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A 1:1 cocrystal of di-μ-chloro-bis{[*N*-(1-hydroxybut-2-yl)salicylideneiminato-*N*,*O*,*O*′]copper(II)} monohydrate and its methanol solvate

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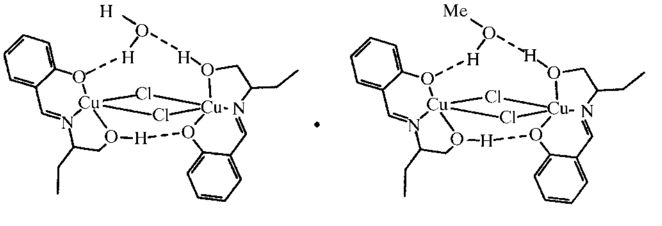
The structure consists of two crystallographically independent and differently solvated binuclear complexes, $\{[Cu_2Cl_2(C_{11}H_{14}NO_2)_2]\cdot CH_4O\}\cdot\{[Cu_2Cl_2(C_{11}H_{14}NO_2)_2]\cdot H_2O\}$. The water and methanol solvate molecules are similarly connected with the complex molecules by two hydrogen bonds. The asymmetrical system of hydrogen bonds breaks up the potential centrosymmetricity of both chelate molecules. All copper(II) centres are in a square-pyramidal environment, with four short bonds in the basal plane formed by two *trans* O atoms and one N atom of the tridentate ligand, and a bridge chloride ion. The fifth axial long bond is formed by a chloride ligand which lies in the basal plane of the neighbouring copper(II) ion.

Comment

The stereochemistry of di-μ-halide-bridged copper(II) dimers has attracted our attention in recent years (Bukowska-Strzyżewska *et al.*, 1997). The present study on the title compound, (I), forms part of our work on the structure of dimeric copper(II) complexes with Schiff bases obtained from aromatic aldehyde and aliphatic amino alcohols. We have previously reported several such compounds and studied their structural features (Bukowska-Strzyżewska & Maniukiewicz, 1992; Maniukiewicz & Bukowska-Strzyżewska, 1994, 1995, 1996). It seems interesting to compare the influence of the solvation or hydration on the shape of the dimeric molecules.



(I)

The view of the two crystallographically independent binuclear complexes (molecules *A* and *B*) with the atom-labelling scheme is shown in Fig. 1. Each copper(II) ion is five-coordinated with approximate square-pyramidal geometry. Apart from small changes in the chemically equivalent bond lengths and angles of molecules *A* and *B*, the largest dissimilarities exist in the geometry of Cu_2Cl_2 cores. The individual Cu—Cl—Cu bridges formed by one short Cu—Cl and one long Cu—Cl bond have distinctly differentiated bond lengths. The short Cu—Cl bonds vary from 2.2550 (11) to 2.2645 (11) Å and the long Cu—Cl bonds from 2.6662 (12) to 2.9112 (13) Å. The Cu···Cu non-bonding distances are 3.450 (1) and 3.422 (1) Å for Cu1···Cu2 and Cu1′···Cu2′, respectively. The central $CuCl_2Cu$ rings are not planar. The dihedral angles change from 21.9 (1) to 23.1 (1)° for Cu1′—Cl1′—Cl2′—Cu2′ and Cu1—Cl1—Cl2—Cu2, respectively.

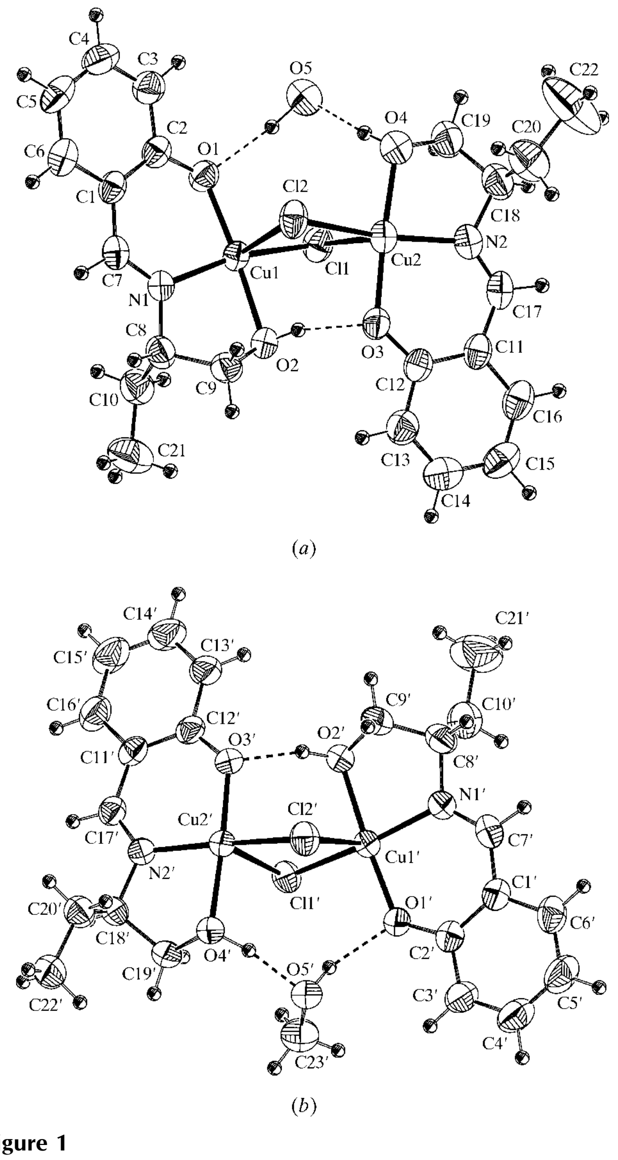


Figure 1
A view of (*a*) the hydrated *A* molecule and (*b*) the *B* molecule solvated by CH_3OH, with the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level.

The asymmetrical system of hydrogen bonds of molecules *A* and *B* is shown in Fig. 1. It spoils the potential centrosymmetricity of the binuclear molecules and induces the deformation of the core $CuCl_2Cu$ rings and the Cu^{II} polyhedra. As can be seen from Table 2, all three hydrogen bonds formed by methanol-solvated complex *B* are distinctly shorter than the bonds formed by molecule *A*. The observed deformation of the Cu^{II} coordination polyhedra from idealized square-pyramidal geometry toward trigonal bipyramidal is also, on average, greater in molecule *B* than in *A*. The deformation parameters τ, computed on the basis of the two maximal valency angles of the Cu atom as $(\alpha_1 - \alpha_2)/60$ (Addison *et al.*, 1985), are 21.9 and 12.6% for the Cu^{II} centres in *A*, and 20.9 and 17.3% for those in *B*.

Experimental

The title compound was prepared by a modification of a previously described procedure (Samus *et al.*, 1987). The complex was prepared by the addition of $CuCl_2{\cdot}2H_2O$ (0.001 mol) to a warm solution containing the ligand (0.001 mol) in methanol (50 ml). The resulting solution was filtered and allowed to cool. Slow evaporation deposited dark-green crystals which were analysed as $[Cu_2Cl_2(C_{11}H_{14}NO_2)_2]_2{\cdot}H_2O{\cdot}CH_3OH$. Analysis found: C 43.55, N 4.56, H 5.46%; calculated: C 43.64, N 4.43, H 5.37%.

Crystal data

$[Cu_2Cl_2(C_{11}H_{14}N_2O_4)_2]_2{\cdot}CH_4O{\cdot}H_2O$
$M_r = 1214.94$
Triclinic, $P\overline{1}$
$a = 12.8770\ (10)$ Å
$b = 15.079\ (2)$ Å
$c = 16.212\ (3)$ Å
$\alpha = 65.10\ (2)^\circ$
$\beta = 71.71\ (2)^\circ$
$\gamma = 69.93\ (2)^\circ$
$V = 2628.4\ (6)$ Å^3
$Z = 2$
$D_x = 1.535$ Mg m^{-3}
D_m measured by flotation in CH_3I/CCl_4
Mo $K\alpha$ radiation
Cell parameters from 15 reflections
$\theta = 10$–20°
$\mu = 1.856$ mm^{-1}
$T = 295\ (2)$ K
Prism, dark green
$0.40 \times 0.35 \times 0.30$ mm

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.907 (3)	Cu1′—O1′	1.894 (3)
Cu1—N1	1.937 (3)	Cu1′—N1′	1.943 (3)
Cu1—O2	2.043 (3)	Cu1′—O2′	2.015 (3)
Cu1—Cl1	2.2646 (11)	Cu1′—Cl1′	2.2615 (11)
Cu1—Cl2	2.6662 (12)	Cu1′—Cl2′	2.7862 (12)
Cu2—O3	1.912 (3)	Cu2′—O3′	1.910 (3)
Cu2—N2	1.945 (3)	Cu2′—N2′	1.943 (3)
Cu2—O4	1.996 (3)	Cu2′—O4′	1.999 (3)
Cu2—Cl2	2.2550 (11)	Cu2′—Cl2′	2.2560 (12)
Cu2—Cl1	2.9112 (13)	Cu2′—Cl1′	2.7752 (12)
O1—Cu1—O2	175.87 (10)	O1′—Cu1′—O2′	175.30 (10)
O1—Cu1—Cl1	95.08 (8)	O1′—Cu1′—Cl1′	93.85 (8)
N1—Cu1—Cl1	162.71 (10)	N1′—Cu1′—Cl1′	162.78 (10)
O2—Cu1—Cl1	88.86 (7)	O2′—Cu1′—Cl1′	90.79 (8)
N1—Cu1—Cl2	99.08 (9)	N1′—Cu1′—Cl2′	101.89 (9)
Cl1—Cu1—Cl2	95.33 (4)	Cl1′—Cu1′—Cl2′	93.01 (4)
O3—Cu2—O4	174.57 (11)	O3′—Cu2′—O4′	175.97 (10)
O3—Cu2—Cl2	92.76 (8)	O3′—Cu2′—Cl2′	92.03 (8)
N2—Cu2—Cl2	167.03 (11)	N2′—Cu2′—Cl2′	165.58 (9)
O3—Cu2—Cl1	89.95 (9)	O3′—Cu2′—Cl1′	90.68 (8)
N2—Cu2—Cl1	102.41 (10)	N2′—Cu2′—Cl1′	99.70 (9)
Cl2—Cu2—Cl1	89.12 (4)	Cl2′—Cu2′—Cl1′	93.42 (4)
Cu1—Cl1—Cu2	82.60 (4)	Cu1′—Cl1′—Cu2′	84.95 (4)
Cu2—Cl2—Cu1	88.62 (4)	Cu2′—Cl2′—Cu1′	84.79 (4)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1···O3	0.85	1.83	2.664 (4)	165
O2′—H1′···O3′	1.00	1.69	2.629 (4)	156
O4—H2···O5	0.85	1.82	2.662 (5)	171
O4′—H2′···O5′	0.98	1.64	2.611 (4)	170
O5—H1*W*···O1	0.98	1.83	2.793 (5)	165
O5′—H5*M*···O1′	0.85	1.89	2.718 (4)	163

Data collection

Siemens *P*3 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.495$, $T_{\max} = 0.573$
9070 measured reflections
8666 independent reflections
7583 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\max} = 25.07^\circ$
$h = 0 \rightarrow 15$
$k = -16 \rightarrow 17$
$l = -18 \rightarrow 19$
2 standard reflections every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.119$
$S = 1.095$
8666 reflections
604 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2 + 2.9616P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.022$
$\Delta\rho_{\max} = 0.72$ e Å^{-3}
$\Delta\rho_{\min} = -0.48$ e Å^{-3}

H atoms attached to O atoms were located directly from the difference map. The remaining H atoms were placed at their calculated positions and refined using a riding model.

Data collection: *P*3 *Software* (Siemens, 1990); cell refinement: *P*3 *Software*; data reduction: *XDISK* in *SHELXTL*/*PC* (Sheldrick, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1033). Services for accessing these data are described at the back of the journal.

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