	$x$	$y$	$z$	$U_{eq}$
Cu(1)	5012 (1)	2515 (1)	2514 (1)	356 (1)
N(11)	7447 (3)	3054 (3)	3095 (2)	380 (10)
C(12)	8377 (4)	4365 (4)	3375 (2)	408 (12)
N(13)	9925 (3)	4284 (3)	3732 (2)	410 (10)
C(14)	9997 (5)	2860 (5)	3687 (3)	518 (15)
C(15)	8457 (5)	2094 (4)	3289 (2)	458 (13)
C(16)	11300 (5)	5541 (5)	4109 (3)	635 (16)
N(21)	5687 (3)	2909 (3)	1391 (2)	348 (9)
C(22)	6531 (4)	4122 (4)	1207 (2)	376 (11)
N(23)	6684 (4)	3992 (3)	379 (2)	385 (10)
C(24)	5887 (5)	2609 (4)	17 (2)	451 (13)
C(25)	5267 (5)	1953 (4)	645 (2)	420 (12)
C(26)	7545 (5)	5130 (5)	-57 (3)	549 (15)
N(31)	2585 (3)	1974 (3)	1928 (2)	344 (9)
C(32)	1661 (4)	665 (4)	1640 (2)	367 (11)
N(33)	106 (3)	750 (3)	1282 (2)	384 (9)
C(34)	43 (5)	2187 (5)	1342 (3)	500 (14)
C(35)	1577 (5)	2939 (4)	1745 (2)	438 (12)
C(36)	-1278 (5)	-489 (5)	897 (3)	616 (16)
N(41)	4339 (3)	2077 (3)	3632 (2)	349 (9)
C(42)	3469 (4)	862 (4)	3795 (2)	394 (12)
N(43)	3281 (4)	959 (3)	4616 (2)	405 (10)
C(44)	4085 (5)	2336 (4)	4997 (2)	459 (13)
C(45)	4736 (5)	3011 (4)	4385 (2)	418 (12)
C(46)	2392 (6)	-195 (5)	5028 (3)	625 (17)
Cu(2)	3580 (1)	7247 (1)	2335 (1)	425 (2)
Cl(1)	5230 (1)	9368 (1)	2180 (1)	479 (3)
Cl(2)	804 (1)	6796 (1)	1928 (1)	653 (4)
Cl(3)	4898 (1)	5587 (1)	2887 (1)	502 (3)
O	8897 (5)	8295 (4)	3240 (3)	868 (16)
Cu(2 <sub>x</sub> )	6445 (13)	7757 (8)	2672 (8)	966 (44)

$2\theta < 45^\circ$ ,  $h 0 \rightarrow 9$ ,  $k -10 \rightarrow 10$ ,  $l -16 \rightarrow 16$ , all unique, 2959 with  $F > 4\sigma(F)$ , transmission 0.58–0.60. Structure solution by direct methods, water H atoms located in difference syntheses and constrained [ $O-H = 0.85 \text{ \AA}$ ,  $H-O-H = 104^\circ$ ,  $U(H) = 1.2U_{eq}(O)$ ]. 283 parameters,  $R = 0.036$ ,  $wR = 0.057$ ,  $g = 0.00038$ , mean  $(\Delta/\sigma) = 0.006$ , max. = 0.07, max.  $(\Delta\rho) = 0.46$ , min. =  $-0.42 \text{ e \AA}^{-3}$ , slope of normal probability plot = 1.75.

Atomic coordinates and equivalent isotropic thermal parameters are given in Tables 1–4.\*

**Discussion.** Selected bond lengths and bond angles for the coordination geometry about the Cu atoms of compounds (1), (2), (3) and (4) are presented in Tables 5–8. Dimensions of the *N*-methylimidazole ligands have not been included: these are very similar to those reported previously (van Ooijen, Reedijk & Spek, 1979; Graves, Hodgson, van Kralingen & Reedijk, 1978, and references therein). The molecular structures of these complexes are represented in Figs. 1–4.

Compound (1): This consists of  $[\text{Cu}(\text{Meim})_4]$  and  $[\text{CuCl}_3]$  moieties, together with water molecules in the crystal structure. The coordinations of Cu(1) by four N atoms and of Cu(2) by three Cl atoms are both

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and complete bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44539 (64 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

essentially planar. The similarity of the dimensions of these complexes to those reported previously for  $\text{Cu}^{\text{II}}(\text{Meim})_4$  (and closely related) complexes (Clegg, Garner & Collison, 1988; McFadden, McPhail, Garner & Mabbs, 1976; Bernarducci, Bharadwaj, Krogh-

Jespersen, Potenza & Schugar, 1983) and  $[\text{Cu}^{\text{I}}\text{Cl}_3]^{2-}$  salts (Brink & MacGillavry, 1949; Brink & van Arkel, 1952) and the need to maintain overall neutrality in the crystal lattice, suggest a basic composition of  $[\text{Cu}^{\text{II}}(\text{Meim})_4]^{2+}[\text{Cu}^{\text{I}}\text{Cl}_3]^{2-}$ . Furthermore, the ESR spectrum obtained for compound (1) is identical within experimental error to that of compound (4) and the values of the parameters are in very close agreement with those found for the related complexes  $[\text{Cu}(\text{Him})_4(\text{H}_2\text{O})_2]\text{F}_2$  and  $[\text{Cu}(\text{Him})_4][\text{BF}_4]\text{F}$ , (Vreugdenhil, Birker, ten Hoedt, Verschoor & Reedijk, 1984) and the two forms of  $[\text{Cu}(\text{Meim})_4(\text{BF}_4)_2]$  (Clegg, Garner & Collison,

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ ) for (2)

	x	y	z	$U_{\text{eq}}$
Cu(1)	-172 (1)	5456 (1)	2790 (1)	498 (5)
Cu(2)	688 (1)	4643 (1)	2141 (1)	501 (5)
Cu(3)	-292 (1)	3815 (1)	2705 (1)	529 (6)
Cu(4)	-935 (1)	4798 (1)	2053 (1)	541 (6)
Cl(12)	1039 (2)	5581 (2)	2614 (1)	679 (13)
Cl(13)	-314 (2)	4514 (1)	3304 (1)	538 (12)
Cl(14)	-1254 (2)	5778 (2)	2475 (1)	687 (13)
Cl(23)	754 (2)	3445 (1)	2333 (1)	708 (14)
Cl(24)	-6 (2)	4909 (2)	1551 (1)	579 (12)
Cl(34)	-1329 (2)	3660 (2)	2275 (1)	716 (13)
O(1)	-184 (4)	4680 (3)	2419 (2)	411 (25)
N(11)	-215 (5)	6237 (4)	3176 (2)	465 (34)
C(12)	242 (7)	6774 (5)	3235 (3)	555 (48)
N(13)	-45 (5)	7206 (5)	3503 (3)	699 (44)
C(14)	-693 (7)	6953 (6)	3623 (4)	770 (59)
C(15)	-780 (7)	6370 (6)	3418 (4)	858 (62)
C(16)	297 (8)	7894 (6)	3638 (4)	909 (65)
N(21)	1588 (5)	4654 (5)	1868 (3)	519 (37)
C(22)	1750 (7)	4731 (6)	1488 (3)	606 (52)
N(23)	2444 (5)	4690 (5)	1426 (3)	696 (43)
C(24)	2748 (7)	4559 (7)	1780 (4)	873 (61)
C(25)	2211 (7)	4523 (7)	2057 (4)	834 (61)
C(26)	2816 (7)	4780 (7)	1031 (3)	844 (60)
N(31)	-362 (6)	2928 (5)	2996 (3)	748 (48)
C(32)	-373 (7)	2802 (6)	3381 (4)	687 (58)
N(33)	-270 (6)	2128 (5)	3467 (3)	756 (45)
C(34)	-225 (12)	1813 (7)	3118 (5)	1629 (113)
C(35)	-279 (14)	2284 (6)	2818 (4)	2303 (155)
C(36)	-220 (9)	1790 (6)	3863 (3)	954 (68)
N(41)	-1679 (5)	4965 (5)	1658 (3)	642 (40)
C(42)	-2270 (6)	5312 (6)	1697 (3)	721 (55)
N(43)	-2661 (6)	5345 (6)	1353 (3)	918 (51)
C(44)	-2292 (7)	5006 (10)	1085 (4)	1343 (89)
C(45)	-1692 (8)	4731 (8)	1261 (4)	1198 (78)
C(46)	-3346 (8)	5720 (8)	1306 (5)	1166 (77)
Cu(5)	7545 (1)	2344 (1)	-613 (1)	493 (5)
Cu(6)	7171 (1)	2506 (1)	296 (1)	485 (5)
Cu(7)	8401 (1)	1537 (1)	42 (1)	451 (5)
Cu(8)	6851 (1)	1104 (1)	-156 (1)	424 (5)
Cl(56)	7315 (2)	3388 (1)	-236 (1)	586 (12)
Cl(57)	8754 (2)	1883 (1)	-619 (1)	555 (12)
Cl(58)	6560 (2)	1617 (1)	-795 (1)	627 (12)
Cl(67)	8304 (2)	2287 (2)	614 (1)	633 (12)
Cl(68)	6197 (2)	1712 (2)	366 (1)	894 (16)
Cl(78)	7836 (1)	391 (1)	53 (1)	503 (11)
O(2)	7497 (3)	1875 (3)	-108 (2)	348 (24)
N(51)	7613 (5)	2774 (4)	-1137 (2)	546 (38)
C(52)	7495 (6)	2464 (5)	-1485 (3)	585 (45)
N(53)	7607 (6)	2864 (4)	-1810 (3)	700 (43)
C(54)	7841 (8)	3450 (7)	-1655 (3)	1048 (70)
C(55)	7853 (7)	3433 (6)	-1238 (4)	758 (56)
C(56)	7543 (9)	2717 (7)	-2251 (3)	975 (66)
N(61)	6826 (5)	3119 (5)	713 (3)	534 (38)
C(62)	7063 (7)	3176 (6)	1076 (4)	713 (58)
N(63)	6641 (6)	3543 (6)	1319 (3)	783 (50)
C(64)	6132 (8)	3754 (8)	1108 (4)	922 (71)
C(65)	6216 (7)	3505 (6)	734 (4)	853 (60)
C(66)	6719 (8)	3675 (8)	1757 (3)	1041 (73)
N(71)	9314 (5)	1198 (4)	196 (3)	456 (36)
C(72)	9471 (5)	603 (6)	357 (3)	480 (47)
N(73)	10163 (5)	519 (5)	456 (2)	652 (40)
C(74)	10453 (7)	1151 (7)	352 (3)	778 (60)
C(75)	9934 (7)	1563 (7)	199 (4)	767 (59)
C(76)	10530 (7)	-113 (7)	634 (4)	786 (55)
N(81)	6227 (4)	306 (4)	-235 (2)	455 (34)
C(82)	6263 (6)	-312 (6)	-37 (3)	523 (47)
N(83)	5754 (5)	-742 (5)	-140 (3)	518 (38)
C(84)	5360 (6)	-404 (6)	-409 (3)	615 (48)
C(85)	5661 (6)	227 (5)	-472 (3)	509 (44)
C(86)	5664 (7)	-1483 (5)	24 (4)	760 (56)
N(9)	2832 (30)	2092 (35)	3193 (21)	10602 (285)
C(91)	2237	2011	3245	10602 (285)
C(92)	1477	1911	3314	10602 (285)

Table 3. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ ) for (3)

	x	y	z	$U_{\text{eq}}$
Cu(1)	1672 (1)	1704 (1)	5409 (1)	402 (3)
Cu(2)	3327 (1)	3184 (1)	5450 (1)	375 (3)
Cu(3)	3179 (1)	1593 (1)	4583 (1)	376 (3)
Cu(4)	1852 (1)	3436 (1)	4615 (1)	391 (3)
O	2498 (5)	2482 (3)	5000	324 (13)
Cl(12)	2453 (1)	2426 (1)	6125 (1)	441 (6)
Cl(13)	2173 (2)	264 (2)	4936 (1)	542 (8)
Cl(14)	489 (1)	2820 (2)	5036 (1)	500 (7)
Cl(23)	4472 (1)	2050 (2)	5074 (1)	670 (9)
Cl(24)	2865 (2)	4694 (2)	5018 (1)	606 (9)
Cl(34)	2484 (1)	2533 (1)	3899 (1)	396 (6)
N(11)	829 (4)	902 (5)	5804 (2)	462 (23)
C(12)	-57 (5)	843 (6)	5755 (3)	487 (29)
N(13)	-423 (4)	188 (5)	6084 (2)	462 (22)
C(14)	282 (6)	-178 (7)	6364 (4)	651 (34)
C(15)	1038 (6)	241 (7)	6192 (4)	679 (35)
C(16)	-1405 (6)	-34 (8)	6132 (4)	734 (38)
N(21)	4201 (4)	3832 (5)	5894 (2)	403 (21)
C(22)	4652 (5)	4680 (6)	5827 (3)	492 (29)
N(23)	5271 (5)	4841 (6)	6194 (3)	622 (27)
C(24)	5175 (6)	4035 (7)	6524 (3)	570 (32)
C(25)	4532 (6)	3443 (6)	6334 (3)	490 (29)
C(26)	5884 (7)	5730 (8)	6235 (4)	838 (43)
N(31)	3834 (4)	681 (5)	4149 (2)	419 (21)
C(32)	4638 (5)	255 (5)	4225 (3)	423 (26)
N(33)	4871 (4)	-373 (5)	3856 (2)	460 (22)
C(34)	4167 (6)	-373 (7)	3512 (3)	626 (35)
C(35)	3536 (5)	293 (6)	3698 (3)	529 (29)
C(36)	5714 (6)	-999 (8)	3809 (3)	662 (36)
N(41)	1220 (4)	4436 (5)	4208 (2)	469 (23)
C(42)	423 (6)	4847 (7)	4291 (3)	607 (34)
N(43)	228 (5)	5534 (5)	3933 (3)	518 (24)
C(44)	953 (7)	5584 (7)	3620 (4)	675 (36)
C(45)	1565 (6)	4921 (7)	3798 (4)	701 (37)
C(46)	-607 (7)	6169 (9)	3898 (4)	901 (46)
Cu(5)	8057 (1)	2481 (1)	7472 (1)	405 (3)
N(51)	8021 (4)	961 (4)	7422 (2)	385 (19)
C(52)	7269 (5)	445 (5)	7403 (3)	450 (26)
N(53)	7413 (4)	-550 (4)	7423 (2)	433 (21)
C(54)	8341 (5)	-675 (5)	7482 (4)	529 (27)
C(55)	8713 (5)	269 (5)	7470 (3)	490 (26)
C(56)	6699 (5)	-1341 (6)	7414 (4)	659 (33)
N(61)	7922 (5)	2313 (5)	8231 (2)	434 (22)
C(62)	7188 (7)	2545 (6)	8499 (3)	576 (32)
N(63)	7361 (5)	2286 (5)	8999 (2)	566 (27)
C(64)	8198 (7)	1882 (7)	9017 (3)	650 (36)
C(65)	8525 (7)	1882 (7)	8545 (3)	628 (35)
C(66)	6701 (7)	2402 (10)	9412 (4)	869 (50)
N(71)	7675 (4)	3939 (4)	7519 (2)	385 (19)
C(72)	8247 (5)	4696 (5)	7469 (3)	504 (26)
N(73)	7819 (5)	5589 (4)	7511 (3)	514 (23)
C(74)	6910 (5)	5388 (6)	7604 (3)	511 (28)
C(75)	6856 (5)	4359 (6)	7601 (3)	494 (28)
C(76)	8270 (8)	6600 (6)	7509 (5)	819 (41)
N(81)	7920 (5)	2583 (5)	6723 (2)	425 (22)
C(82)	7176 (6)	2489 (7)	6452 (3)	586 (32)
N(83)	7271 (5)	2671 (6)	5965 (3)	578 (26)
C(84)	8177 (7)	2942 (10)	5914 (4)	892 (46)
C(85)	8569 (6)	2839 (8)	6379 (3)	668 (38)
C(86)	6574 (8)	2576 (10)	5562 (4)	981 (56)
Cl(51)	9769 (1)	2795 (1)	7505 (1)	520 (6)
Cl(52)	5455 (1)	2103 (1)	7446 (1)	526 (6)

1988), *i.e.*  $g_{\parallel} \approx 2.25$  and  $g_{\perp} \approx 2.04$ . The cations and anions of compound (1) are arranged in chains (Fig. 1), each anion linking two cations *via* axial Cu...Cl contacts of 2.922 (2) and 3.007 (2) Å; Cl...Cu...Cl is 178.0 (2)° and the Cu...Cl vectors are inclined at 87.0 (1)° to the Cu—N bonds, thus completing a tetragonally distorted octahedral coordination of the Cu atom of the cation. However, there is a minor disorder of the Cu atom of the anion which results in a small contribution from the arrangement *B* in the majority arrangement *A* (Fig. 5). The relative contribution of these two components is 0.919:0.081 (2).

Compound (1) is of interest as a mixed-valence Cu<sup>II</sup>...Cu<sup>I</sup>...Cu<sup>II</sup>...Cu<sup>I</sup> system of the Class I type described by Robin & Day (1967), and the arrangement has some similarities to Pd<sup>II</sup>...Pd<sup>I</sup>...Pd<sup>II</sup>...Pd<sup>I</sup> systems (Cotton & Wilkinson, 1980).

Compound (2): [Cu<sub>4</sub>OCl<sub>6</sub>(Meim)<sub>4</sub>] (Fig. 2), the major product of the reaction, is presumably formed when traces of water are present. Similar observations have been made in the reaction of 4-methylthiazole (van

Ooijen & Reedijk, 1978) and it is consistent with observations made by Gill & Sterns (1970). The [Cu<sub>4</sub>OCl<sub>10-n</sub>L<sub>n</sub>]<sup>n-4</sup> type of structure is well known and has been fully characterized for a variety of ligands, *L*, coordinated to copper through N, O or Cl [*L* = 2-methylpyridine (Gill & Sterns, 1970), pyridine

Table 6. Selected bond lengths (Å) and angles (°) for (2)

Cu(1) Cl(12)	2.380 (4)	Cu(2) Cl(12)	2.470 (4)
Cu(1) Cl(13)	2.493 (3)	Cu(2) Cl(23)	2.372 (3)
Cu(1) Cl(14)	2.382 (4)	Cu(2) Cl(24)	2.416 (3)
Cu(1)-O(1)	1.924 (6)	Cu(2)-O(1)	1.895 (7)
Cu(1)-N(11)	1.967 (8)	Cu(2) N(21)	1.931 (9)
Cu(3) Cl(13)	2.396 (3)	Cu(4)-Cl(14)	2.411 (3)
Cu(3) Cl(23)	2.440 (4)	Cu(4)-Cl(24)	2.435 (3)
Cu(3) Cl(34)	2.449 (4)	Cu(4)-Cl(34)	2.409 (4)
Cu(3) O(1)	1.912 (6)	Cu(4)-O(1)	1.886 (7)
Cu(3)-N(31)	1.950 (9)	Cu(4)-N(41)	1.952 (9)
Cu(5) Cl(56)	2.389 (3)	Cu(6)-Cl(56)	2.456 (3)
Cu(5) Cl(57)	2.454 (3)	Cu(6)-Cl(67)	2.428 (4)
Cu(5) Cl(58)	2.401 (4)	Cu(6)-Cl(68)	2.397 (4)
Cu(5)-O(2)	1.904 (6)	Cu(6)-O(2)	1.906 (6)
Cu(5) N(51)	1.929 (8)	Cu(6)-N(61)	1.926 (9)
Cu(7) Cl(57)	2.392 (3)	Cu(8)-Cl(58)	2.402 (3)
Cu(7) Cl(67)	2.384 (3)	Cu(8)-Cl(68)	2.426 (4)
Cu(7) Cl(78)	2.430 (3)	Cu(8) Cl(78)	2.412 (3)
Cu(7) O(2)	1.897 (7)	Cu(8) O(2)	1.918 (6)
Cu(7)-N(71)	1.915 (9)	Cu(8)-N(81)	1.944 (8)

Table 4. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{Å}^2 \times 10^4$ ) for (4)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Cu(1)	5000	5000	0	330 (2)
O(1)	7536 (3)	4687 (3)	-216 (2)	537 (10)
N(11)	4133 (3)	2740 (3)	-418 (2)	386 (10)
Cl(12)	4518 (4)	1866 (3)	-1024 (2)	463 (14)
N(13)	3702 (3)	399 (3)	-1172 (2)	496 (12)
Cl(14)	2739 (4)	347 (4)	-645 (2)	561 (16)
Cl(15)	3008 (4)	1790 (4)	-194 (2)	521 (15)
Cl(16)	3829 (6)	-905 (4)	-1813 (3)	823 (22)
N(21)	5725 (3)	4844 (3)	1330 (2)	358 (10)
Cl(22)	7173 (4)	4903 (3)	1780 (2)	381 (12)
N(23)	7327 (3)	4785 (3)	2639 (2)	378 (10)
Cl(24)	5892 (4)	4631 (4)	2749 (2)	516 (15)
Cl(25)	4910 (4)	4660 (4)	1942 (2)	504 (15)
Cl(26)	8804 (4)	4763 (4)	3319 (2)	572 (15)
Cu(2)	5000	0	5000	345 (2)
O(2)	4809 (3)	2534 (2)	4720 (2)	594 (11)
N(31)	6871 (3)	236 (3)	4546 (2)	374 (10)
Cl(32)	7177 (4)	-828 (3)	4016 (2)	436 (13)
N(33)	8480 (3)	-279 (3)	3817 (2)	419 (11)
Cl(34)	9057 (4)	1222 (4)	4243 (2)	469 (14)
Cl(35)	8051 (4)	1529 (4)	4687 (2)	441 (13)
Cl(36)	9164 (5)	-1116 (5)	3207 (3)	669 (19)
N(41)	6428 (3)	1018 (3)	6309 (2)	361 (10)
Cl(42)	6882 (4)	277 (4)	6934 (2)	425 (13)
N(43)	7776 (3)	1231 (3)	7744 (2)	499 (12)
Cl(44)	7880 (4)	2659 (4)	7627 (2)	584 (16)
Cl(45)	7059 (4)	2522 (4)	6751 (2)	494 (14)
Cl(46)	8486 (6)	781 (6)	8591 (3)	895 (24)
Cl(1)	30 (1)	3313 (1)	935 (1)	490 (3)
Cl(2)	2389 (1)	4456 (1)	4656 (1)	527 (3)
O(3)	1145 (6)	2129 (4)	2704 (2)	1293 (24)

Table 5. Selected bond lengths (Å) and angles (°) for (1)

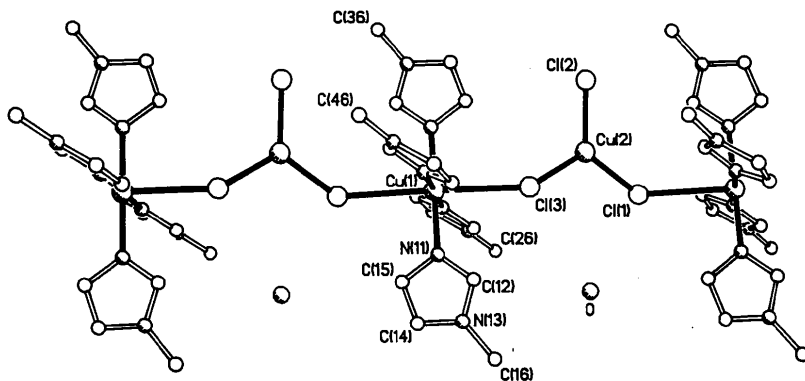
Cu(1)-N(11)	2.020 (3)	Cu(1)-N(21)	2.011 (3)
Cu(1)-N(31)	2.016 (3)	Cu(1)-N(41)	2.014 (3)
Cu(2)-Cl(1)	2.259 (1)	Cu(2)-Cl(2)	2.224 (1)
Cu(2)-Cl(3)	2.246 (1)		
N(11)-Cu(1)-N(21)	90.2 (1)	N(11)-Cu(1)-N(31)	179.7 (1)
N(21)-Cu(1)-N(31)	89.6 (1)	N(11)-Cu(1)-N(41)	89.8 (1)
N(21)-Cu(1)-N(41)	178.8 (1)	N(31)-Cu(1)-N(41)	90.4 (1)
Cl(1)-Cu(2)-Cl(2)	121.8 (1)	Cl(1)-Cu(2)-Cl(3)	116.4 (1)
Cl(2)-Cu(2)-Cl(3)	121.7 (1)		
Cl(12)-Cu(1)-Cl(13)	110.2 (1)	Cl(12)-Cu(2)-Cl(23)	120.7 (1)
Cl(12)-Cu(1)-Cl(14)	134.1 (1)	Cl(12)-Cu(2)-Cl(24)	120.8 (1)
Cl(13)-Cu(1)-Cl(14)	113.2 (1)	Cl(23)-Cu(2)-Cl(24)	116.6 (1)
Cl(12)-Cu(1)-O(1)	86.1 (2)	Cl(12)-Cu(2)-O(1)	84.1 (2)
Cl(13)-Cu(1)-O(1)	83.4 (2)	Cl(23)-Cu(2)-O(1)	87.1 (2)
Cl(14)-Cu(1)-O(1)	84.6 (2)	Cl(24)-Cu(2)-O(1)	85.1 (2)
Cl(12)-Cu(1)-N(11)	97.2 (3)	Cl(12)-Cu(2)-N(21)	93.1 (3)
Cl(13)-Cu(1)-N(11)	95.2 (2)	Cl(23)-Cu(2)-N(21)	95.2 (3)
Cl(14)-Cu(1)-N(11)	93.2 (3)	Cl(24)-Cu(2)-N(21)	95.5 (3)
O(1)-Cu(1)-N(11)	176.8 (3)	O(1)-Cu(2)-N(21)	177.1 (3)
Cl(13)-Cu(3)-Cl(23)	126.6 (1)	Cl(14)-Cu(4)-Cl(24)	120.9 (1)
Cl(13)-Cu(3)-Cl(34)	122.6 (1)	Cl(14)-Cu(4)-Cl(34)	116.1 (1)
Cl(23)-Cu(3)-Cl(34)	108.7 (1)	Cl(24)-Cu(4)-Cl(34)	120.8 (1)
Cl(13)-Cu(3)-O(1)	86.3 (2)	Cl(14)-Cu(4)-O(1)	84.6 (2)
Cl(23)-Cu(3)-O(1)	84.8 (2)	Cl(24)-Cu(4)-O(1)	84.7 (2)
Cl(34)-Cu(3)-O(1)	84.2 (2)	Cl(34)-Cu(4)-O(1)	85.9 (2)
Cl(13)-Cu(3)-N(31)	93.9 (3)	Cl(14)-Cu(4)-N(41)	94.8 (3)
Cl(23)-Cu(3)-N(31)	93.2 (3)	Cl(24)-Cu(4)-N(41)	92.7 (3)
Cl(34)-Cu(3)-N(31)	97.5 (3)	Cl(34)-Cu(4)-N(41)	97.4 (3)
O(1)-Cu(3)-N(31)	177.7 (4)	O(1)-Cu(4)-N(41)	176.6 (3)
Cu(1)-Cl(12)-Cu(2)	79.9 (1)	Cu(1)-O(1)-Cu(2)	109.3 (3)
Cu(1)-Cl(13)-Cu(3)	80.1 (1)	Cu(1)-O(1)-Cu(3)	110.2 (3)
Cu(1)-Cl(14)-Cu(4)	80.8 (1)	Cu(2)-O(1)-Cu(3)	107.7 (3)
Cu(2) Cl(23)-Cu(3)	79.4 (1)	Cu(1)-O(1)-Cu(4)	109.3 (3)
Cu(2)-Cl(24)-Cu(4)	79.6 (1)	Cu(2)-O(1)-Cu(4)	110.3 (3)
Cu(3)-Cl(34)-Cu(4)	79.7 (1)	Cu(3)-O(1)-Cu(4)	110.1 (3)
Cl(56)-Cu(5)-Cl(57)	118.1 (1)	Cl(56)-Cu(6)-Cl(67)	109.4 (1)
Cl(56)-Cu(5)-Cl(58)	118.1 (1)	Cl(56)-Cu(6)-Cl(68)	125.9 (1)
Cl(57)-Cu(5)-Cl(58)	121.2 (1)	Cl(67)-Cu(6)-Cl(68)	122.0 (1)
Cl(56)-Cu(5)-O(2)	85.3 (2)	Cl(56)-Cu(6)-O(2)	83.4 (2)
Cl(57)-Cu(5)-O(2)	83.4 (2)	Cl(67)-Cu(6)-O(2)	84.9 (2)
Cl(58)-Cu(5)-O(2)	85.1 (2)	Cl(68)-Cu(6)-O(2)	85.4 (2)
Cl(56)-Cu(5)-N(51)	97.6 (2)	Cl(56)-Cu(6)-N(61)	98.2 (3)
Cl(57)-Cu(5)-N(51)	94.7 (3)	Cl(67)-Cu(6)-N(61)	95.2 (3)
Cl(58)-Cu(5)-N(51)	94.0 (3)	Cl(68)-Cu(6)-N(61)	93.0 (3)
O(2)-Cu(5)-N(51)	177.0 (3)	O(2)-Cu(6)-N(61)	178.2 (3)
Cl(57)-Cu(7)-Cl(67)	126.1 (1)	Cl(58)-Cu(8)-Cl(68)	108.8 (1)
Cl(57)-Cu(7)-Cl(78)	112.7 (1)	Cl(58)-Cu(8)-Cl(78)	131.5 (1)
Cl(67)-Cu(7)-Cl(78)	119.4 (1)	Cl(68)-Cu(8)-Cl(78)	117.2 (1)
Cl(57)-Cu(7)-O(2)	85.2 (2)	Cl(58)-Cu(8)-O(2)	84.8 (2)
Cl(67)-Cu(7)-O(2)	86.4 (2)	Cl(68)-Cu(8)-O(2)	84.3 (2)
Cl(78)-Cu(7)-O(2)	84.9 (2)	Cl(78)-Cu(8)-O(2)	85.0 (2)
Cl(57)-Cu(7)-N(71)	94.9 (3)	Cl(58)-Cu(8)-N(81)	93.4 (2)
Cl(67)-Cu(7)-N(71)	93.4 (3)	Cl(68)-Cu(8)-N(81)	99.1 (3)
Cl(78)-Cu(7)-N(71)	95.2 (3)	Cl(78)-Cu(8)-N(81)	93.9 (3)
O(2)-Cu(7)-N(71)	179.7 (2)	O(2)-Cu(8)-N(81)	176.5 (3)
Cu(5)-Cl(56)-Cu(6)	80.2 (1)	Cu(5)-O(2)-Cu(6)	110.0 (3)
Cu(5)-Cl(57)-Cu(7)	80.2 (1)	Cu(5)-O(2)-Cu(7)	110.4 (3)
Cu(5)-Cl(58)-Cu(8)	80.4 (1)	Cu(6)-O(2)-Cu(7)	108.7 (3)
Cu(6)-Cl(67)-Cu(7)	79.9 (1)	Cu(5)-O(2)-Cu(8)	108.4 (3)
Cu(6)-Cl(68)-Cu(8)	80.7 (1)	Cu(6)-O(2)-Cu(8)	109.5 (3)
Cu(7)-Cl(78)-Cu(8)	80.3 (1)	Cu(7)-O(2)-Cu(8)	109.8 (3)

Table 7. Selected bond lengths (Å) and angles (°) for (3)

Cu(1)—O	1.923 (5)	Cu(2)—O	1.937 (5)
Cu(1)—Cl(12)	2.411 (2)	Cu(2)—Cl(12)	2.418 (2)
Cu(1)—Cl(13)	2.397 (2)	Cu(2)—Cl(23)	2.460 (3)
Cu(1)—Cl(14)	2.482 (3)	Cu(2)—Cl(24)	2.398 (2)
Cu(1)—N(11)	1.934 (6)	Cu(2)—N(21)	1.938 (6)
Cu(3)—O	1.897 (5)	Cu(4)—O	1.877 (5)
Cu(3)—Cl(13)	2.477 (2)	Cu(4)—Cl(14)	2.427 (2)
Cu(3)—Cl(23)	2.375 (3)	Cu(4)—Cl(24)	2.472 (3)
Cu(3)—Cl(34)	2.422 (2)	Cu(4)—Cl(34)	2.425 (2)
Cu(3)—N(31)	1.923 (6)	Cu(4)—N(41)	1.942 (7)
Cu(5)—N(51)	2.016 (5)	Cu(5)—N(61)	2.032 (6)
Cu(5)—N(71)	2.013 (6)	Cu(5)—N(81)	2.000 (6)
Cu(5)—Cl(51)	2.542 (2)		
O—Cu(1)—Cl(12)	86.2 (1)	O—Cu(2)—Cl(12)	85.7 (1)
O—Cu(1)—Cl(13)	86.5 (1)	O—Cu(2)—Cl(23)	83.5 (2)
Cl(12)—Cu(1)—Cl(13)	125.5 (1)	Cl(12)—Cu(2)—Cl(23)	114.0 (1)
O—Cu(1)—Cl(14)	84.0 (2)	O—Cu(2)—Cl(24)	86.0 (1)
Cl(12)—Cu(1)—Cl(14)	114.1 (1)	Cl(12)—Cu(2)—Cl(24)	123.3 (1)
Cl(13)—Cu(1)—Cl(14)	118.6 (1)	Cl(23)—Cu(2)—Cl(24)	120.5 (1)
O—Cu(1)—N(11)	178.3 (2)	O—Cu(2)—N(21)	177.1 (2)
Cl(12)—Cu(1)—N(11)	95.5 (2)	Cl(12)—Cu(2)—N(21)	94.8 (2)
Cl(13)—Cu(1)—N(11)	92.4 (2)	Cl(23)—Cu(2)—N(21)	93.7 (2)
Cl(14)—Cu(1)—N(11)	95.5 (2)	Cl(24)—Cu(2)—N(21)	96.2 (2)
O—Cu(3)—Cl(13)	84.8 (2)	O—Cu(4)—Cl(14)	86.5 (2)
O—Cu(3)—Cl(23)	86.7 (2)	O—Cu(4)—Cl(24)	85.2 (2)
Cl(13)—Cu(3)—Cl(23)	116.6 (1)	Cl(14)—Cu(4)—Cl(24)	121.4 (1)
O—Cu(3)—Cl(34)	84.0 (1)	O—Cu(4)—Cl(34)	84.4 (1)
Cl(13)—Cu(3)—Cl(34)	113.4 (1)	Cl(14)—Cu(4)—Cl(34)	120.5 (1)
Cl(23)—Cu(3)—Cl(34)	127.9 (1)	Cl(24)—Cu(4)—Cl(34)	116.2 (1)
O—Cu(3)—N(31)	178.1 (3)	O—Cu(4)—N(41)	178.2 (3)
Cl(13)—Cu(3)—N(31)	94.3 (2)	Cl(14)—Cu(4)—N(41)	95.3 (2)
Cl(23)—Cu(3)—N(31)	95.2 (2)	Cl(24)—Cu(4)—N(41)	93.8 (2)
Cl(34)—Cu(3)—N(31)	94.8 (2)	Cl(34)—Cu(4)—N(41)	94.8 (2)
Cu(1)—O—Cu(2)	107.7 (1)	Cu(1)—O—Cu(3)	109.1 (2)
Cu(2)—O—Cu(3)	109.0 (3)	Cu(1)—O—Cu(4)	110.5 (3)
Cu(2)—O—Cu(4)	109.1 (2)	Cu(3)—O—Cu(4)	111.4 (1)
Cu(1)—Cl(12)—Cu(2)	80.4 (1)	Cu(1)—Cl(13)—Cu(3)	79.3 (1)
Cu(1)—Cl(14)—Cu(4)	79.0 (1)	Cu(2)—Cl(23)—Cu(3)	80.4 (1)
Cu(2)—Cl(24)—Cu(4)	79.3 (1)	Cu(3)—Cl(34)—Cu(4)	80.1 (1)
N(51)—Cu(5)—N(61)	87.4 (3)	N(51)—Cu(5)—N(71)	162.3 (2)
N(61)—Cu(5)—N(71)	90.9 (2)	N(51)—Cu(5)—N(81)	90.0 (3)
N(61)—Cu(5)—N(81)	168.4 (3)	N(71)—Cu(5)—N(81)	88.2 (3)
N(51)—Cu(5)—Cl(51)	101.0 (2)	N(61)—Cu(5)—Cl(51)	94.6 (2)
N(71)—Cu(5)—Cl(51)	96.6 (2)	N(81)—Cu(5)—Cl(51)	97.0 (2)

Table 8. Selected bond lengths (Å) and angles (°) for (4)

Cu(1)—O(1)	2.518 (3)	Cu(2)—O(2)	2.511 (3)
Cu(1)—N(11)	2.002 (2)	Cu(2)—N(31)	2.008 (3)
Cu(1)—N(21)	2.033 (3)	Cu(2)—N(41)	2.028 (2)
O(1)—Cu(1)—N(11)	87.2 (1)	O(2)—Cu(2)—N(31)	89.4 (1)
O(1)—Cu(1)—N(21)	91.3 (1)	O(2)—Cu(2)—N(41)	90.2 (1)
N(11)—Cu(1)—N(21)	90.1 (1)	N(31)—Cu(2)—N(41)	90.8 (1)

Fig. 1. The chain structure of (1). H atoms and the minor disorder component are omitted. The atom-labelling scheme for the *N*-methylimidazole ligands is shown for one ligand only; the others (in all structures) follow the same scheme.

(Kilburn & Dunitz, 1967), piperidine (Simonov, Yampol'skaya, Dvorkin, Ablov, Malinovskii & Matuzenko, 1980), 3-quinuclidinone (Dickinson, Helm, Baker, Black & Watson, 1977), hexamethylenetetramine (Pickardt & Rautenberg, 1982), triphenylphosphine oxide (Bertrand, 1967; Simonov, Dvorkin, Yampol'skaya & Zavodnik, 1982), triethylphosphine oxide (Churchill, de Boer & Mendak, 1975), *N*-methyl-2-pyrrolidinone (Churchill & Rotella, 1979), dimethylformamide (Nifontova, Lavrent'ev, Letuchii & Khidekel, 1982), or chloride (Bertrand & Kelley, 1969; Harlow & Simonsen, 1977; Holt, Holt & Vlasse, 1979; Belford, Fenton & Truter, 1972)] following reactions of  $\text{CuCl}_2$  with the corresponding ligand and a source of oxygen. Compounds of this type have attracted attention, not only because of their structure, but also in view of their unusual magnetic properties (Jones, Sams & Thompson, 1983) and catalytic activity (Davies, El-Shazly, Rupich, Churchill & Rotella, 1978).

$[\text{Cu}_4\text{OCl}_6(\text{Meim})_4]$  consists of a tetrahedron of copper(II) atoms at the centre of which is a  $\mu_4$ -oxide ion and above each of the six edges of which is a  $\mu_2$ -chloride ion: the structure is completed by one *N*-methylimidazole ligand bonded to each Cu atom. The central  $\mu_4$ -oxide ion, O(1), is approximately tetrahedrally coordinated to four  $\text{Cu}^{\text{II}}$  atoms. The average Cu—O distance is 1.904 Å and the Cu—O—Cu angles vary between 107.7 and 110.3°. Examples of an oxide ion forming four  $\sigma$  bonds to surrounding atoms are relatively rare. The classic example is basic beryllium acetate,  $[\text{Be}_4\text{O}(\text{CH}_3\text{CO}_2)_6]$  (Bragg & Morgan, 1923; Morgan & Astbury, 1926; Pauling & Sherman, 1934; Semenenko, 1958; Tulinsky, 1959); other such species, upon which X-ray diffraction studies have been carried out, include  $[\text{Zn}_4\text{O}(\text{CH}_3\text{CO}_2)_6]$  (Koyama & Saito, 1954) and  $[\text{Mg}_4\text{OBr}_6(\text{Et}_2\text{O})_4]$  (Stucky & Rundle, 1964). Each of the Cu atoms of  $[\text{Cu}_4\text{OCl}_6(\text{Meim})_4]$  has a coordination geometry which is essentially trigonal bipyramidal, with O and N atoms in axial positions and Cl atoms in the three equatorial sites.

Compound (3): This is a co-crystallized product, consisting of  $[\text{Cu}_4\text{OCl}_6(\text{Meim})_4]$ , one  $[\text{Cu}(\text{Meim})_4\text{Cl}]^+$  cation (Fig. 3), and one chloride anion per asymmetric unit. The structure of  $[\text{Cu}_4\text{OCl}_6(\text{Meim})_4]$  is essentially the same as found in compound (2). The one-sided axial coordination of a discrete tetrakis(*N*-methylimidazole)-copper(II) unit obtained in  $[\text{Cu}(\text{Meim})_4\text{Cl}]^+$  is novel and results in a tetragonal pyramidal coordination of the  $\text{Cu}^{\text{II}}$  which is displaced by  $0.257 \text{ \AA}$  from the mean plane of the four coordinated N atoms in the direction of the Cl atom. The chloride anion lies  $3.843 \text{ \AA}$  away from the nearest Cu atom in a direction opposite to the axial chlorine ( $\text{Cl}-\text{Cu}\cdots\text{Cl} = 177.9^\circ$ ). The Cu-N bond lengths vary from  $2.000$  (6) to  $2.036$  (6)  $\text{Å}$

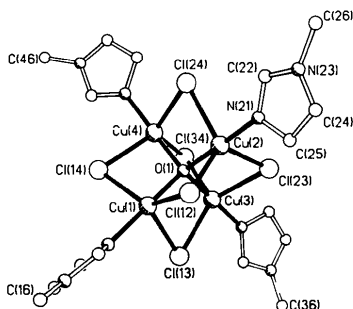


Fig. 2. The structure of one molecule of (2).

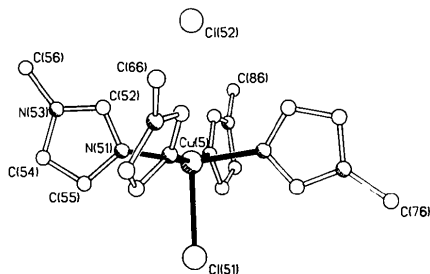


Fig. 3. The  $[\text{Cu}(\text{Meim})_4\text{Cl}]$  ion pair in (3).

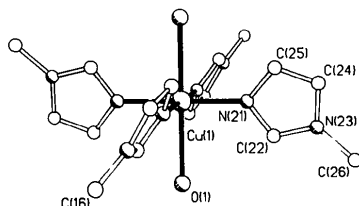


Fig. 4. The structure of (4).

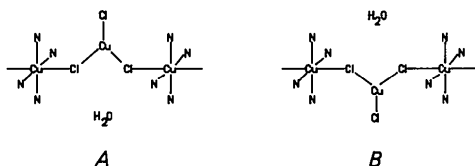


Fig. 5. The disorder components in the structure of (1).

(average  $2.015 \text{ \AA}$ ) and are typical of tetrakis(imidazole or *N*-methylimidazole)copper(II) complexes. Tetragonal pyramidal coordination of  $\text{Cu}^{\text{II}}$  by imidazole and/or imidazolate and chloride ligands has previously been observed in the polymeric  $[\text{Cu}(\text{imidazole})_2\text{Cl}_2]$  (Lundberg, 1972b) and  $[\text{Cu}(\text{imidazole})_2(\text{imidazolate})\text{Cl}]$  (Lundberg, 1972a) complexes. The former contains chains of  $\text{Cu}^{\text{II}}$  atoms bridged by  $\mu_2\text{-Cl}$  ligands and in the latter the  $\text{Cu}^{\text{II}}$  atoms are bridged by imidazole ligands with Cl occupying an axial position.

Compound (4): An example of pseudo-octahedral coordination of the  $[\text{Cu}(\text{Meim})_4]^{2+}$  cation occurs in compound (4) (Fig. 4),  $[\text{Cu}(\text{Meim})_4(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ , with the presence of two water molecules as axial ligands. The Cu-O bond lengths of  $2.511$  (3) and  $2.518$  (3)  $\text{Å}$  indicate a rather weak attachment and these Cu-O distances are in the range observed for semi-coordination (Hathaway & Tomlinson, 1970; Hathaway & Billing, 1970), but are shorter than the values of  $2.638 \text{ \AA}$  observed by Vreugdenhil *et al.* (1984) for the compound  $[\text{Cu}(\text{Him})_4(\text{H}_2\text{O})_2]\text{F}_2$ , in which the strong hydrogen-bonding interaction weakens the axial interaction of the water molecules with the Cu ion. (4) contains two crystallographically independent cations, each located on a centre of symmetry. The ligand water molecules and the additional water of crystallization are hydrogen-bonded to the chloride anions, to form a three-dimensional network (Fig. 6). Each O atom forms two  $\text{O}\cdots\text{Cl}$  contacts of  $3.133\text{--}3.170 \text{ \AA}$ , which are roughly collinear with the O-H bonds [ $\text{Cl}\cdots\text{O}\cdots\text{Cl} = 94.3, 90.0, 118.6^\circ$ ]. Thus, each chloride anion has three neighbouring water molecules, with  $\text{O}\cdots\text{Cl}\cdots\text{O}$  ranging from  $74.4$  to  $146.7^\circ$ . No precautions were taken to exclude moisture during recrystallization of (4). Free access of air was allowed and undried solvents were employed; thus, the presence of water molecules is not surprising.

The chemical analysis of the crude product (4a) from which (4) was obtained by recrystallization is consistent with its formulation as impure  $[\text{Cu}(\text{Meim})_4\text{-Cl}]\text{Cl}$ , one of the components observed in the structure of (3).

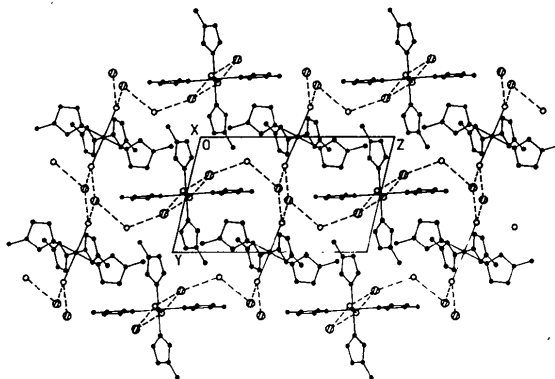


Fig. 6. Projection of the structure of (4) along the *a* axis.

Table 9. Selected mean-planes data

Plane number	Atoms	R.m.s. $\Delta$ (Å)	Other $\Delta$ (Å)	For atom	Dihedral angle to plane No. 1 (°)
Compound (1)					
1	N(11), N(21), N(31), N(41)	0.009	0.012	Cu(1)	
2	Ligand 1*	0.002	0.022	Cu(1)	80.6
3	Ligand 2	0.003	-0.067	Cu(1)	56.2
4	Ligand 3	0.002	-0.020	Cu(1)	81.3
5	Ligand 4	0.001	0.020	Cu(1)	55.7
6	Cl(1), Cl(2), Cl(3)	0	0.021	Cu(2)	58.7
Compound (2)					
1	Ligand 1	0.002	-0.148	Cu(1)	
2	Ligand 2	0.012	-0.023	Cu(2)	
3	Ligand 3	0.011	-0.349	Cu(3)	
4	Ligand 4	0.016	0.087	Cu(4)	
5	Ligand 5	0.001	0.099	Cu(5)	
6	Ligand 6	0.009	-0.301	Cu(6)	
7	Ligand 7	0.010	0.096	Cu(7)	
8	Ligand 8	0.009	-0.097	Cu(8)	
Compound (3)					
1	N(51), N(61), N(71), N(81)	0.053	0.257	Cu(5)	
2	Ligand 5	0.011	0.218	Cu(5)	85.9
3	Ligand 6	0.011	-0.045	Cu(5)	59.6
4	Ligand 7	0.005	-0.008	Cu(5)	79.5
5	Ligand 8	0.017	0.176	Cu(5)	84.9
6	Ligand 1	0.005	-0.037	Cu(1)	
7	Ligand 2	0.007	0.159	Cu(2)	
8	Ligand 3	0.004	-0.084	Cu(3)	
9	Ligand 4	0.013	0.049	Cu(4)	
Compound (4)					
1	N(11), N(21), N(11)', N(21)'	0	0	Cu(1)	
2	Ligand 1	0.005	-0.038	Cu(1)	57.8
3	Ligand 2	0.003	0.016	Cu(1)	80.9
4	N(31), N(41), N(31)', N(41)'	0	0	Cu(2)	74.0
5	Ligand 3	0.002	-0.060	Cu(2)	51.0†
6	Ligand 4	0.002	-0.065	Cu(2)	83.0†

\* Atoms fitted are the five ring N and C atoms.

† Dihedral angle to plane No. 4.

In each of the four structures described above, all of the Meim ligands are essentially planar (Table 9). In the  $[\text{Cu}(\text{Meim})_4]^{2+}$ ,  $[\text{Cu}(\text{Meim})_4\text{Cl}]^+$  and  $[\text{Cu}(\text{Meim})_4(\text{H}_2\text{O})_2]^{2+}$  cations of (1), (3) and (4) the Meim ligand planes are rotated at various angles to the  $\text{N}_4$  mean plane of the Cu coordination with no obvious systematic pattern. Wide variation has been observed in the orientation of the imidazole rings with respect to the  $(\text{Cu})\text{N}_4$  plane for other tetrakis(imidazole)copper(II) complexes (McFadden *et al.*, 1976; Bernarducci *et al.*, 1983; Akhtar, Goodgame, Rayner-Canham & Skapski, 1968; Ivarsson, 1973; Prout, Allison & Rossotti, 1971; Fransson & Lundberg, 1972; Kashaev, Zel'bst, Demidov, Frolov, Chipanina, Domnina & Skvortsova, 1978).

Compounds (2), (3) and (4) are all  $\text{Cu}^{\text{II}}$  complexes (like the initial starting complex  $[\text{CuCl}_2(\text{Meim})_2]$ ), whereas (1) is a mixed-valence species. Although reaction of 4-methylthiazole with copper (II) chloride has also produced several complexes containing Cl and 4-Metz ligands (Marsh, Hatfield & Hodgson, 1983), it is interesting that none of them is analogous to any of the products described here, except that  $[\text{Cu}_4\text{OCl}_5(4\text{-Metz})_4]$  is obtained when, and only when, water is present. One of the 4-Metz complexes,  $[\text{Cu}_2(4\text{-Metz})_4\text{Cl}_3]$ ,

is a mixed-valence system; although it has an analogous empirical formula to that of (1), the two structures are quite different.

The role of  $\text{K}_2[\text{S}_2\text{-o-xyl}]$  in the preparation of complexes (1) to (4) is unclear, except that it appears to act as a reducing agent for the generation of  $\text{Cu}^{\text{I}}$  in product (1). However, in no instance does this versatile ligand appear coordinated to copper in the products of this reaction sequence.

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## **gauche Conformer of Bis[tricarbonyl(cyclopentadienyl)molybdenum]**

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**Abstract.** [ $\{\text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5)\}_2$ ],  $M_r = 490.1$ , monoclinic,  $I2$  (non-conventional setting of  $C2$ , No. 5),  $a = 10.332$  (1),  $b = 8.009$  (1),  $c = 10.366$  (1) Å,  $\beta = 109.063$  (9)°,  $V = 810.8$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.01$  g cm<sup>-3</sup>,  $\text{Mo } K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 15.4$  cm<sup>-1</sup>,  $F(000) = 476$ ,  $T = 295$  K,  $R = 0.047$  for 613 observed reflections. The asymmetric unit is one-half of the dimeric molecule, which has  $C_2$  (2) symmetry. The Mo–Mo bond is 3.2239 (11) Å. Each Mo atom is coordinated to three C (carbonyl) at 1.94–1.97 Å and five C (Cp) at 2.27–2.39 Å. A remarkable feature of the structure is an intramolecular contact of 2.44 (2) Å between two carbon atoms separated by three bonds.

**Introduction.** The stable (*trans*) conformer (1) of the title compound (2) was one of the first organometallic structures to be reported (Wilson & Shoemaker, 1956,

1957), its preparation having been reported only slightly earlier (Wilkinson, 1954; Cotton, Liehr & Wilkinson, 1955). We obtained crystals of (2) as a minor product in the reaction of  $\text{Mo}(\text{Cp})(\text{CO})_3\text{Cl}$  (3) with  $\text{Me}_3\text{SiNMe}_2$  (4), a reaction being carried out to prepare the species [ $\{\text{Mo}(\text{Cp})(\text{CO})(\text{NMe}_2)\}_2$ ] (Keable & Kilner, 1987).

**Experimental.** A freshly prepared toluene solution of (4) (from  $\text{LiNMe}_2$  and  $\text{Me}_3\text{SiCl}$  in toluene, the precipitated  $\text{LiCl}$  having been filtered off) was reacted with (3) at 320 K. Small bright-red plates were found in the crude yield of this reaction, and one with dimensions 0.25 × 0.25 × 0.025 mm was selected for a structure determination. Enraf–Nonius CAD-4 diffractometer.  $\text{Mo } K\alpha$  radiation, graphite monochromator. Lattice parameters refined from the setting angles for 18