Variable Stereochemistry in Binuclear Complexes of Copper(II)

By C. A. BEAR, J. M. WATERS, and T. N. WATERS*
(*Department of Chemistry, University of Auckland, New Zealand*)

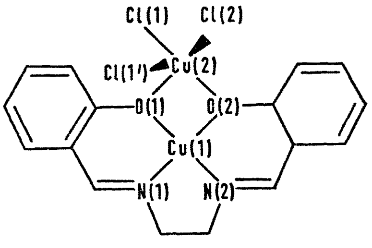
Summary An X-ray structural study of two binuclear complexes of copper(II) shows that small stereochemical changes at one metal centre can have a large effect on the geometry at the other.

BINUCLEAR complexes of copper(II) have long been recognised as providing special electronic and structural situations as the detailed and continuing studies of copper(II) acetate monohydrate demonstrate.[1] In this and similar compounds molecular structure is based on the bridging role of the carboxylate ligands and electron spin pairing occurs. Neither the geometry nor the electronic phenomena is unique however, and binuclear complexes may be formed by what can be regarded as molecular dimerisation, as in the γ-modification of bis-(N-methylsalicylaldiminato)copper(II)[2] or NN'-ethylenebis(salicylaldiminato)copper(II),[3] or through bridging atoms, rather than groups, as in acetylacetone–mono-(o-hydroxyanil)copper(II).[4] These compounds also show evidence for electron pairing and are generally planar molecules, or nearly so, the copper atoms being four-co-ordinate. The former have five-co-ordinate metal centres as a result of plane to plane bonding between two monomeric species.

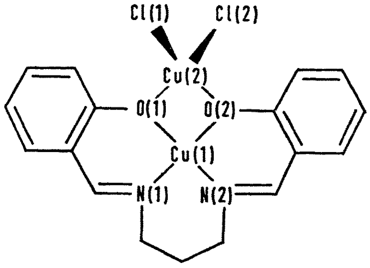
Recently, Harris and Sinn and their co-workers[5] have prepared a new series of compounds with the electronic properties characteristic of many binuclear complexes but which also include a mixture of ligands, typically salicylaldimines and halogens, not previously found. It follows that bonding geometries about the two copper centres may now be dissimilar and the possibility that the stereochemistry may involve tetrahedral co-ordination and be subject to manipulation by appropriate changes to the ligands has led us to examine two compounds by X-ray methods.

Dichloro - [NN' - ethylenebis(salicylideneiminato)copper(II)] copper(II)—(I), monoclinic, a = 9·791(6), b = 16·780(6), c = 10·536-(5) Å, β = 100·80(1)°, $P2_1/n$, $Z = 4$. Intensity data were collected on a Hilger and Watts automatic diffractometer, 1548 amplitudes (of intensity $> 3\sigma$) being recorded with Mo-K_α-radiation. The current R-factor is 0·079 with refinement continuing. Dichloro-[NN'-propylenebis(salicylideneiminato)copper(II)] copper(II)—(II), monoclinic, a = 11·15(2), b = 8·438(8), c = 18·17(2) Å, β = 97·63(6)°, $P2_1/c$, $Z = 4$. Intensity data were again collected by diffractometry, 2112 values being recorded. The current R-factor, refinement continuing, is 0·077.

(I) and (II) are diagrammatic representations of the molecules. Relevant bond lengths and angles are listed in the Table. It will be seen that the stereochemistry about the copper atoms, Cu(1), chelated to the Schiff base, are approximately planar in both complexes with a slight but significant tetrahedral distortion apparent in (II), presumably reflecting the less rigid requirements of a ligand containing a propylene bridge. At the two remaining copper centres, Cu(2), different situations exist. In (II) a large tetrahedral component is apparent, as indicated by the angles subtended at the metal.



(I)



(II)

Selected bond lengths and angles

(I)			
Cu(1)–O(1)	1·89(1) Å	O(1)–Cu(1)–O(2)	85·0(5)
Cu(1)–O(2)	1·92(1)	O(1)-Cu(1)–N(1)	95·7(5)
Cu(1)–N(1)	1·90(1)	O(1)–Cu(1)–N(2)	174·3(5)
Cu(1)–N(2)	1·91(1)	O(2)–Cu(1)–N(1)	175·6(5)
		O(2)–Cu(1)–N(2)	93·9(5)
Cu(2)–O(1)	2·30(1)	N(1)–Cu(1)–N(2)	85·8(5)
Cu(2)–O(2)	1·98(1)		
Cu(2)–Cl(1)	2·288(5)	O(1)–Cu(2)–O(2)	73
Cu(2)–Cl(2)	2·240(5)	O(1)–Cu(2)–Cl(1)	104·5(3)
O(1)–Cu(2)–Cl(1′)	96·1(3)°	O(1)–Cu(2)–Cl(2)	110
		O(2)–Cu(2)–Cl(1)	174·3(3)
		O(2)–Cu(2)–Cl(2)	93
O(2)–Cu(2)–Cl(1′)	90·1(3)	Cl(1)–Cu(2)–Cl(2)	93·0(2)
Cl(1)–Cu(2)–Cl(1′)	84·8(2)		
Cl(2)–Cu(2)–Cl(1′)	153·7(2)	Cu(1)–O(1)–Cu(2)	95·3(4)
Cu(2)–Cl(1′)–Cu(2′)	95·2(2)	Cu(1)–O(2)–Cu(2)	105·7(5)
(II)			
Cu(1)–O(1)	1·94(1) Å	O(1)–Cu(1)–O(2)	77·7(5)°
Cu(1)–O(2)	1·96(1)	O(1)–Cu(1)–N(1)	92·7(5)
Cu(1)–N(1)	1·95(1)	O(1)–Cu(1)–N(2)	166·7(5)
Cu(1)–N(2)	1·96(1)	O(2)–Cu(1)–N(1)	169·7(5)
		O(2)–Cu(1)–N(2)	89·4(5)
Cu(2)–O(1)	2·01(1)	N(1)–Cu(1)–N(2)	100·3(5)
Cu(2)–O(2)	1·96(1)		
Cu(2)–Cl(1)	2·179(5)	O(1)–Cu(2)–O(2)	76·1(5)
Cu(2)–Cl(2)	2·176(5)	O(1)–Cu(2)–Cl(1)	113·2(3)
		O(1)–Cu(2)–Cl(2)	125·3(3)
Cu(1)–O(1)–Cu(2)	101·4(5)°	O(2)–Cu(2)–Cl(1)	133·5(4)
Cu(1)–O(2)–Cu(2)	103·0(5)	O(2)–Cu(2)–Cl(2)	102·5(4)
		Cl(1)–Cu(2)–Cl(2)	106·3(2)

This pseudo-tetrahedral environment has been predicted on steric grounds,[5] but another solution to steric problems is to be found in complex (I). Here the stereochemistry about Cu(2) is that of a tetragonal pyramid with one of the basal positions being occupied by a chlorine atom Cl(1′), from a neighbouring molecule. The oxygen atom O(1) takes the apical position, a role consistent with the longer Cu(2)–O(1) bond length of 2·30 Å. This compound is thus polymeric in the solid with a bridging chlorine as well as bridging oxygen atoms between metal centres. It seems likely that this network disappears in the monohydrate,[5] the water molecule occupying the co-ordination position of Cl(1) in a non-bridging role.

The adoption of a pseudo-tetrahedral geometry by copper centres bonded to halogens cannot therefore be assumed. Nor can the bridging oxygen atoms be assumed as equally effective in transmitting magnetic interactions. The results seem to agree, however, with the suggestion[6] that the more tetrahedral the co-ordination geometry imposed by the Schiff base the more tetrahedral will be the geometry at the other copper centre [Cu(2) in this instance]. The small distortion towards the tetrahedral imposed by the Schiff base in (II), presumably as a response to steric interactions between *N*-bonded methylene groups in the longer and more flexible alkyl bridge, is regarded as favouring a tetrahedral, rather than tetragonal pyramidal, geometry at Cu(2). Small adjustments to geometry at one centre are thus associated with large stereochemical changes at the other, a magnification in the present instance which must alter the electronic properties of the complexes and their ability to bind an additional ligand at Cu(2).

Similarly, the observations which indicate that the geometry at Cu(1) becomes more planar when a binuclear species is formed[6] receives some support in that the tetrahedral distortion in (II) is very slight. In this connection the marked changes in stereochemistry towards strict molecular planarity are reminiscent of those seen in mononuclear tetradentate Schiff base complexes of copper(II) when they are hydrogen bonded at an oxygen donor.[7] Possible explanations for these have been given[8] and we believe that the same effect is likely when another positive centre, in this instance a copper ion, interacts with the oxygen atoms. Since changes in hydrogen bond strength bring large changes in stereochemistry in the mononuclear complexes it is reasonable to suggest that small adjustments in electronic properties, through the monodentate ligands of Cu(2), may again produce a magnified overall result in the binuclear compounds.

Both steric and electronic influences seem important and even in a series of very similar complexes the same structures and properties should not be assumed.

(*Received, March* 30*th*, 1971; *Com.* 459.)

---

[1] R. W. Jotham and S. F. A. Kettle, *J. Chem. Soc.* (*A*), 1969, 2821.
[2] D. Hall, Sylvia V. Sheat, and T. N. Waters, *J. Chem. Soc.* (*A*), 1968, 460.
[3] D. Hall and T. N. Waters, *J. Chem. Soc.*, 1960, 2644.
[4] G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1965, 1979.
[5] S. J. Gruber, C. M. Harris, and E. Sinn, *Inorg. Chem.*, 1968, **7**, 268.
[6] S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1805.
[7] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 396, 400.
[8] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 406.