Crystal and Molecular Structure of Di-μ-[4,6,6-trimethyl-3,7-diazanon-3-ene-1,9-diolato(1—)-*ONN'*,μ-*O'*]-dicopper(II) Diperchlorate

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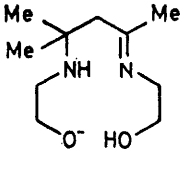
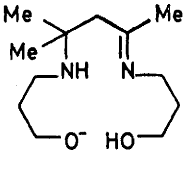
The structure of the title compound, formed by reaction of copper(II) perchlorate, 2-aminoethanol, and acetone, has been determined by *X*-ray diffractometry. It is monoclinic, space group $P2_1/c$, a = 8.4495(6), b = 23.612(5), c = 8.3041(8) Å, and β = 115.43(1)°; R = 0.066. The compound contains centrosymmetric di-μ-oxo-bridged dimeric cations, with the copper atoms in distorted square-pyramidal co-ordination. The bridging oxo-groups, and the amine and imine donor groups, are co-ordinated in the basal plane and the hydroxyl group of the quadridentate ligand is co-ordinated in the apical site. An analogous compound with the ligand 5,7,7-trimethyl-4,8-diazaundeca-4-ene-1,11-diol has been prepared from copper(II) perchlorate, 3-aminopropan-1-ol, and acetone. This is diamagnetic, or nearly so, implying complete spin pairing *via* the di-μ-oxo bridge, although spin pairing of the title compound is not significant.

THE reaction of some copper(II) salts, 2-aminoethanol (monoethanolamine), and acetone (and other methyl ketones) to yield products with quadridentate ligands formed by linking the amino-groups of two aminoethyl residues by a three-carbon amino–imine bridge derived from two acetone residues has been reported.[1,†] The 2-aminoethanol derivatives were assigned structures on the basis of i.r. spectra and chemical properties, particularly their hydrolysis by acid to yield mesityl oxide as the only carbonyl product. With acetone and copper perchlorate the product $[\{CuL^1\}_2][ClO_4]_2$ was formed with one of the hydroxy-groups of the ligand deprotonated, as often occurs for simple aminoethanol complexes of Cu^{II}. We now report an *X*-ray crystallographic study of this compound. The reaction is extended to include the preparation of the analogous compound, $[\{CuL^2\}_2][ClO_4]_2$, with three linked six-membered chelate rings obtained by reaction of 3-aminopropan-1-ol, copper(II) perchlorate, and acetone.



L^1



L^2

The *N*-isopropylideneaminoethanol structures assigned to some copper(II) compounds by other workers are questioned and reformulation with the quadridentate ligand (L^1) is proposed.

EXPERIMENTAL

Samples of $[\{CuL^1\}_2][ClO_4]_2$ and $[\{CuL^1\}_2][NO_3]_2$ were prepared as previously reported.[1] Small crystals of $[\{CuL^1\}_2][ClO_4]_2$ were obtained as monoclinic plates by adding a few drops of water to a hot ethanolic solution of the compound. One of the largest, 0.05 × 0.15 × 0.24 mm in the crystallographic *a*, *b*, *c* directions, was selected for *X*-ray crystallographic analysis. Its lack of size necessitated the use of Cu-K_α radiation in spite of its large absorption coefficient.

Bis(5,7,7-*trimethyl*-4,8-*diazaundeca*-4-*ene*-1,11-*diolato*)-*dicopper*(II) *Diperchlorate*, $[\{CuL^2\}_2][ClO_4]_2$.—The stoicheiometry of this compound was assumed as dimeric by analogy with that of L^1. Copper(II) perchlorate tetrahydrate (10 g) dissolved in acetone (20 cm^3) was added with stirring to 3-aminopropan-1-ol (10 g) in acetone (20 cm^3). The solution was heated for a few minutes and propan-2-ol was added until the mixture became turbid. The dark green crystalline product was filtered off after *ca.* 1 d and recrystallised from hot acetone–ethanol (Found: C, 36.7; H, 6.5; Cu, 25.9. $C_{24}H_{50}Cl_2N_4O_{12}$ requires C, 36.7; H, 6.4; Cu, 16.2%).

Crystal Data.—$C_{20}H_{42}Cl_2Cu_2N_4O_{12}$, M = 728.7, Monoclinic, a = 8.449 5(6), b = 23.612(5), c = 8.304 1(8) Å, β = 115.43(1)° (standard deviations from the least-squares fit of parameters to the diffractometer setting angles of 12 reflections), U = 1 496 Å^3, D_m = 1.61 (by flotation), Z = 2, D_c = 1.617 g cm^{-3}, $F(000)$ = 756. Cu-K_α radiation, λ = 1.541 8 Å, μ = 39.82 cm^{-1}. Space group $P2_1/c$.

Data were collected on a Hilger–Watts Y290 automated four-circle diffractometer using the 2θ–ω technique with a 2θ scan of 1.40° stepped at a rate of 0.01° s^{-1}. The diameter of the primary beam collimator was 0.5 mm and that of the secondary collimator was 3.5 mm. Of the total of 2 242 reflections collected, 1 308 had an intensity greater than 3σ. ($\sigma = \{I + [t/(t_1 + t_2)]^2(B_1 + B_2) + (pI)^2\}^{\frac{1}{2}}$ where I = total counts in time t and B_1 and B_2 are the background counts in times t_1 and t_2; the parameter p was assigned a preliminary value of 0.05.[4]) The heavy-atom method was successfully used in the solution of the structure, the second electron-density map revealing the positions of all the non-hydrogen atoms. Block-diagonal least-squares refinement was then undertaken. The real part of the anomalous-dispersion effect was applied to the scattering factor for Cu^0. Values of the scattering factors of copper and chlorine were taken from ref. 5, those of the remaining atoms from ref. 6. The weighting scheme was of the form $w = 4F^2/\sigma^2(F^2)$. Restraints on the refinement model were gradually relaxed to accommodate anisotropic vibration and the need to include hydrogen atoms. The latter were first located on a

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[†] Related compounds were formed with (hydroxyethyl)-ethylenediamine, acetone, and copper(II) [2] or nickel(II).[3]

[1] V. C. Patel and N. F. Curtis, *J. Chem. Soc.* (*A*), 1968, 1265.

[2] M. N. Hughes, M. Underhill, and K. J. Rutt, *J.C.S. Dalton*, 1972, 1219.

[3] V. C. Patel and N. F. Curtis, *J. Chem. Soc.* (*A*), 1969, 1607.

[4] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

[5] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[6] ' International Tables for *X*-Ray Crystallography,' ed. K. Lonsdale, Kynoch Press, Birmingham, 1962, vol. 3.

difference map and then included in the model at calculated positions at a fixed isotropic temperature factor of 5.0 Å.[2] At each relaxation a statistical test[7] was applied to justify correspondence with physical reality. Convergence for a model containing all the atoms, with non-hydrogen atoms assumed to undergo anisotropic thermal motion, gave *R* 0.066. As Figures 1 and 2 show, it seemed important at this point to check the placement of hydrogen atoms about the ligand oxygen atoms. Initially only O(2) was found to have an attached hydrogen, H(111), and this assignment was unequivocally supported by a difference synthesis computed for a model which omitted H(111). There were no other significant peaks in the vicinity of O(1) and O(2), nor elsewhere in the map.

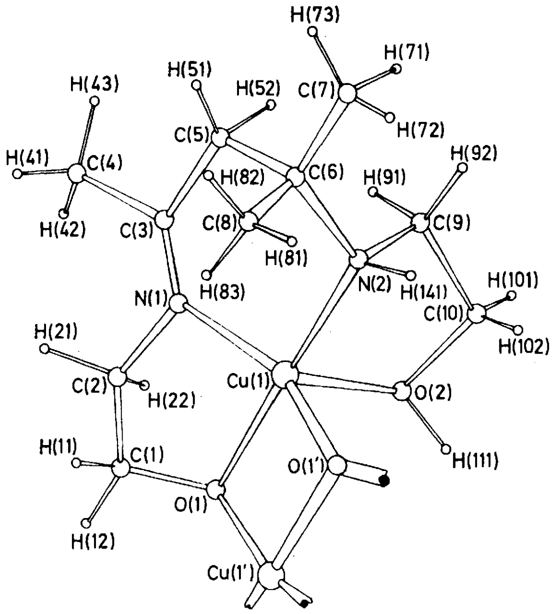

FIGURE 1 Numbering scheme for the crystallographic asymmetric unit (half a molecular unit). The perchlorate oxygen atoms are numbered O(3)—O(6)

TABLE 1

Atom co-ordinates with standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Cu(1)	−0.001 9(1)	0.446 51(6)	0.409 9(1)
Cl(1)	0.296 6(2)	0.369 5(1)	0.031 0(3)
C(1)	0.326 0(11)	0.482 3(5)	0.650 6(14)
C(2)	0.364 8(11)	0.434 4(5)	0.557 4(13)
C(3)	0.218 5(10)	0.345 7(5)	0.473 6(12)
C(4)	0.387 5(12)	0.313 5(5)	0.533 8(14)
C(5)	0.059 9(12)	0.306 4(5)	0.395 4(14)
C(6)	−0.122 5(11)	0.329 4(5)	0.374 6(13)
C(7)	−0.260 2(13)	0.285 1(5)	0.282 4(14)
C(8)	−0.116 2(12)	0.343 0(5)	0.558 4(12)
C(9)	−0.178 5(12)	0.381 1(5)	0.087 8(12)
C(10)	−0.213 9(13)	0.440 3(5)	0.006 8(12)
O(1)	0.160 8(7)	0.505 3(3)	0.535 0(8)
O(2)	−0.075 3(8)	0.475 3(3)	0.123 0(8)
O(3)	0.432 2(11)	0.396 3(5)	0.183 0(12)
O(4)	0.232 1(11)	0.324 0(4)	0.097 3(12)
O(5)	0.365 2(11)	0.347 7(5)	−0.086 2(10)
O(6)	0.154 1(13)	0.407 9(4)	−0.062 3(13)
N(1)	0.207 1(8)	0.398 5(4)	0.481 1(9)
N(2)	−0.167 7(9)	0.385 7(4)	0.272 2(9)

The structure-factor data are listed in Supplementary Publication No. SUP 22006 (9 pp.).* The final positional parameters and amplitudes of vibration are in Tables 1 and 2, and the calculated bond lengths and angles are in Tables 3 and 4.

TABLE 2

Root-mean-square amplitudes of vibration (Å)

Atom			
Cu(1)	0.187	0.209	0.223
Cl(1)	0.181	0.197	0.215
C(1)	0.117	0.206	0.288
C(2)	0.146	0.215	0.246
C(3)	0.120	0.200	0.253
C(4)	0.185	0.218	0.254
C(5)	0.159	0.195	0.268
C(6)	0.161	0.207	0.248
C(7)	0.120	0.255	0.267
C(8)	0.163	0.200	0.248
C(9)	0.154	0.213	0.228
C(10)	0.140	0.223	0.264
O(1)	0.111	0.178	0.241
O(2)	0.175	0.205	0.241
O(3)	0.229	0.267	0.394
O(4)	0.184	0.297	0.331
O(5)	0.200	0.279	0.365
O(6)	0.223	0.312	0.340
N(1)	0.136	0.193	0.197
N(2)	0.145	0.173	0.191

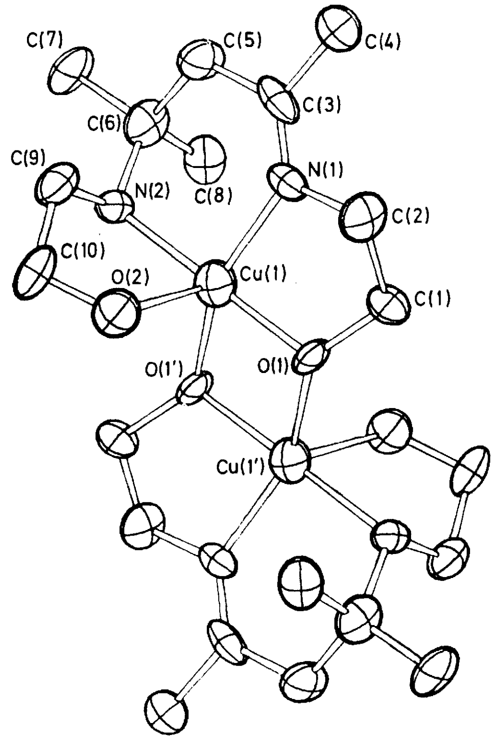

FIGURE 2 ORTEP diagram of the complex ion (omitting hydrogen atoms)

DISCUSSION

Structure of $[\{CuL^1\}_2][ClO_4]_2$.—The structural investigation confirms that the product of the 2-aminoethanol–acetone–copper(II) perchlorate reaction does contain the

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue. Items less than 10pp. are supplied as full-size copies.

[7] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

quadridentate ligand formed by linking the amino-groups of two aminoethyl residues by a three-carbon amine–imine bridge as originally proposed. The formula requires that one of the hydroxy-groups of the free ligand is deprotonated. A hydrogen atom was unambiguously observed in an expected position for the aminoethanol residue bonded *via* the amino-group, showing that the ligand present is L^1. A dimeric cation is present, with the deprotonated hydroxyl oxygen atoms of each ligand serving as a bridging group, and with the copper atom in distorted square-pyramidal co-ordination. An ORTEP diagram of the cation is shown in Figure 2. Deviations from selected planes through the cation are listed in Table 5.

TABLE 3

Calculated bond lengths (Å) with standard deviations in parentheses

Cu(1)–O(1)	1.916(6)	C(2)–N(1)	1.47(1)
Cu(1)–O(1′) *	1.958(6)	C(3)–C(4)	1.50(2)
Cu(1)–O(2)	2.292(6)	C(3)–C(5)	1.53(2)
Cu(1)–N(1)	1.966(6)	C(3)–N(1)	1.25(1)
Cu(1)–N(2)	1.988(8)	C(5)–C(6)	1.57(2)
Cl(1)–O(3)	1.44(1)	C(6)–C(7)	1.51(2)
Cl(1)–O(4)	1.42(1)	C(6)–C(8)	1.54(1)
Cl(1)–O(5)	1.43(1)	C(6)–N(2)	1.54(1)
Cl(1)–O(6)	1.44(1)	C(9)–C(10)	1.52(2)
C(1)–C(2)	1.49(2)	C(9)–N(2)	1.50(1)
C(1)–O(1)	1.42(1)	C(10)–O(2)	1.42(1)

* The prime refers to the atom at $-x, 1 - y, 1 - z$.

TABLE 4

Calculated bond angles (°) with standard deviations in parentheses

O(1)–Cu(1)–O(2)	99.2(5)	C(1)–O(1)–Cu(1′)	129.6(7)
O(1)–Cu(1)–O(1′)	81.8(5)	Cu(1)–O(2)–C(10)	108.0(8)
O(1)–Cu(1)–N(1)	85.0(5)	Cu(1)–N(1)–C(2)	109.0(8)
O(1)–Cu(1)–N(2)	177.6(6)	Cu(1)–N(1)–C(3)	129.6(8)
O(2)–Cu(1)–N(1)	106.9(5)	Cu(1)–N(2)–C(6)	111.1(8)
O(2)–Cu(1)–N(2)	78.9(5)	Cu(1)–N(2)–C(9)	111.1(8)
N(1)–Cu(1)–N(2)	94.3(6)	C(2)–N(1)–C(3)	121.4(9)
O(2)–Cu(1)–O(1′)	99.4(5)	C(4)–C(3)–C(5)	111.8(9)
N(1)–Cu(1)–O(1′)	152.0(6)	C(4)–C(3)–N(1)	124.6(9)
N(2)–Cu(1)–O(1′)	99.8(5)	C(5)–C(3)–N(1)	123.6(9)
O(3)–Cl(1)–O(4)	106.6(8)	C(3)–C(5)–C(6)	118.5(9)
O(3)–Cl(1)–O(5)	110.9(8)	C(5)–C(6)–C(7)	108.7(9)
O(3)–Cl(1)–O(6)	111.2(8)	C(5)–C(6)–C(8)	110.4(9)
O(4)–Cl(1)–O(5)	109.1(8)	C(5)–C(6)–N(2)	111.0(9)
O(4)–Cl(1)–O(6)	108.3(8)	C(7)–C(6)–C(8)	109.9(9)
O(5)–Cl(1)–O(6)	110.5(8)	C(7)–C(6)–N(2)	111.5(9)
C(2)–C(1)–O(1)	108.2(9)	C(8)–C(6)–N(2)	105.4(9)
C(1)–C(2)–N(1)	107.7(9)	C(6)–N(2)–C(9)	113.2(9)
Cu(1)–O(1)–Cu(1′)	98.2(6)	C(10)–C(9)–N(2)	107.3(9)
C(1)–O(1)–Cu(1)	111.0(7)	C(9)–C(10)–O(2)	106.7(9)

Co-ordination about the copper atom. The copper atom is in approximately square-pyramidal co-ordination with the two nitrogen atoms and the two bridging oxygen atoms forming the basal plane and the hydroxyl oxygen atom in the apical co-ordination site. The basal plane shows a tetrahedral distortion, with the copper atom approximately collinear with O(1) and N(2) [O(1)–Cu–N(2) 178, N(1)–Cu–O(1′) 152°]. This could be viewed as a displacement of the copper atom towards the apical site. The apical oxygen, O(2), is displaced by *ca.* 10° from the tetragonal axis in the direction of N(2). The alternative consideration of the co-ordination sphere as a distorted trigonal bipyramid with a collinear O(1)–Cu–N(2) axis appears less appropriate. [Angles in the 'equatorial plane' are N(1)–Cu–O(1′) 152, N(1)–Cu–O(2) 107, and O(2)–Cu–O(1′) 99°.] The copper–oxygen and –nitrogen bond lengths are normal for such compounds, with the copper–apical-oxygen distance somewhat longer than the others.

Configuration and conformation of the ligand. The two five-membered chelate rings adopt *gauche* conformations with O–Cu–N bond angles of 85 (basal) and 79° (apical) respectively. The values are comparable with those observed for other compounds with 2-aminoethanol moieties.[8,9] The six-membered chelate ring having dihedral angles of −15, 0, −19, 53, −60, and 40° in the sequence Cu–N(1), N(1)–C(3), *etc.*, clearly adopts a half-chair conformation [Table 5, plane (*ii*)]. The N–Cu–N bond angle is 94.3° and the methyl substituents of the chelate ring lie away from the occupied apical co-ordination site. The imino-group is approximately planar [Table 5, plane (*iii*)] and C=N is 1.25 Å. The conformation present is thus similar to that observed for other compounds with the same trimethyl-substituted amine–imine six-membered chelate ring,[10] in particular the only such copper compound reported, *trans*-bis(2-amino-4-imino-2-methylpentane)copper(II) nitrate[11] which is formed by reaction of copper(II) nitrate, acetone, and ammonia. The structures described all show evidence for bond-angle strain in this chelate ring, particularly in the large C–C–C bond angle at the central methylene group (118° in the present instance).

TABLE 5

Planes of best fit through selected atoms and deviations (Å) of the atoms from the planes (in square brackets). The equations are of the form $AX + BY + CZ - D = 0$ where the orthogonal axes X, Y, Z are related to the cell axes x, y, z by $X = x + z\cos\beta$, $Y = y$, and $Z = z\sin\beta$

Plane (*i*) N(1), N(2), O(1), O(1′)

$$0.331\,9X + 0.403\,0Y - 0.852\,9Z + 0.950 = 0$$

[N(1) −0.22, N(2) 0.19, O(1) 0.25, O(1′) −0.22, Cu 0.19, Cu′ −0.15]

Plane (*ii*) Cu, N(2), C(3), C(5)

$$0.054\,5X + 0.132\,8Y - 0.837\,4Z - 1.872\,0 = 0$$

[Cu −0.08, N(2) 0.09, C(3) 0.10, C(5) −0.11, N(1) 0.15, C(6) −0.71]

Plane (*iii*) Cu, N(1), C(3)

$$0.384\,5X + 0.079\,4Y - 0.919\,8Z + 2.557\,9 = 0$$

[C(2) −0.05, C(4) −0.01, C(5) 0.06]

Plane (*iv*) Cu, O(1), N(1)

$$0.481\,5X + 0.246\,2Y - 0.841\,2Z - 0.702 = 0$$

[C(1) −0.39, C(2) 0.24]

Plane (*v*) Cu, O(2), N(2)

$$-0.847\,6X + 0.530\,5Y + 0.088\,8Z + 6.873 = 0$$

[C(9) −0.55, C(10) 0.20]

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[8] J. A. Bertrand and C. E. Kirkwood, *Inorg. Chim. Acta*, 1970, **4**, 192.

[9] J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta*, 1970, **4**, 203.

[10] D. A. Swann, T. N. Waters, and N. F. Curtis, *J.C.S. Dalton*, 1972, 1115 and refs. therein.

[11] F. Hanic and M. Serator, *Chem. Zvesti*, 1964, **18**, 572.

The cation contains a number of chiral features, with the halves of the dimer centrosymmetrically related. The *R* chirality for the co-ordinated secondary amine, N(2), determines the chirality of the six-membered chelate ring as δ, and this, with the planarity of the imino-group, then determines the chirality of the basal-plane five-membered chelate ring as λ. Either λ or δ chirality is possible for the apical five-membered chelate ring but models suggest that for the *R* configuration the observed δ configuration is the least strained.

The di-μ-oxo-bridge. Planarity of the Cu_2O_2 ring is required by the centre of symmetry. The Cu–O distances are unequal [Cu–O(1) 1.916, Cu–O(1′) 1.985 Å]. The O(1)–Cu–O(1′) angle is 81.8° and the Cu–Cu distance is 2.929 Å. Di-μ-oxo-bridged dimeric structures are relatively common for Cu^{II}, both planar and non-planar rings being found.[12-15] Spin pairing *via* the oxygen bridges occurs in some instances, and evidence suggests that spin pairing is facilitated when the oxygen atoms are trigonally bonded, inhibited when they are tetrahedrally bonded.[16] In $[\{CuL^1\}_2][ClO_4]_2$ the angles about the oxygen atoms approximate more closely to the tetrahedral configuration, the oxygen atom lying well out of the Cu–Cu′–C(1) plane.

Perchlorate ion. The oxygen atoms of the perchlorate ion show a higher thermal vibration than the other non-hydrogen atoms, as is common. The observed bond lengths (1.42—1.44 Å) are slightly lower than the expected value (1.46 Å). A correction based on the method of Cruickshank[17] brings the values into the range 1.46—1.48 Å.

Intermolecular approaches and hydrogen bonding. Short contacts which could be interpreted as hydrogen bonds exist between the hydroxyl oxygen atoms O(2) and the perchlorate oxygen atom O(6) (2.83 Å), between the secondary amino-nitrogen N(2) and the perchlorate oxygen atom O(3) of another perchlorate ion (3.15 Å), and between the two hydroxyl oxygen atoms, O(2), of different cations (3.06 Å). Consideration of the hydrogen-atom positions supports assignment of hydrogen bonds between O(2) and O(6), and between N(2) and O(3) but not between O(2) and O(2″) (Table 6).

The structure thus consists of parallel chains of $[\{CuL^1\}_2]^{2+}$ cations linked by hydrogen-bonded perchlorate ions. The cell constants are shown in Figure 3.

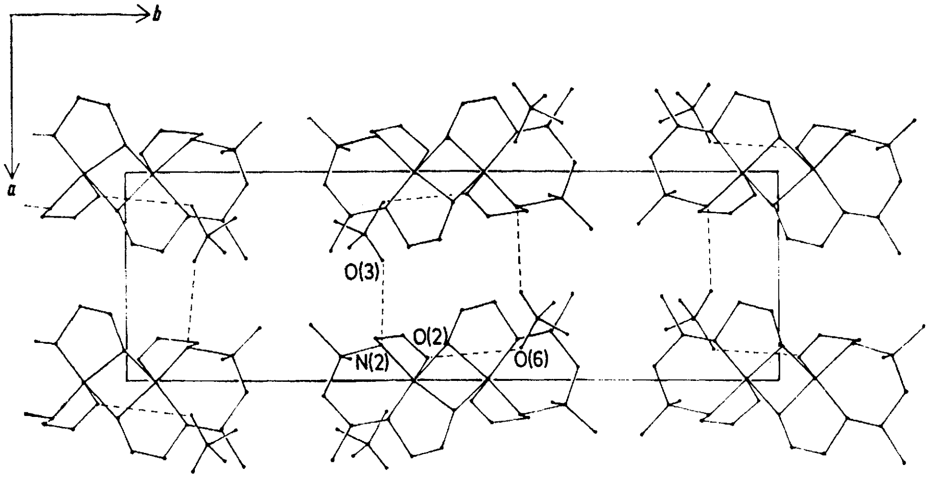

FIGURE 3 Contents of the unit cell projected down *c* showing hydrogen bonds

Magnetic and Spectral Properties.—The room-temperature magnetic susceptibilities of $[\{CuL^1\}_2][ClO_4]_2$ and the nitrate salt were reported by Patel and Curtis.[1] Effective magnetic moments, calculated assuming the validity of the Curie law, were 1.83 B.M.* for both compounds, on the lower side of the normal range for Cu^{II}. In view of the dimeric structure found for $[\{CuL^1\}_2][ClO_4]_2$, the susceptibility was remeasured over the range 100—300 K and found to obey the Curie–Weiss law with $\theta = 25 \pm 5$ K, giving $\mu = 1.71$ B.M.).† The compound $[\{CuL^2\}_2][ClO_4]_2$ is diamagnetic ‡ at room temperature (*i.e.* a singlet ground state) and is therefore formulated as a dimer (or possible higher-order polymer), with complete spin pairing. Examples have previously been reported[9] for related oxo-bridged dimers based on the ligands L^3

TABLE 6

Hydrogen-bonding geometry (bonds in Å, angles in °)

O(2) · · · O(6)	2.83	N(2) · · · O(3)	3.15
O(2)–H(111)	1.1	N(2)–H(141)	1.1
H(111) · · · O(6)	1.8	H(141) · · · O(3)	2.1
O(2)–H(111)–O(6)	161	N(2)–H(141)–O(3)	153

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

† The reported room-temperature susceptibility was reproduced; the lower value of μ arises from the use of the Curie–Weiss relation with $\theta = 25$ K and does not indicate significant spin pairing in this temperature region.

‡ This result follows from the experimental measurement, the calculated diamagnetic correction, and the assumed temperature-independent paramagnetism.

[12] G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1965, 1979.

[13] D. Hall, J. E. Wallace, J. M. Waters, and T. N. Waters, *J. Inorg. Chem.*, 1970, **32**, 1847.

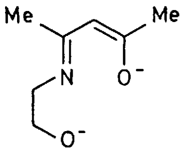
[14] R. S. Sager, R. J. Williams, and W. H. Watson, *Inorg. Chem.*, 1967, **6**, 951.

[15] E. D. Estes and D. J. Hodgson, *Inorg. Chem.*, 1975, **14**, 334.

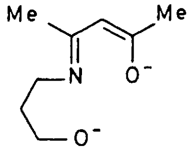
[16] Y. Muto, M. Kato, H. B. Jonassen, and H. M. Ramaswamy, *Bull. Chem. Soc. Japan*, 1967, **40**, 1535.

[17] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 575; 1961, **14**, 896.

and L^4, where changing the chelate ring containing the bridging oxygen atom from five- to six-membered greatly enhances the spin pairing. It has been suggested that the larger chelate ring permits the adoption of a trigonal, rather than tetrahedral, arrangement about the oxygen atom and that this facilitates spin pairing.[16] In $[\{CuL^1\}_2][ClO_4]_2$ the bonding about the bridging oxygen atoms is not planar and therefore offers some support for the proposal. In this connection we note that in a number of di-μ-hydroxo-copper(II) dimers the coupling constant, J, is a linear function of the CuOCu angle, α, J being 0 at $\alpha = 97.7°$.[18-20] The value of this angle in $[\{CuL^1\}_2][ClO_4]_2$ is 98.2(6)° and since no deviation from the Curie–Weiss law was detectable down to 100 K the value of J must be very small.

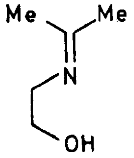


L^3



L^4

Artemenko and his co-workers [21,22] reported the preparation of a number of compounds formulated as *N*-isopropylideneamino-derivatives of copper(II) compounds of 2-aminoethanol. One compound, formulated as $[Cu(HL^5)(L^5)][NO_3]$, is isomeric with $[CuL^1][NO_3]$, which presumably has a dimeric structure analogous to the perchlorate. In view of the rapid formation of compounds of the quadridentate ligand L^1 whenever copper(II) salts, acetone, and 2-aminoethanol (or aminoethanol, copper compounds, and acetone) are mixed, it appears improbable that a separate series of simple imino-complexes could be prepared under these conditions. Artemenko reported magnetic-susceptibility measurements, over a temperature range, for this series of compounds and in several instances sub-normal magnetic moments were observed. In particular, the value of 1.16 B.M. for $[Cu(HL^5)(L^5)][NO_3]$ prompted us to remeasure the susceptibility of $[CuL^1][NO_3]$. For well crystalline samples the ' normal ' magnetic moment of 1.83 B.M. reported by Patel and Curtis [1] was reproduced. For rapidly crystallised samples, which were powdery in character, lower magnetic moments were observed, individual samples showing a range of values between 1.16 and 1.83 B.M. The samples all had the same chemical composition and it is likely that the rapidly crystallised samples contain a varying proportion of some isomeric form having appreciable spin pairing. Another dimeric copper(II) compound which crystallises in two forms exhibiting quite different spin pairing has been reported.[23]



HL^5

Absorption Spectra.—Dark blue $[\{CuL^1\}_2][ClO_4]_2$ and dark green $[\{CuL^2\}_2][ClO_4]_2$ are quite different in appearance, but their reflectance spectra are similar, both showing a *d–d* band at *ca.* 17 000 cm^{-1} and a more intense band at *ca.* 26 000 cm^{-1}.* Many oxygen-bridged dimeric copper(II) compounds show a moderately intense band in the 20 000—30 000 cm^{-1} region, which has been assigned to a charge transfer from an orbital of the bridging oxygen atom to a *d* orbital of the copper ion.[24-26] The band is normally present only when appreciable spin pairing occurs, and it has been suggested that the presence of the band is diagnostic of spin pairing. However, the appearance of the band for $[\{CuL^1\}_2][ClO_4]_2$, which has no significant spin pairing, indicates that this presumption is not necessarily correct. The absence of the band in a methanol solution of $[\{CuL^1\}_2][ClO_4]_2$ may indicate dissociation of the dimer, or some conformational change which renders the spectrum ' normal ' for a dimer without spin pairing.

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* Electronic spectra: $[\{CuL^1\}_2][ClO_4]_2$ (reflectance) 16 000 and 26 400; (in methanol solution) 16 700(85) and 37 000 (sh) (*ca.* 7 000); $[CuL^2][ClO_4]$ (reflectance) 16 700 and 25 500; (in methanol) 38 000 (4 200), 26 000 (1 360), and 16 300(67) cm^{-1}. Molar absorbances (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. The band at *ca.* 26 000 cm^{-1} is assigned to a transition of the metal–imine chromophore.

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