X-Ray Structure Analyses and Magnetic Correlation of Four Copper(II) Complexes

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Summary Magnetic properties of a series of antiferromagnetic binuclear complexes correlate closely with their structures, as determined by single crystal, *X*-ray diffraction analyses.

UNIT cell parameters (Table 1) have been measured for single crystals of dimeric bromo-(*N*-ethylsalicylaldimino)-copper(II), $[CuC_9H_{10}NOBr]_2$ (Ia), of the analogous chloro-compound $[CuC_9H_{10}NOCl]_2$ (Ib), of $[CuC_9H_9NOCl]_2$, (IIa), which contains the same non-hydrogen atoms as (Ib), and of dimeric chloro-(*N*-methylsalicylaldimino) copper(II), [Cu-

Crystallographic data (*distances in* Å, *angles in degrees; e.s.d.'s in parentheses*)

	(Ia)	(Ib)	(Ic)	(IIa)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a	10·77	9·989(1)	6·998(2)	7·639(2)
b	7·48	7·441(1)	10·165(2)	18·527(3)
c	7·92	8·396(1)	7·189(2)	14·633(3)
α	114·3	122·56(1)	90·32(1)	90
β	96·9	98·74(1)	105·77(1)	116·93(1)
γ	116·0	104·28(1)	115·51(1)	90
Z	1	1	1	4
Number of reflections	—	1316	514	841
R	—	0·039	0·045	0·115

(Ia) cell constants determined directly from precession films and structure deduced from (Ib).

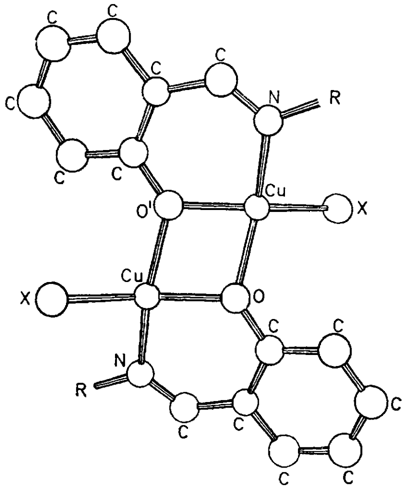

FIGURE 1. trans-*Bis*[*halogeno*(N-*alkylsalicylaldimino*)*copper*(II)] *complexes:* (Ia; R = Et, X = Br), (Ib; R = Et, X = Cl), *and* (Ic; R = X = Cl).

$C_8H_8NOCl]_2$(Ic).[1,2] For (Ib), (Ic), and (IIa) three-dimensional intensity data were collected using a Hilger and Watts four-circle automatic diffractometer and Zr-filtered Mo-K_α X-radiation. These structures were solved using normal Fourier techniques and full-matrix least-squares refinements. Structure (Ia) is not isomorphous with (Ib) but photographs of their *h0l* reciprocal lattice layers are superimposable and show only those differences in intensities consequent upon substituting bromine (Ia) for chlorine (Ib) in isostructural molecules. The exact Cu_2O_2 planes of these molecules are stacked approximately normally to the *b*-axes of their triclinic cells. Consequently this cell dimension does not change much between the two compounds. a, c, α, and γ do change and reflect a shift of adjacent stacks parallel to the *b*-axis to accommodate the change in halogen atom radius.

The four structures contain well separated, neutral, binuclear complex molecules. In (Ia), (Ib), and (Ic) centres of symmetry are imposed on these molecules, while in structure (IIa) all atoms are crystallographically independent. Intramolecular dimensions are listed in Table 2 and Figure 2.

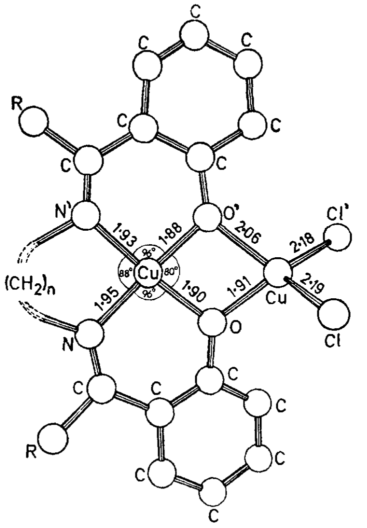

FIGURE 2. cis-*Bis[chloro(alkylsalicylaldimino)copper*(II)] *complexes:* (IIa; R = Me, n = 2), (IIb; R = H, n = 2), *and* (IIc; R = H, n = 3); [*bond lengths*(Å) *and angles* (*degrees*) *refer to* (IIa)].

Pressure dependence of magnetic susceptibility in the range 1—3000 atmospheres was measured as previously described.[3]

Replacement of bromine in (Ia) by chlorine, to form (Ib), has little effect on the magnetism. The structures of (Ia) and (Ib) are believed to be very similar from the diffraction data, no great structural effect on the magnetism would be expected, and an electronic effect, which might have been expected, is not evident. On the other hand, slight changes in the stereochemistry of copper, while retaining the same ligand atoms [(Ib) → (Ic), the same atoms surround copper at about the same distances, but at different angles, so that the deviation from planarity is greater in (Ic)] weakens the antiferromagnetic coupling between the copper atoms [coupling constant $J = -240\ \text{cm}^{-1} \rightarrow J = -146\ \text{cm}^{-1}$ in (Ib) → (Ic)]. Replacement of Et by Me remote from the copper atoms [(Ib) → (Ic)] cannot be considered important as a direct electronic effect, when the effect of replacing bromine with chlorine on copper itself is of much lesser importance.

TABLE 2

Interatomic distances (Å) *and bond angles* (°)

Distances	(Ib)	(Ic)	Angles	(Ib)	(Ic)	Angles around Cu′ in (IIa)	
Cu–Cu[a]	3·05	3·041	O–Cu–O′	76·8	77·4	O–Cu′–O′	75
Cu–O	1·97	1·98	O–Cu–Cl	100·7	101·6	O–Cu′–Cl	100
Cu–O′	1·923	1·92	O–Cu–N	154·1	154·1	O′–Cu–Cl′	108
Cu–N	1·950	1·93	O′–Cu–N	92·1	94·5	Cl–Cu′–Cl′	106
Cu–X	2·202	2·20	O′–Cu–Cl	154·0	149·8	O–Cu′–Cl′	140
			N–Cu–Cl	99·3	96·7	O′–Cu′–Cl	132

[a] This distance is 3·01 Å in (IIa).

(IIa), which is almost isomeric with (I), contains copper atoms with two different stereochemistries as expected.[4] After this structure had been solved, Waters *et al.* reported similar structures for (IIb) and (IIc),[5] except that in (IIb) the possibility[2] of linkage through the halogen atoms of adjacent molecules was realised, making copper five-co-ordinate, and simultaneously weakening one of the Cu–O bonds (2·3 Å). Here again, there is a weakening antiferromagnetic interaction in the direction (IIa) → (IIb), which must be attributed largely to the structural effect of weakening the Cu–Cu bridging linkage.

Owing the accident of five-co-ordination in (IIb), the pair of complexes (IIb) and (IIc) do not form part of the same series, but (IIa) and (IIc) are analogues, with the latter containing the more distorted copper atoms. However, (IIa) does not suffer from this problem, and (IIa) and (IIc) form part of a series in which, again, decreasing antiferromagnetic interaction correlates with increasing distortion from planar environment.

Although the magnetic properties of the complexes are very dependent upon temperature, we find that they are not significantly sensitive to pressure up to 3000 atmospheres, indicating that there is little difference in volume between the singlet and triplet forms of the molecules. This compares interestingly with the lack of volume change on electron pairing in the antiferromagnetic copper(II) acetate[3] and the dramatic volume decrease (and metal–metal bond length decrease) upon electron pairing in ferric dithiocarbamates.[6] Although the bond angles are different, (Ib) and (Ic) have essentially the same metal–ligand bond lengths and hence about the same volume, despite the fact that (Ic) contains twice as many triplet state molecules as (Ib). This, together with the pressure effect, suggests that there is little difference between the singlet and triplet molecules in this type of system, and the strength of antiferromagnetic interaction is very sensitive to small changes in the bond angles.

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