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The new three-dimensional supramolecule bis{μ-2-[(4-hydroxybenzoyl)hydrazonomethyl]phenolato}bis[aquacopper(II)] dinitrate

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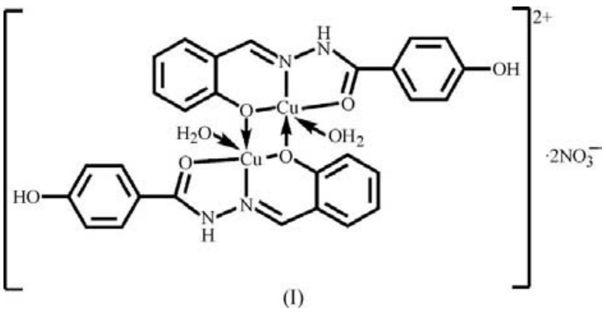
In the title centrosymmetric binuclear complex, $[Cu_2(C_{14}H_{11}N_2O_3)_2(H_2O)_2](NO_3)_2$, the two metal centres are bridged by the phenolate O atoms of the ligand, forming a Cu_2O_2 quadrangle. Each Cu atom has a distorted square-pyramidal geometry, with the basal donor atoms coming from the *O*,*N*,*O*′-tridentate ligand and a symmetry-related phenolate O atom. The more weakly bound apical donor O atom is supplied by a coordinated water molecule. When a further weak Cu···O interaction with the 4-hydroxy O atom of a neighbouring cation is considered, the extended coordination sphere of the Cu atom can be described as distorted octahedral. This interaction leads to two-dimensional layers, which extend parallel to the (100) direction. The two-dimensional polymeric structure contrasts with other reported structures involving salicylaldehyde benzoylhydrazone ligands, which are usually discrete mono- or dinuclear Cu complexes. The nitrate anions are involved in a three-dimensional hydrogen-bonding network, featuring intermolecular N—H···O and O—H···O hydrogen bonds.

Comment

N-Salicylideneacylhydrazines, acting either as neutral, mono- or dianionic *O*,*N*,*O*′-tridentate Schiff base ligands, have received intense attention owing to their structural and functional diversities (Iskander *et al.*, 2000*a*,*b*, 2004; Yin & Liu, 2002; Li & Liu, 2004). A large number of monomeric and dimeric copper(II) complexes have been prepared, characterized and proved to have magnetic properties (Iskander *et al.*, 2000*a*,*b*, 2004; Chan *et al.*, 1995; Ainscough *et al.*, 1995; Sangeetha *et al.*, 1999). An area of particular significance is the relation between the molecular magnetic properties and the intermolecular interactions of this type of dimeric copper(II) complex. Strong intermolecular interactions, such as hydrogen bonding, can be associated with subtle effects on the molecular magnetic properties of a compound. As part of our continuing investigations of these types of Schiff base ligands and their copper(II) compounds, we have synthesized and reported a new Schiff base ligand, 4-hydroxy-*N*′-(2-hydroxybenzylidene)benzohydrazide (H_3L; Lin *et al.*, 2007). H_3L is not only a potentially tetradentate ligand containing both chelating and bridging units, but also can be involved in hydrogen-bond formation with available hydrogen donor sites. In many cases, these hydrogen bonds dictate interesting molecular packing arrangements in the solid state. We report here the title compound, (I), with the H_3L ligand in its monodeprotonated tridentate form.



(I)

The molecular structure of complex (I), as shown in Fig. 1, consists of a centrosymmetric dimeric cation, $[Cu_2(H_2L)_2(H_2O)_2]^{2+}$, accompanied by two nitrate anions, where the ligand is monoanionic and tridentate. Phenolate atom O1 bridges the two Cu atoms with one short and one long Cu—O bond (Table 1), resulting in a Cu···Cu distance of 2.987 (1) Å. Each Cu^{II} atom exists in a slightly distorted square-pyramidal geometry. The basal plane is defined by atoms N1, O1 and O2 from the ligand and the symmetry-related atom O1($-x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z$), while the axial site is occupied by the water molecule. Owing to the Jahn–Teller effect, the pendant water O atom has weak bonding interactions with the Cu^{II} atom [Cu1—O1*W* = 2.452 (3) Å]. However, this distance is somewhat longer than that in some related Cu compounds (Sangeetha *et al.*, 1999; Chan *et al.*, 1995). The Cu—N and other Cu—O distances (Table 1) are similar to the corresponding values observed in related copper(II) complexes

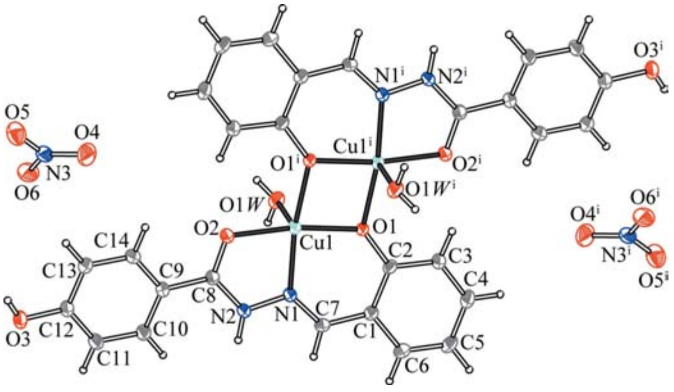


Figure 1
A view of the title complex, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $-x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z$.]

(Iskander *et al.*, 2000*b*, 2004). The remaining protonated phenol group has very weak bonding interactions with atom Cu1^{vi} [Cu1$^{vi}\cdots$O3 = 2.803 (2) Å; symmetry code: (vi) $-x+\frac{1}{2}$, $y+\frac{1}{2}$, $-z+\frac{1}{2}$] of a neighbouring dimeric cation, and at the same time it is involved in intermolecular hydrogen bonding, as shown in Fig. 2. Overall, the geometry of the Cu atom is considered as distorted octahedral. Inclusion of this latter weak interaction leads to the overall structure consisting of two-dimensional layers, which extend parallel to the (100) direction.

The six-membered N1/C7/C1/C2/O1/Cu1 ring and the five-membered O2/C8/N2/N1/Cu1 chelate ring are almost planar, with a dihedral angle of 3.79 (10)° between them. The C7═N1 bond distance of 1.281 (3) Å in the title complex confirms its assignment as a double bond; at the same time, the N1—N2 and C8—N2 bond lengths of 1.384 (3) and 1.331 (3) Å indicate that they are single bonds, all of which are in agreement with the corresponding values reported in other mono-deprotonated *N*-salicylideneacylhydrazine complexes (Iskander *et al.*, 2000*b*, 2004). The uncoordinated nitrate anions are involved in forming a complex intermolecular hydrogen-bonding network. The dimers interact *via* N2—H2$\cdots$O4^{iii}, O3—H3$\cdots$O1*W*^{ii} and O1*W*—H12$\cdots$O6^{v} hydrogen bonds [symmetry codes: (ii) $x, -y, z+\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (v) $x, -y, z-\frac{1}{2}$; Table 2] and extend to form a layer of dimers parallel to the (100) plane, as shown in Fig. 2. Layers of coordinated water molecules and nitrate anions alternate with the complex molecule layers along the *a* direction and further join these two-dimensional sheets into a three-dimensional network *via* the O1*W*—H11$\cdots$O5^{iv} interaction [symmetry code: (iv) $-x, y, -z+\frac{1}{2}$; Fig. 3]. Two nitrate anions and two coordinated water molecules form a chair-shaped ring through intermolecular hydrogen bonding (as shown in Fig. 3).

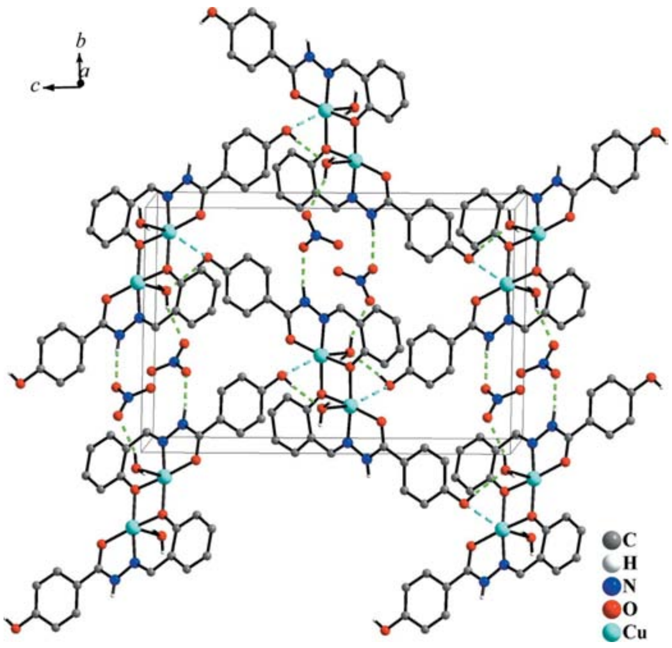


Figure 2
A hydrogen-bonded layer of dimers parallel to the (100) plane, with H atoms on C atoms omitted for clarity. (In the electronic version of the paper, green dashed lines indicate hydrogen bonds and cyan dashed lines indicate the weak interactions between Cu and protonated phenol O atoms.)

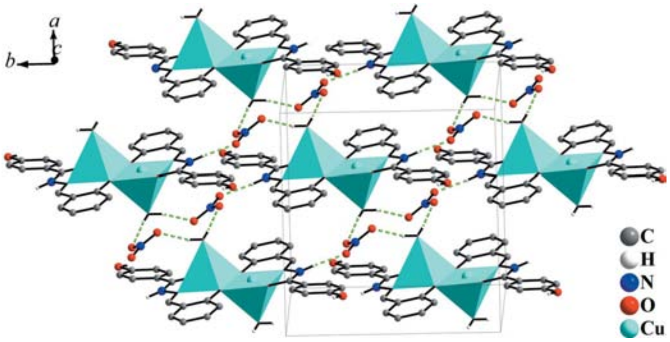
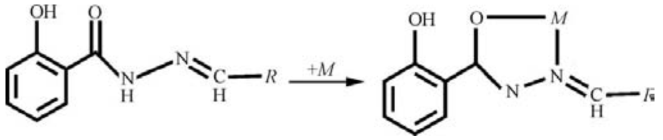


Figure 3
A hydrogen-bonded layer of dimers parallel to the (001) plane. H atoms not involved in hydrogen bonding have been omitted. Dashed lines indicate hydrogen bonds. The Cu coordination is here regarded as a square pyramid, not considering the weak bonding interactions.

The 4-hydroxy group in the ligand of the title complex forms a strong intermolecular hydrogen bond and a weak interaction with the Cu atom of a neighbouring cation. In metal complexes of the corresponding 2-hydroxy ligand it is also common for this potential donor not to coordinate strongly to the metal, but rather to form strong intramolecular hydrogen bonds. These compounds are usually mononuclear (Sur *et al.*, 1993; Tai *et al.*, 2007) (as shown in the scheme below), but one dinuclear uranium complex has been reported (Gatto *et al.*, 2004).



The IR spectrum of the free ligand shows a series of bands at *ca* 3210, 1670, 1602, 1543 and 1343 cm^{-1} due to υ_{N-H}, $\upsilon_{C=O}$, $\upsilon_{C=N}$, δ_{N-H} and υ_{C-N}, respectively. In (I), these bands appear at *ca* 3352, 1612, 1600, 1538 and 1326 cm^{-1}, respectively. The presence of υ_{N-H}, $\upsilon_{C=O}$ and δ_{N-H} in (I) indicates that the hydrazone molecule reacts in the keto–amine form. Moreover, the shift of both $\upsilon_{C=O}$ and $\upsilon_{C=N}$ to lower frequencies relative to the free ligand suggests that the ligand acts as a monoanionic *O*,*N*,*O*′-tridentate ligand (Iskander *et al.*, 2000*a*, 2004). On the other hand, the intense band at *ca* 1380 cm^{-1} is characteristic of the nitrate anion (Nakamoto, 1986). In addition, the existence of υ_{Cu-N} and υ_{Cu-O} at *ca* 630 and 436 cm^{-1}, respectively, further confirms the coordination of the metal with the hydroxy O atom and the amine N atom (Nakamoto, 1986).

These results indicate that the addition of hydroxy substituents to the benzoyl ring of the salicylaldehyde benzoylhydrazone ligand facilitates the ability of the ligand simultaneously to chelate and bridge metal ions and form strong hydrogen-bonding interactions, which results in coordination polymers and extended hydrogen-bonding networks.

Experimental

$Cu(NO_3)_2 \cdot 3H_2O$ (0.2 mmol, 48.4 mg) was added to an ethanol solution (20 ml) containing 4-hydroxy-*N*′-(2-hydroxybenzylidene)benzohydrazide (0.2 mmol, 51.2 mg). The resulting mixture was stirred for 1.5 h and then filtered. Dark-blue block-shaped crystals were obtained from the solution after two weeks.

Crystal data

$[Cu_2(C_{14}H_{11}N_2O_3)_2(H_2O)_2](NO_3)_2$
$M_r = 797.62$
Monoclinic, $C2/c$
$a = 13.815$ (8) Å
$b = 12.109$ (4) Å
$c = 18.787$ (8) Å
$\beta = 106.55$ (2)°
$V = 3013$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.50$ mm^{-1}
$T = 293$ (2) K
0.28 × 0.23 × 0.19 mm

Data collection

Rigaku Weissenberg IP diffractometer
Absorption correction: empirical (using intensity measurements) (*TEXRAY*; Molecular Structure Corporation, 1999)
$T_{min} = 0.668$, $T_{max} = 0.753$
14501 measured reflections
3442 independent reflections
2803 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.114$
$S = 1.09$
3442 reflections
242 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Atoms H11, H12, H3 and H2 were located in difference Fourier maps and were then included in the refinement with O—H distances restrained to 0.79 (2), 0.82 (2) and 0.74 (3) Å, respectively, and the N—H distance to 0.85 (2) Å. Other H atoms were positioned geometrically and treated as riding [C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$].

Data collection: *TEXRAY* (Molecular Structure Corporation, 1999); cell refinement: *TEXRAY*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *SHELXL97*.

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Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.928 (2)	Cu1—O1^i	1.9651 (17)
Cu1—O1	1.9400 (17)	Cu1—O1*W*	2.452 (3)
Cu1—O2	1.9606 (17)		
N1—Cu1—O1	91.36 (8)	O2—Cu1—O1^i	107.28 (7)
N1—Cu1—O2	80.94 (8)	N1—Cu1—O1*W*	99.49 (9)
O1—Cu1—O2	170.71 (8)	O1—Cu1—O1*W*	95.25 (8)
N1—Cu1—O1^i	171.36 (8)	O2—Cu1—O1*W*	91.18 (9)
O1—Cu1—O1^i	80.20 (7)	O1^i—Cu1—O1*W*	83.25 (8)

Symmetry code: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O1*W*^{ii}	0.74 (3)	2.03 (3)	2.764 (3)	174 (3)
N2—H2···O4^{iii}	0.851 (17)	1.998 (18)	2.847 (3)	175 (3)
O1*W*—H11···O5^{iv}	0.794 (18)	1.997 (19)	2.789 (4)	176 (3)
O1*W*—H12···O6^{v}	0.821 (18)	1.94 (2)	2.748 (3)	167 (4)

Symmetry codes: (ii) $x, -y, z+\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x, y, -z+\frac{1}{2}$; (v) $x, -y, z-\frac{1}{2}$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3086). Services for accessing these data are described at the back of the journal.

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