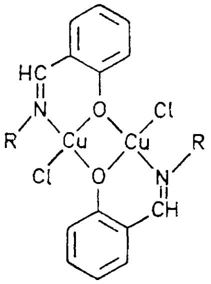
Crystal and Molecular Structure of the Tetranuclear Copper Complex Di-μ-chloro-bis{chloro[*NN*′-ethylenebis(salicylideneiminato)copper(II)]-copper(II)}

By **Cedric A. Bear, Joyce M. Waters, and T. Neil Waters** * Chemistry Department, University of Auckland, New Zealand

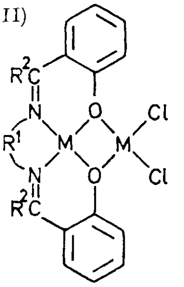
The reaction product formed between *NN*′-ethylenebis(salicylaldiminato)copper(II), Cu(salen), and copper(II) chloride has been subjected to a three-dimensional *X*-ray analysis. The monoclinic cell has *a* = 7·791(6), *b* = 16·780(6), *c* = 10·536(5) Å, β = 100·80(9)°; space group, $P2_1/n$. The structure was solved from diffractometer data by the heavy-atom method and refined by block-diagonal least squares to *R* 0·069. The tetranuclear molecular structure has chlorine atoms bridging binuclear species Cu(salen)CuCl$_2$. The copper atoms bonded by the organic ligands are four-co-ordinate with a planar donor stereochemistry; the remaining copper atoms are five-co-ordinate with donors in a distorted tetragonal pyramidal geometry.

Extensive work[1-8] has demonstrated the ability of Schiff-base–metal complexes to act as bidentate chelating agents in the formation of multinuclear species. Associated spectral and magnetic phenomena have been studied. Typically, the co-ordination of bidentate *trans*-planar complexes leads to symmetrical products (I) whereas quadridentate compounds lead to species of type (II).

(I)

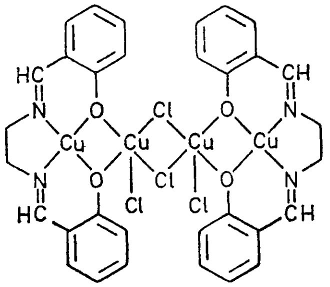


(II)



(III) R^1 = CH$_2$·CH$_2$, R^2 = H
(IV) R^1 = CH$_2$·CH$_2$, R^2 = Me

We have examined the bimolecular structure of the binuclear complex arising from the reaction between *NN*′-ethylenebis(salicylaldiminato)copper(II) and copper(II) chloride, not because of any doubt about its overall geometry, but because the presence of two metal centres close together has possible stereochemical implications. The steric requirements of a planar complex acting as a ligand have been likened[5] to those of 2,2′-biquinolyl (biq) which are said to force a pseudotetrahedral structure on the complexes Cu(biq)X$_2$ and [Cu(biq)$_2$](ClO$_4$)$_2$.[2] Thus the electronic absorption spectra of both [Cu(salen)CuCl$_2$]$_2$ (III) and Cu(salen)CuCl$_2$,H$_2$O have been interpreted in terms of such a distorted tetrahedral stereochemistry at the copper centre which binds chlorine, with the stereochemistry at the other centre more nearly planar than in the free Cu(salen) molecule.[2] It has been suggested that this structure avoids the juxtaposition of two planar metal centres for the steric reasons mentioned above, or of two tetrahedral centres which would imply closer approach between the metal atoms.



EXPERIMENTAL

Crystals were prepared by slowly diffusing copper(II) chloride in aqueous ethanol and *NN*′-ethylenebis(salicylaldiminato)copper(II) in chloroform into one another. The product was black, as is the non-hydrated form.[4]

Crystal Data.—C$_{32}$H$_{28}$Cl$_4$Cu$_4$N$_4$O$_4$, *M* = 928, Monoclinic, *a* = 7·791(6), *b* = 16·780(6), *c* = 10·536(5) Å, β = 100·80(9)° (obtained by a least-squares fit to 12 reflexions located by four-circle diffractometry), *U* = 1353 Å^3, D_m = 1·82, *Z* = 2, D_c = 1·81. Space group = $P2_1/n$. Cu-K_α radiation, λ = 1·5418 Å, μ(Cu-K_α) = 16·08 cm^{-1}.

Intensity data were collected on a Hilger and Watts automatic diffractometer by the θ–ω step-scan technique and corrected for absorption effects to give a total of 1543 independent reflexions, for which $|F_o|^2 \geqslant 3\sigma(F_o{}^2)$. The phase problem was solved conventionally by the heavy-atom method. Initial use of electron-density maps reduced the *R* factor, based on all non-hydrogen atoms, to 0·151, at which point block-diagonal least-squares refinement was begun. With the copper and chlorine atoms assumed to have anisotropic motion *R* converged to 0·084, reaching a final value of 0·069 after incorporation of hydrogen atoms (with fixed temperature factors, *B* 5·0 Å^2) and vibrational anisotropy for all other atoms, the reduction having statistical significance. The weighting scheme, based on counting statistics,[9] gave approximately constant values of $\langle w\Delta^2\rangle$ over $|F_o|$ ranges. Final positional parameters are listed in Table 1 and the root-mean-square amplitudes of vibration in Table 2. The Figure shows the numbering scheme. Bond lengths and bond angles are in Tables 3 and

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[1] E. Sinn and C. M. Harris, *Co-ordination Chem. Rev.*, 1969, **4**, 391.

[2] C. M. Harris, H. R. H. Patil, and E. Sinn, *Inorg. Chem.*, 1967, **6**, 1102.

[3] S. J. Gruber, C. M. Harris, and E. Sinn, *Inorg. Chem.*, 1968, **7**, 268.

[4] S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1805.

[5] S. J. Gruber, C. M. Harris, and E. Sinn, *Inorg. Chem.*, 1968, **7**, 268.

[6] C. M. Harris, and E. Sinn, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2723.

[7] R. B. Coles, C. M. Harris, and E. Sinn, *Inorg. Chem.*, 1969, **8**, 2607.

[8] C. M. Harris, J. M. James, P. J. Milham, and E. Sinn, *Inorg. Chim. Acta*, 1969, **3**, 81.

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

TABLE 1

Atom positions

Atom	x/a	y/b	z/c
Cu(1)	0·1373(2)	0·3453(1)	0·3902(2)
Cu(2)	0·4261(2)	0·4246(1)	0·3997(2)
Cl(1)	0·5277(4)	0·5454(2)	0·3770(5)
Cl(2)	0·4816(5)	0·3760(3)	0·2181(5)
O(1)	0·192(1)	0·4516(6)	0·368(1)
O(2)	0·333(1)	0·3241(6)	0·435(1)
N(1)	−0·056(1)	0·3655(7)	0·359(1)
N(2)	0·085(1)	0·2359(7)	0·397(1)
C(1)	−0·142(2)	0·294(1)	0·368(2)
C(2)	−0·065(2)	0·222(1)	0·348(2)
C(11)	0·105(1)	0·513(1)	0·344(1)
C(12)	−0·037(1)	0·509(1)	0·333(2)
C(13)	−0·120(2)	0·580(1)	0·311(2)
C(14)	−0·061(1)	0·652(1)	0·297(2)
C(15)	0·080(2)	0·656(1)	0·303(2)
C(16)	0·166(1)	0·588(1)	0·328(1)
C(17)	−0·116(1)	0·434(1)	0·341(2)
C(21)	0·396(1)	0·255(1)	0·475(2)
C(22)	0·318(2)	0·184(1)	0·479(2)
C(23)	0·391(2)	0·112(1)	0·521(2)
C(24)	0·530(2)	0·116(1)	0·556(2)
C(25)	0·606(2)	0·181(1)	0·556(2)
C(26)	0·541(2)	0·252(1)	0·516(2)
C(27)	0·167(2)	0·177(1)	0·439(2)
H(1a) *	−0·24(2)	0·30(1)	0·30(2)
H(1b)	−0·17(2)	0·29(1)	0·46(2)
H(2a)	−0·08(2)	0·21(1)	0·25(2)
H(2b)	−0·10(2)	0·17(1)	0·40(2)
H(13)	−0·23(2)	0·58(1)	0·30(2)
H(14)	−0·13(2)	0·70(1)	0·28(2)
H(15)	0·13(2)	0·71(1)	0·29(2)
H(16)	0·28(2)	0·59(1)	0·33(2)
H(17)	−0·23(2)	0·43(1)	0·33(2)
H(23)	0·33(2)	0·06(1)	0·52(2)
H(24)	0·58(2)	0·06(1)	0·59(2)
H(25)	0·72(2)	0·18(1)	0·59(2)
H(26)	0·60(2)	0·31(1)	0·51(2)
H(27)	0·11(2)	0·12(1)	0·44(2)

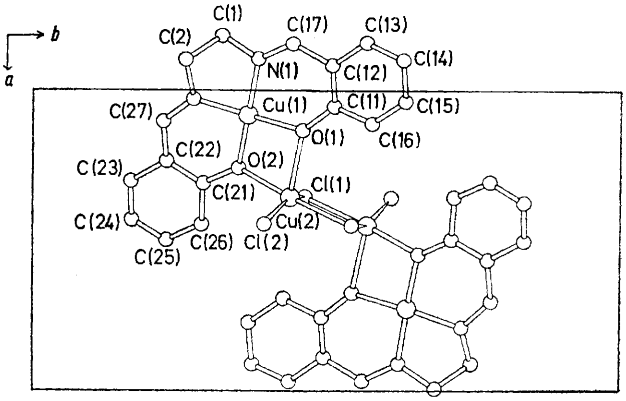
* Hydrogens numbered to correspond with the atoms to which they are bonded.

TABLE 2

Root-mean-square amplitudes of vibration

	Axis		
Atom	Minor	Medium	Major
Cu(1)	0·135	0·178	0·239
Cu(2)	0·138	0·174	0·238
Cl(1)	0·135	0·208	0·268
Cl(2)	0·196	0·230	0·290
O(1)	0·149	0·182	0·278
O(2)	0·150	0·180	0·288
N(1)	0·116	0·155	0·254
N(2)	0·136	0·191	0·240
C(1)	0·152	0·216	0·334
C(2)	0·037	0·274	0·311
C(11)	0·018	0·197	0·216
C(12)	0·091	0·203	0·257
C(13)	0·159	0·238	0·279
C(14)	0·097	0·143	0·324
C(15)	0·191	0·220	0·243
C(16)	0·031	0·196	0·259
C(17)	0·087	0·230	0·271
C(21)	0·121	0·173	0·230
C(22)	0·150	0·211	0·252
C(23)	0·164	0·262	0·302
C(24)	0·151	0·238	0·268
C(25)	0·185	0·244	0·274
C(26)	0·136	0·195	0·248
C(27)	0·132	0·188	0·271

4. Structure factors are listed in Supplementary Publication No. SUP 20954 (4 pp.).†



Numbering scheme and unit cell outline. (Hydrogens are numbered for the atoms to which they are attached.)

TABLE 3

Bond lengths (Å)

Cu(1)–O(1)	1·89(1)	C(15)–C(16)	1·41(2)
Cu(1)–O(2)	1·92(1)	C(21)–C(22)	1·42(2)
Cu(1)–N(1)	1·89(1)	C(21)–C(26)	1·41(2)
Cu(1)–N(2)	1·91(1)	C(22)–C(23)	1·42(3)
Cu(2)–Cl(1)	2·290(4)	C(22)–C(27)	1·47(2)
Cu(2)–Cl(1′)	2·365(4)	C(23)–C(24)	1·34(3)
Cu(2)–Cl(2)	2·239(6)	C(24)–C(25)	1·38(3)
Cu(2)–O(1)	2·30(1)	C(25)–C(26)	1·39(3)
Cu(2)–O(2)	1·99(1)	C(1)–H(1a)	1·1(2)
O(1)–C(11)	1·33(2)	C(1)–H(1b)	1·1(2)
O(2)–C(21)	1·34(2)	C(2)–H(2a)	1·1(2)
N(1)–C(1)	1·48(2)	C(2)–H(2b)	1·1(2)
N(1)–C(17)	1·29(2)	C(13)–H(13)	1·1(2)
N(2)–C(2)	1·49(2)	C(14)–H(14)	1·1(2)
N(2)–C(27)	1·29(2)	C(15)–H(15)	1·1(2)
C(1)–C(2)	1·46(3)	C(16)–H(16)	1·1(2)
C(11)–C(12)	1·39(2)	C(17)–H(17)	1·1(2)
C(11)–C(16)	1·41(2)	C(23)–H(23)	1·1(2)
C(12)–C(13)	1·43(3)	C(24)–H(24)	1·1(2)
C(12)–C(17)	1·48(2)	C(25)–H(25)	1·1(2)
C(13)–C(14)	1·35(3)	C(26)–H(26)	1·1(2)
C(14)–C(15)	1·37(2)	C(27)–H(27)	1·1(2)

TABLE 4

Bond angles (°)

O(1)–Cu(1)–O(2)	85·1(7)	Cu(1)–N(2)–C(27)	126(1)
O(1)–Cu(1)–N(1)	96·0(7)	C(2)–N(2)–C(27)	120(1)
O(1)–Cu(1)–N(2)	174·9(7)	N(1)–C(1)–C(2)	111(1)
O(2)–Cu(1)–N(1)	175·6(7)	N(2)–C(2)–C(1)	108(1)
O(2)–Cu(1)–N(2)	94·1(7)	O(1)–C(11)–C(12)	125(1)
N(1)–Cu(1)–N(2)	85·1(7)	O(1)–C(11)–C(16)	117(1)
Cl(1)–Cu(2)–Cl(1′)	84·8(4)	C(12)–C(11)–C(16)	119(1)
Cl(1)–Cu(2)–Cl(2)	93·0(4)	C(11)–C(12)–C(13)	120(1)
Cl(1)–Cu(2)–O(1)	104·6(6)	C(11)–C(12)–C(17)	125(1)
Cl(1)–Cu(2)–O(2)	174·3(6)	C(13)–C(12)–C(17)	116(1)
Cl(1′)–Cu(2)–Cl(2)	153·6(4)	C(12)–C(13)–C(14)	121(1)
Cl(1′)–Cu(2)–O(1)	95·7(6)	C(13)–C(14)–C(15)	119(1)
Cl(1′)–Cu(2)–O(2)	90·1(6)	C(14)–C(15)–C(16)	122(1)
Cl(2)–Cu(2)–O(1)	110·1(6)	C(11)–C(16)–C(15)	119(1)
Cl(2)–Cu(2)–O(2)	92·7(6)	N(1)–C(17)–C(12)	122(1)
O(1)–Cu(2)–O(2)	73·3(7)	O(2)–C(21)–C(22)	121(1)
Cu(2)–Cl(1)–Cu(2′)	95·2(5)	O(2)–C(21)–C(26)	120(1)
Cu(1)–O(1)–C(11)	125(1)	C(22)–C(21)–C(26)	119(1)
Cu(2)–O(1)–C(11)	140(1)	C(21)–C(22)–C(23)	119(1)
Cu(1)–O(1)–Cu(2)	95·3(7)	C(21)–C(22)–C(27)	125(1)
Cu(1)–O(2)–Cu(2)	105·6(7)	C(23)–C(22)–C(27)	116(1)
Cu(1)–O(2)–C(21)	128(1)	C(22)–C(23)–C(24)	121(1)
Cu(2)–O(2)–C(21)	126(1)	C(23)–C(24)–C(25)	121(1)
Cu(1)–N(1)–C(1)	114(1)	C(24)–C(25)–C(26)	121(1)
Cu(1)–N(1)–C(17)	127(1)	C(21)–C(26)–C(25)	120(1)
C(1)–N(1)–C(17)	119(1)	N(2)–C(27)–C(22)	125(1)
Cu(1)–N(2)–C(2)	113(1)		

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue. (Items less than 10 pp. are supplied as full size copies.)

DISCUSSION

The notable feature of the molecular structure is that it is dimeric and contains four copper atoms. The asymmetric ' half ' of the centrosymmetric dimer is the expected binuclear complex but a sharing of the ligand atoms Cl(1) and Cl(1′) ensures the five-co-ordination of two copper centres and the tetranuclear structure. The stereochemical arrangement of the chlorine bridges is such as to reduce to a minimum contact between the two ' halves ' of the molecule.

The geometry about Cu(2) [and Cu(2′)] may be described as distorted tetragonal pyramidal (Table **5**), atoms O(1) being in the apical position with Cu(2)–O(1) 2·30 Å. This arrangement is clearly a satisfactory solution to the steric problem presented by the adjacent copper centres in the binuclear ' half ' of the molecule and one which is fully in line with expectation for this metal. The steric demands of the Cu(salen) moiety which suggest that the stereochemistry at Cu(2) cannot also be planar are therefore met without the assumption of tetrahedral geometry.

TABLE 5

Bond angles (°) subtended at Cu(2)

Cl(1′)–Cu(2)–Cl(2)	153·6	Cl(1)–Cu(2)–O(1)	104·6
Cl(1′)–Cu(2)–O(1)	95·7	Cl(1)–Cu(2)–O(2)	174·3
Cl(2)–Cu(2)–O(1)	110·1	Cl(1′)–Cu(2)–O(2)	90·1
Cl(1)–Cu(2)–Cl(1′)	84·8	Cl(2)–Cu(2)–O(2)	92·7
Cl(1)–Cu(2)–Cl(2)	93·0	O(1)–Cu(2)–O(2)	73·3

TABLE 6

Planes of best fit

The equations of planes are referred to a set of orthogonal axes and given in the cosine form $AX + BY + CZ + D = 0$. The transformation to cell axes is: $X = x + z\cos\beta$, $Y = y$, $Z = z\sin\beta$. Displacements (Å) of relevant atoms are given in square brackets.

Plane (i): Co-ordination plane, O(1), O(2), N(1), N(2)

$$0{\cdot}183X - 0{\cdot}136Y - 0{\cdot}974Z + 4{\cdot}610 = 0$$

[O(1) 0·08, O(2) −0·08, N(1) −0·08, N(2) 0·08, Cu(1) −0·01, Cu(2) 0·23, C(1) −0·16, C(2) 0·35]

Plane (ii): Benzene ring, C(11)—(16)

$$0{\cdot}071X - 0{\cdot}159Y - 0{\cdot}985Z + 4{\cdot}839 = 0$$

[C(12) * 0·01, Cu(1) −0·02, O(1) −0·04, N(1) 0·11, C(17) 0·07]

Plane (iii): Benzene ring C(21)—(26)

$$0{\cdot}278X - 0{\cdot}195Y - 0{\cdot}941Z + 4{\cdot}654 = 0$$

[C(24) * 0·02, Cu(1) −0·12, O(2) 0·02, N(2) 0·03, C(27) 0·01]

Plane (iv): Co-ordination plane: Cl(1), Cl(1′), Cl(2), O(2)

$$-0{\cdot}856X + 0{\cdot}411Y - 0{\cdot}313Z + 1{\cdot}510 = 0$$

[Cl(1) 0·27, Cl(1′) −0·27, Cl(2) −0·27, O(2) 0·28, Cu(2) 0·25]

Plane (v): Ring Cu(1), Cu(2), O(1), O(2)

$$0{\cdot}138X - 0{\cdot}228Y - 0{\cdot}964Z + 5{\cdot}192 = 0$$

[Cu(1) 0·06, Cu(2) 0·05, O(1) −0·05, O(2) −0·06]

* Atom in defining plane showing largest deviation therefrom.

Comparison of appropriate regions of the molecule with the simple Cu(salen) complex[10] shows some significant changes. Thus the plane-to-plane dimeric bonding which ensures five-co-ordination of the copper atom in Cu(salen) is no longer present, Cu(1) being bonded only to the four donor atoms of the quadridentate ligand. This part of the molecule is indeed more nearly planar as has been deduced from its spectrum. This is clear from the planes of best fit (Table **6**), when the displacement of copper atoms from the salicylidene residues is considered. In Cu(salen) itself these distances are 0·40 and 0·47 Å, testifying to a large ' umbrella ' distortion in this complex, as against the 0·06 and 0·14 Å in (III). We believe that the reason for this lies not in the presence of an adjacent distorted stereochemistry but in an electronic effect resulting from the in-plane bonding of a positive centre, *i.e.* Cu(2), to the oxygen donor atoms. The consequences of interactions with the positive dipole in a hydrogen bond has been demonstrated to be a closer approximation to molecular planarity and a decrease in co-ordination number[11,12] similar to that seen with Cu(1). However, the ethylene bridging atoms C(1) and C(2) are still asymmetrically displaced[13] from the mean co-ordination plane [defined by N(1), N(2), O(1), O(2)] by −0·16 and 0·35 Å.

In the tetranuclear molecule there are three four-membered rings containing copper atoms. The mean plane through Cu(1), Cu(2), O(1), and O(2) shows that this ring, and its centrosymmetrically related partner, are not quite planar, the atom displacements being ±0·05 Å. The other ring [Cu(2), Cu(2′), Cl(1), Cl(1′)] is necessarily planar by symmetry. The Cu(1) · · · Cu(2) distance is 3·109 Å, the Cu(2) · · · Cu(2′) distance 3·439 Å. The antiferromagnetic interaction observed[4] can clearly be accounted for by a superexchange mechanism involving O(2) and perhaps O(1), if not by direct copper–copper spin pairing. That O(2) is in approximately trigonal hybridisation with bond angles of 128, 126, and 106°, and is almost equidistant from the two copper atoms suggests that it provides the most likely pathway.

There is only one intermolecular approach less than the sum of van der Waals radii; C(15) · · · C(22^{I}) 3·34 Å [C(22^{I}) at $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$]. There are thus no packing constraints between molecules.

Comparison of the present molecular structure with that of (IV)[14] has ascribed the weaker antiferromagnetic interaction in (III) to the lengthened Cu(1)–Cu(2) bridging consequent upon the five-co-ordination of Cu(2). The interesting structural question is whether the quinque-covalency is an accident of crystal packing or whether it is an electronic requirement of one complex. The copper–nitrogen bond lengths are at the limit of being significantly different in the two compounds,

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[10] D. Hall and T. N. Waters, *J. Chem. Soc.*, 1960, 2644.

[11] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 406.

[12] H. C. Freeman, ' The Biochemistry of Copper,' eds. J. Peisach, P. Aisen, and W. E. Blumberg, Academic Press, New York, 1966, p. 105.

[13] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 400.

[14] E. Sinn and W. T. Robinson, *J.C.S. Chem. Comm.*, 1972, 359.

assuming the same standard deviations (0·01 Å) for both; mean 1·90 in (III) and 1·94 Å in (IV). Since it is known that there is a close interaction between electronic state and structure in salicylaldimine, and other, complexes of copper(II) [11,12] it should not be assumed that the differences between the two compounds have a purely ' packing origin '.

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