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Structure of Chloro{*N*-[2-(4-imidazolyl)ethyl]salicylideneaminato}copper(II) Monohydrate

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Abstract. $[CuCl(C_{12}H_{11}N_3O)].H_2O$, $M_r = 330{\cdot}25$, orthorhombic, $Pccn$, $a = 18{\cdot}952\ (9)$, $b = 19{\cdot}680\ (9)$, $c = 15{\cdot}028\ (8)$ Å, $V = 5605{\cdot}1\ (9)$ Å^3, $Z = 16$, $D_x = 1{\cdot}584$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 17{\cdot}5$ cm^{-1}, $F(000) = 2688$, $T = 293$ K, $R = 0{\cdot}059$ for 2569 observed data with $I \geq 2{\cdot}58\sigma(I)$. There are two independent molecules in the asymmetric unit. In each molecule the Cu atom is four-coordinate in an essentially square-planar environment with three of the basal coordination positions occupied by the donor atoms of the ligand whilst the fourth position is occupied by a chloride ion. The coordination is completed by a long, but significant (3·0 Å av.), bond between the Cu atom of one molecule and the chloride ion of a symmetry-related counterpart. This results in the existence of dimeric units in which the coordination of the metal atom is best described as belonging to the 4 + 1 type.

Introduction. Histidine and tyrosine residues are, generally, thought to be involved at many biological copper sites. In order to characterize the properties of a copper ion in such an environment, we started investigating systematically copper complexes of ligands involving a diamine in addition to a salicyl moiety. In a previous study, we reported on the behaviour of complexes of ligands involving a salicyl group together with an aminoalkylpyridine (Latour, Leonard, Limosin, Povey & Tandon, 1985; Latour, Tandon & Povey, 1989). In the present contribution, we describe the structural properties of the chlorocopper(II) complex of the ligand resulting from the condensation of histamine with salicylaldehyde.

Experimental. Histamine dihydrochloride (0·555 g; 3 mmol) was dissolved in 50 ml of aqueous 0·1 *M* sodium hydroxide solution. To this solution was added salicylaldehyde (0·366 g; 3 mmol) in 25 ml of absolute ethanol. The yellow reaction mixture was stirred for 30 min and, after addition of a solution of copper(II) nitrate trihydrate (0·793 g; 3 mmol) in 10 ml of water, it turned dark green. After stirring for 2 h, the resulting

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solution was filtered and then concentrated to about 20 ml. Upon cooling down to room temperature, crystals separated which were collected, washed with absolute ethanol and dried in vacuum.

Compound crystallizes as dark-green irregular prisms; accurate unit-cell parameters from a least-squares analysis using 25 accurately centred reflections ($17 \leq \theta \leq 21°$) measured on a CAD-4 diffractometer from a crystal of dimensions $0{\cdot}4 \times 0{\cdot}4 \times 0{\cdot}3$ mm. 4879 unique reflections (including systematic absences) with $(\sin\theta)/\lambda \leq 0{\cdot}57$ Å^{-1}, range of *hkl*: $h\,0\rightarrow21$, $k\,0\rightarrow22$, $l\,0\rightarrow17$, standard reflection 006 measured every 1 h of exposed X-ray time, reduced to 4382 after removal of systematic absences. D_m not determined. Enraf–Nonius CAD-4 diffractometer with graphite monochromator on incident beam, ω–2θ scanning mode with variable scan speed 3·33–0·45° min^{-1} in ω. Lorentz–polarization and empirical absorption correction (from φ-scan data) applied (maximum and minimum transmissions 0·99, 0·91). Space group (No. 56) determined from systematic absences. Structure solved by heavy-atom method. Full-matrix least-squares refinement with H-atom positions from geometrical criteria. Disordered solvent molecule (H_2O) identified from difference synthesis, two discrete peaks given fixed occupancy of 0·5 and temperature factors allowed to refine. 321 parameters refined: atomic coordinates and anisotropic thermal parameters for all non-H atoms, H-atom parameters not refined, two molecules refined independently with no constraints on geometry. $\sum w(|F_o - F_c|)^2$ minimized with $w = [\sigma^2(I) + (0{\cdot}06F^2)^2]^{-1/2}$, $S = 1{\cdot}531$, $R = 0{\cdot}059$, $wR = 0{\cdot}078$ for 2569 (59%) observed reflections [$I \geq 2{\cdot}58\sigma(I)$]. Max. and min. excursions on final difference Fourier map 0·4, –0·5 e Å^{-3}, max. shift/e.s.d. 0·01. Scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations were carried out on a DEC PDP 11/73 computer using the *SDP-Plus* system (Frenz, 1983). Atomic parameters are given in Table 1.*

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic thermal parameters* (Å^2)

The B_{eq} values are calculated according to the equation $B_{eq} = \frac{4}{3}\sum_i\sum_j B_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	B_{eq}(Å^2)
Cu(1*A*)	0·32379 (6)	0·17683 (5)	0·36216 (7)	2·90 (2)
Cl(1*A*)	0·3393 (2)	0·2912 (1)	0·3468 (2)	4·14 (6)
O(1*A*)	0·3656 (4)	0·1681 (3)	0·2474 (4)	4·1 (2)
N(1*A*)	0·2910 (4)	0·0817 (4)	0·3615 (5)	3·0 (2)
N(2*A*)	0·3187 (4)	0·1827 (4)	0·4941 (5)	2·9 (2)
N(3*A*)	0·3270 (4)	0·2233 (4)	0·6303 (5)	3·2 (2)
C(1*A*)	0·3060 (5)	0·0372 (5)	0·3003 (6)	3·4 (2)
C(2*A*)	0·3465 (5)	0·0482 (5)	0·2237 (6)	3·4 (2)
C(3*A*)	0·3751 (5)	0·1119 (5)	0·1991 (6)	3·4 (2)
C(4*A*)	0·4163 (6)	0·1166 (5)	0·1214 (7)	4·5 (2)
C(5*A*)	0·4246 (6)	0·0592 (6)	0·0670 (7)	4·9 (3)
C(6*A*)	0·3949 (7)	–0·0016 (6)	0·0871 (7)	5·5 (3)
C(7*A*)	0·3565 (6)	–0·0074 (5)	0·1658 (7)	4·4 (2)
C(8*A*)	0·2467 (6)	0·0584 (5)	0·4358 (6)	3·5 (2)
C(9*A*)	0·2877 (6)	0·0617 (5)	0·5228 (6)	3·4 (2)
C(10*A*)	0·3031 (5)	0·1318 (4)	0·5532 (6)	2·8 (2)
C(11*A*)	0·3066 (5)	0·1571 (5)	0·6372 (6)	3·1 (2)
C(12*A*)	0·3328 (5)	0·2370 (5)	0·5415 (6)	3·3 (2)
Cu(1*B*)	0·82773 (6)	0·18833 (6)	0·28264 (7)	2·87 (2)
Cl(1*B*)	0·7067 (1)	0·1715 (1)	0·2744 (2)	4·15 (6)
O(1*B*)	0·8299 (3)	0·1516 (3)	0·1649 (4)	3·5 (1)
N(1*B*)	0·9283 (4)	0·2150 (4)	0·2788 (5)	3·0 (2)
N(2*B*)	0·8280 (4)	0·1855 (4)	0·4148 (5)	3·2 (2)
N(3*B*)	0·7917 (5)	0·1732 (4)	0·5522 (5)	3·7 (2)
C(1*B*)	0·9714 (5)	0·1985 (5)	0·2172 (7)	3·7 (2)
C(2*B*)	0·9550 (5)	0·1584 (5)	0·1391 (6)	3·2 (2)
C(3*B*)	0·8860 (5)	0·1366 (4)	0·1177 (6)	2·9 (2)
C(4*B*)	0·8768 (5)	0·0965 (5)	0·0407 (6)	3·3 (2)
C(5*B*)	0·9337 (6)	0·0793 (5)	–0·0112 (7)	4·3 (2)
C(6*B*)	1·0004 (6)	0·1029 (6)	0·0068 (7)	4·6 (3)
C(7*B*)	1·0107 (5)	0·1413 (6)	0·0813 (7)	4·6 (3)
C(8*B*)	0·9563 (5)	0·2539 (5)	0·3531 (6)	3·8 (2)
C(9*B*)	0·9566 (5)	0·2109 (6)	0·4369 (6)	4·3 (2)
C(10*B*)	0·8852 (5)	0·1942 (5)	0·4710 (6)	3·4 (2)
C(11*B*)	0·8613 (6)	0·1878 (5)	0·5558 (6)	4·1 (2)
C(12*B*)	0·7742 (5)	0·1732 (5)	0·4671 (6)	3·6 (2)
O(3)	0·1514 (9)	–0·0190 (7)	0·231 (1)	8·3 (5)
O(4)	0·0708 (9)	0·004 (1)	0·275 (1)	13·1 (9)

O(3) and O(4) were allocated fixed occupancies of 0·5.

Discussion. As illustrated in Fig. 1, the coordination around the copper ion can be described as belonging to the 4 + 1 type. Three equatorial positions are occupied by the donor atoms of the ligand, and the fourth by a chloride. The apical position is filled by a second chloride from a neighbouring molecule, thus forming a dimer. The apical copper–chloride distance is far longer than the equatorial one: 3·16 (1) Å for molecule *A* and 2·84 (1) Å for molecule *B* *vs* 2·281 (1) and 2·321 (12) Å, respectively. The Cu—Cu distance is

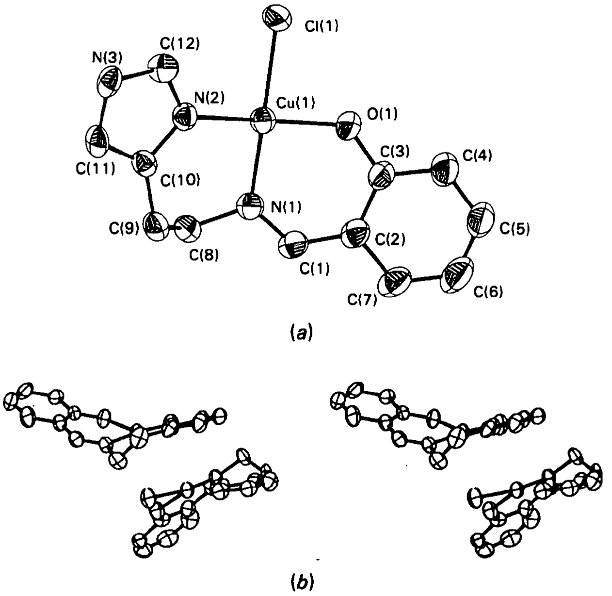

Fig. 1. (*a*) Structure of the complex showing the numbering scheme used. Thermal ellipsoids are shown at 50% probability. (*b*) Stereoview of the dimeric unit.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, C—H bond lengths, torsion angles for non-H atoms and a selection of least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51518 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu(1*A*)	Cl(1*A*)	2·281 (1)	Cu(1*B*)	Cl(1*B*)	2·321 (12)
Cu(1*A*)	O(1*A*)	1·906 (2)	Cu(1*B*)	O(1*B*)	1·911 (10)
Cu(1*A*)	N(1*A*)	1·972 (3)	Cu(1*B*)	N(1*B*)	1·977 (13)
Cu(1*A*)	N(2*A*)	1·988 (5)	Cu(1*B*)	N(2*B*)	1·987 (12)
O(1*A*)	C(3*A*)	1·334 (7)	O(1*B*)	C(3*B*)	1·312 (12)
N(1*A*)	C(1*A*)	1·302 (15)	N(1*B*)	C(1*B*)	1·277 (13)
N(1*A*)	C(8*A*)	1·471 (7)	N(1*B*)	C(8*B*)	1·455 (12)
N(2*A*)	C(10*A*)	1·370 (10)	N(2*B*)	C(10*B*)	1·384 (13)
N(2*A*)	C(12*A*)	1·312 (9)	N(2*B*)	C(12*B*)	1·311 (12)
N(3*A*)	C(11*A*)	1·363 (10)	N(3*B*)	C(11*B*)	1·351 (15)
N(3*A*)	C(12*A*)	1·366 (9)	N(3*B*)	C(12*B*)	1·321 (12)
C(1*A*)	C(2*A*)	1·40 (2)	C(1*B*)	C(2*B*)	1·448 (14)
C(2*A*)	C(3*A*)	1·41 (2)	C(2*B*)	C(3*B*)	1·414 (14)
C(2*A*)	C(7*A*)	1·41 (2)	C(2*B*)	C(7*B*)	1·408 (12)
C(3*A*)	C(4*A*)	1·408 (9)	C(3*B*)	C(4*B*)	1·411 (13)
C(4*A*)	C(5*A*)	1·404 (8)	C(4*B*)	C(5*B*)	1·374 (13)
C(5*A*)	C(6*A*)	1·357 (9)	C(5*B*)	C(6*B*)	1·374 (12)
C(6*A*)	C(7*A*)	1·394 (9)	C(6*B*)	C(7*B*)	1·364 (11)
C(8*A*)	C(9*A*)	1·523 (10)	C(8*B*)	C(9*B*)	1·518 (12)
C(9*A*)	C(10*A*)	1·484 (11)	C(9*B*)	C(10*B*)	1·485 (11)
C(10*A*)	C(11*A*)	1·359 (11)	C(10*B*)	C(11*B*)	1·358 (11)

Cl(1*A*)	Cu(1*A*)	O(1*A*)	86·80 (7)	Cl(1*B*)	Cu(1*B*)	O(1*B*)	85·3 (4)
Cl(1*A*)	Cu(1*A*)	N(1*A*)	167·47 (9)	Cl(1*B*)	Cu(1*B*)	N(1*B*)	171·4 (5)
Cl(1*A*)	Cu(1*A*)	N(2*A*)	92·9 (2)	Cl(1*B*)	Cu(1*B*)	N(2*B*)	93·0 (5)
O(1*A*)	Cu(1*A*)	N(1*A*)	92·32 (9)	O(1*B*)	Cu(1*B*)	N(1*B*)	93·0 (5)
O(1*A*)	Cu(1*A*)	N(2*A*)	158·1 (2)	O(1*B*)	Cu(1*B*)	N(2*B*)	156·1 (5)
N(1*A*)	Cu(1*A*)	N(2*A*)	92·6 (2)	N(1*B*)	Cu(1*B*)	N(2*B*)	91·9 (5)
C(1*A*)	N(1*A*)	C(8*A*)	116·8 (7)	C(1*B*)	N(1*B*)	C(8*B*)	117·1 (9)
C(10*A*)	N(2*A*)	C(12*A*)	106·6 (6)	C(10*B*)	N(2*B*)	C(12*B*)	105·5 (8)
C(11*A*)	N(3*A*)	C(12*A*)	106·5 (6)	C(11*B*)	N(3*B*)	C(12*B*)	106·5 (8)
N(1*A*)	C(1*A*)	C(2*A*)	127· (1)	N(1*B*)	C(1*B*)	C(2*B*)	126· (1)
C(1*A*)	C(2*A*)	C(3*A*)	124· (2)	C(1*B*)	C(2*B*)	C(3*B*)	123·2 (8)
C(1*A*)	C(2*A*)	C(7*A*)	117· (2)	C(1*B*)	C(2*B*)	C(7*B*)	118·0 (9)
C(3*A*)	C(2*A*)	C(7*A*)	118· (1)	C(3*B*)	C(2*B*)	C(7*B*)	118·7 (8)
O(1*A*)	C(3*A*)	C(2*A*)	122·7 (9)	O(1*B*)	C(3*B*)	C(2*B*)	123·9 (8)
O(1*A*)	C(3*A*)	C(4*A*)	118·1 (5)	O(1*B*)	C(3*B*)	C(4*B*)	118·0 (9)
C(2*A*)	C(3*A*)	C(4*A*)	119·1 (9)	C(2*B*)	C(3*B*)	C(4*B*)	118·1 (8)
C(3*A*)	C(4*A*)	C(5*A*)	119·5 (6)	C(3*B*)	C(4*B*)	C(5*B*)	120·4 (9)
C(4*A*)	C(5*A*)	C(6*A*)	122·3 (6)	C(4*B*)	C(5*B*)	C(6*B*)	121·8 (8)
C(5*A*)	C(6*A*)	C(7*A*)	118·5 (6)	C(5*B*)	C(6*B*)	C(7*B*)	118·8 (8)
C(2*A*)	C(7*A*)	C(6*A*)	122·0 (8)	C(2*B*)	C(7*B*)	C(6*B*)	122·0 (9)
N(1*A*)	C(8*A*)	C(9*A*)	110·4 (5)	N(1*B*)	C(8*B*)	C(9*B*)	110·1 (8)
C(8*A*)	C(9*A*)	C(10*A*)	113·8 (6)	C(8*B*)	C(9*B*)	C(10*B*)	114·0 (7)
N(2*A*)	C(10*A*)	C(9*A*)	121·5 (7)	N(2*B*)	C(10*B*)	C(9*B*)	122·0 (7)
N(2*A*)	C(10*A*)	C(11*A*)	109·0 (7)	N(2*B*)	C(10*B*)	C(11*B*)	107·5 (8)
C(9*A*)	C(10*A*)	C(11*A*)	129·5 (8)	C(9*B*)	C(10*B*)	C(11*B*)	130·4 (8)
N(3*A*)	C(11*A*)	C(10*A*)	107·1 (6)	N(3*B*)	C(11*B*)	C(10*B*)	107·9 (8)
N(2*A*)	C(12*A*)	N(3*A*)	110·8 (7)	N(2*B*)	C(12*B*)	N(3*B*)	112·6 (9)

4·061 (2) Å for molecule *A* and 3·821 (1) Å for molecule *B*. The Cu—Cl—Cu angles are 93·6 (1) and 94·9 (1)° in the two independent molecules of the cell. The Cu—O and Cu—N bond distances are unexceptional, and do not show the shortening observed for the nitrate derivative of a similar ligand (Latour *et al.*, 1989). Table 2 summarizes the bond distances and angles within the dimeric unit.

A notable feature of the coordination is the distortion of the basal plane of each monomeric coordination polyhedron towards a tetrahedral arrangement. This is exemplified by the calculation of a least-squares plane through N(1), Cl(1), N(2) and O(1). For both molecules of the dimeric unit, there are deviations from the best plane averaging about 0·3 Å in opposite directions for the pairs of atoms N(2), O(1) and N(1), Cl(1).

A disordered water molecule is present in the lattice and in one of its two proposed positions it makes a possible hydrogen bond [3·18 (1) Å] with the Cl atom of molecule *A*. There are further significant contacts, probably electrostatic between N(3) and O(1) of adjacent molecules [translation $x, \frac{1}{2}-y, \frac{1}{2}+z$: 2·86 (2) Å for molecule *A* and 2·89 (2) Å for molecule *B*].

Dichloro-bridged dicopper complexes have been widely studied over the past decade in an attempt to correlate their structural and magnetic properties (Roundhill *et al.*, 1979; Marsh, Patel, Hatfield & Hodgson, 1983; Landee & Greeney, 1986). Several structural situations have been described according to the overall geometry (trigonal bipyramid, tetragonal pyramid) of the copper coordination sphere and the positions (equatorial *vs* axial) of the bridging atoms. In these compounds, the Cu—Cl—Cu angles span the range 84–102° while the long Cu—Cl distances lie between 2·6 and 3·4 Å. The present complex exhibits values in the middle of both domains. A small magnetic interaction between the two copper centres could be expected from these results. However, the magnetic data down to 6 K failed to reveal any significant interaction and they have been fitted to the Curie–Weiss equation with a Weiss constant of −0·15 K, indicative of a very small interaction.

In solution, the chloride ion is probably dissociated since the conductivity amounts to about 30 µS cm^{-1} for a millimolar Me$_2$SO solution, which corresponds to a 1:1 electrolyte. The occurrence of a *d–d* transition at 645 nm (= 70 mol^{-1} cm^{-1}) and the observation of an axial EPR spectrum ($g = 2{\cdot}25$, $A = 175G$, $g = 2{\cdot}065$) strongly suggest that the chromophore possesses tetragonal symmetry. Moreover, a strong phenoxide-to-copper charge-transfer band is detected at 368 nm (= 5000 mol^{-1} cm^{-1}), thus confirming the presence of the ligand. So, it is plausible that in solution the two chlorides are replaced by solvent molecules and that the resulting complex retains a roughly square-pyramidal geometry.

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