

## *cis*-Diaqua[*(E)*-2-(2-oxidobenzylidene-amino- $\kappa^2N,O$ )benzoato- $\kappa O$ ]-copper(II): tubes built from O—H...O hydrogen-bonding, $\pi$ – $\pi$ and C—H... $\pi$ interactions

 Li-Ping Lu,<sup>a</sup> Shu-Qin Yao<sup>a,b</sup> and Miao-Li Zhu<sup>a\*</sup>

<sup>a</sup>Institute of Molecular Science, Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry, Shanxi University, Taiyuan, Shanxi 030006, People's Republic of China, and <sup>b</sup>School of Chemistry and Materials Science, Shanxi Normal University, Linfen, Shanxi 041004, People's Republic of China  
Correspondence e-mail: miaoli@sxu.edu.cn

Received 17 March 2006

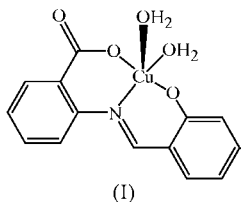
Accepted 11 April 2006

Online 29 April 2006

In the title compound,  $[\text{Cu}(\text{C}_{14}\text{H}_9\text{NO}_3)(\text{H}_2\text{O})_2]$ , pairs of complexes are linked into dimers by three O—H...O hydrogen bonds. Strong O—H...O hydrogen bonds link the dimers into one-dimensional chains that further assemble into tubes through  $\pi$ – $\pi$  and C—H... $\pi$  interactions.

### Comment

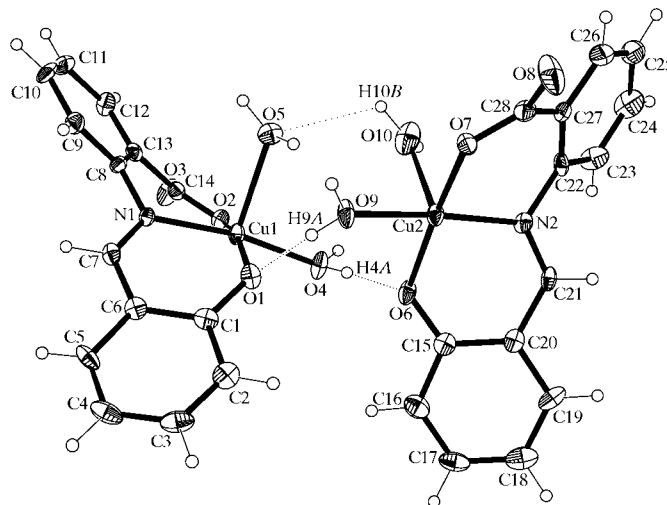
(*E*)-2-(2-Hydroxybenzylideneamino)benzoic acid is a tridentate ligand, many of whose metal complexes have been studied (Clague *et al.*, 1993; Asgedom *et al.*, 1997; Dey *et al.*, 1999; Redshaw & Elsegood, 2001; Rosair *et al.*, 2002; Shan *et al.*, 2003). As a result of our interest in Schiff base metal complexes as model compounds for the study of the active sites of metalloenzymes, we have investigated the title compound, (I), and we report its structure here.



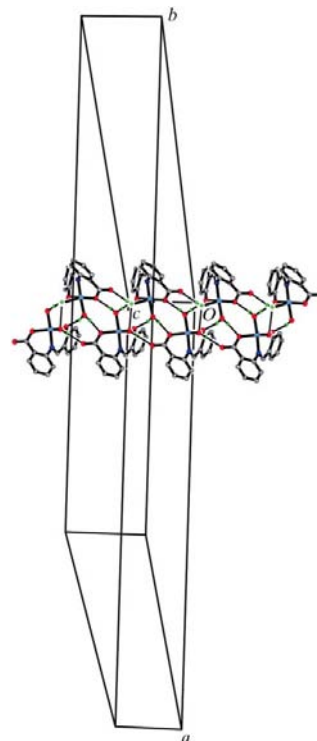
Compound (I) (Fig. 1) has two independent  $\text{Cu}(\text{C}_{14}\text{H}_9\text{NO}_3)$  complex molecules in the asymmetric unit. In each complex, the Cu atom is coordinated by one N and four O atoms from two water molecules and one (*E*)-2-(2-hydroxybenzylidene-amino)benzoic acid molecule, adopting a square-pyramidal geometry similar to that in  $[\text{Cu}(\text{C}_{14}\text{H}_9\text{NO}_3)(\text{C}_5\text{H}_5\text{N})_2]\cdot\text{H}_2\text{O}$  (Li *et al.*, 1995), but there the Cu atom is four-coordinate with a square geometry (Gao *et al.*, 2000). Although the two complex molecules in (I) have the same coordination environments, the corresponding bonds around atoms Cu1 and Cu2

are significantly different (Table 1), especially the Cu—O distances between the Cu atom and the apical water ligands. The two aryl rings in each complex make dihedral angles of 58.7 (2) and 58.4 (2)°. The two complexes are connected to each other by three strong O—H...O hydrogen bonds to form a dimer in which the Cu...Cu distance is 4.674 (1) Å.

The supramolecular interactions (Table 2) are illustrated in Figs. 2 and 3. Four intermolecular O—H...O hydrogen bonds, with two coordinated water molecules as hydrogen-bond



**Figure 1**  
The structure of (I), with displacement ellipsoids drawn at the 30% probability level for non-H atoms. Dotted lines indicate hydrogen bonds.



**Figure 2**  
The one-dimensional chain along the *c* axis, constructed from O—H...O hydrogen bonding.

donors and two carboxyl O atoms of the organic ligand as acceptors, link the dimers into one-dimensional chains along the *c* axis (Fig. 2). Because of the relatively strong intermolecular hydrogen bonding, neighbouring dimers are connected closely, the Cu1···Cu2(*x*, *y*, *z* + 1) separation being 5.304 (1) Å, leaving atoms Cu1 and Cu2 arranged in a zigzag shape in the chains. Six such chains, related to one another by a rotation of 60° in the (001) plane, are connected through  $\pi$ - $\pi$  stacking interactions between the C1-C6 and C15-C20 aryl rings, with Cg1···Cg2(*y*, -*x* + *y*, -*z* + 1) (Cg1 is the centroid of the C1-C6 ring and Cg2 is the centroid of the C15-C20 ring), Cg1···Cg2(*y*, -*x* + *y*, -*z* + 2), Cg2···Cg1(*x* - *y*, *x*, -*z* + 1) and Cg2···Cg1(*x* - *y*, *x*, -*z* + 2) distances of 3.677 (3),

3.548 (3), 3.677 (4) and 3.548 (4) Å, and interplanar spacings of 3.250, 3.263, 3.279 and 3.302 Å, respectively, assembling the six chains into a tube (Fig. 3). Additionally, a C-H··· $\pi$  interaction (Fig. 3*a*) between the C23-H23 group and the C8-C13 aryl ring (centroid Cg3) in a neighbouring chain, with a C23···Cg3(*x* - *y*, *x*, -*z* + 2) separation of 3.618 (9) Å, also takes part in the stabilization of the tubes.

Large voids in the structure were examined using *PLATON* (Spek, 2003). In the three-dimensional structure of (I), there are three channels along the *c* axis (Fig. 3), accounting in total for 1518.3 Å<sup>3</sup> per unit cell, *i.e.* some 11.4% of the total volume. The channels lie along a threefold inversion centre with an average cross-sectional area of *ca* 70.6 Å<sup>2</sup> and an average diameter of *ca* 9.5 Å. The channels in (I) appear to be occupied by water molecules; their behaviour is intractable, possibly due to dynamic disorder.

## Experimental

Compound (I) was synthesized by adding an ethanol solution (15 ml) of (*E*)-2-(2-hydroxybenzylideneamino)benzoic acid (0.120 g) to an aqueous solution (5 ml) of Cu(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O (0.102 g). The mixed solution was refluxed at 333 K for 2 h; the pH was then adjusted to 7 with 0.1 mol dm<sup>-3</sup> NaOH and the solution was filtered while it cooled to room temperature. Dark-blue needle-shaped crystals of (I) were obtained from the filtrate at room temperature after two weeks.

### Crystal data

[Cu(C<sub>14</sub>H<sub>9</sub>NO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>]  
*M<sub>r</sub>* = 338.81  
 Trigonal, *R* $\bar{3}$   
*a* = 46.263 (2) Å  
*c* = 7.2030 (7) Å  
*V* = 13350.9 (15) Å<sup>3</sup>  
*Z* = 36

*D<sub>x</sub>* = 1.517 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 $\mu$  = 1.49 mm<sup>-1</sup>  
*T* = 298 (2) K  
 Needles, dark-blue  
 0.24 × 0.09 × 0.01 mm

### Data collection

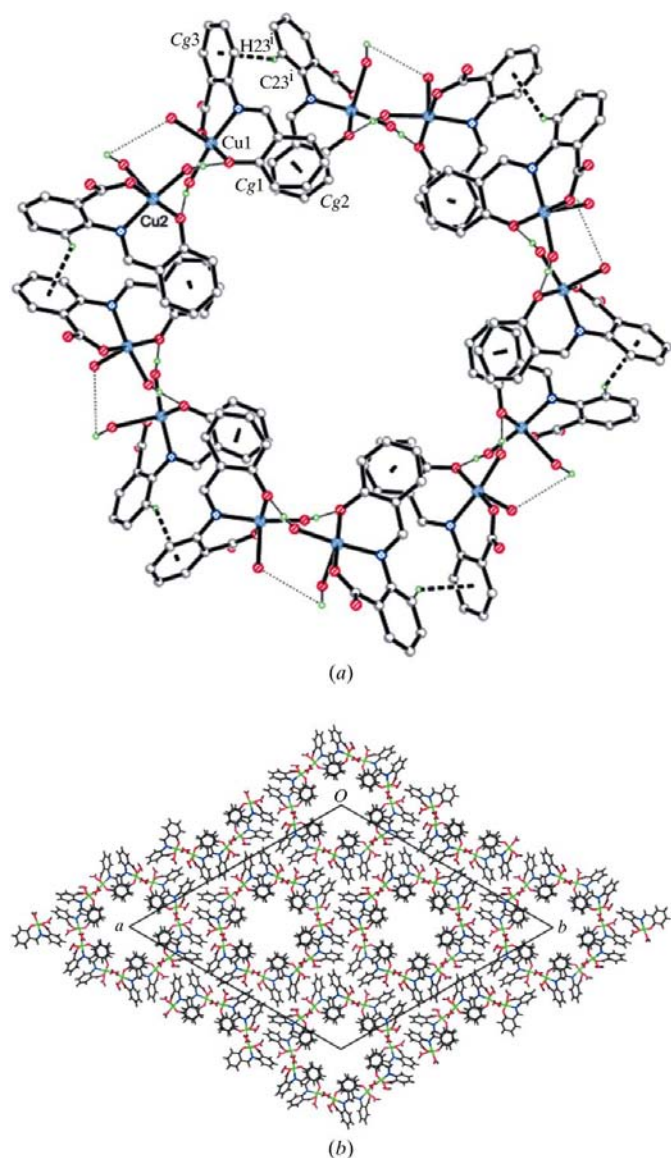
Bruker SMART 1K CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)  
*T<sub>min</sub>* = 0.715, *T<sub>max</sub>* = 0.985

5220 measured reflections  
 5220 independent reflections  
 3659 reflections with *I* > 2σ(*I*)  
 $\theta_{\max}$  = 25.0°

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.072  
*wR*(*F*<sup>2</sup>) = 0.160  
*S* = 1.04  
 5220 reflections  
 379 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2 + 7.9408P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.63 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.61 \text{ e } \text{Å}^{-3}$



**Figure 3**

(*a*) The six-membered ring built from  $\pi$ - $\pi$  stacking and C-H··· $\pi$  interactions (dashed lines), with centroid (0, 0, 0). Dotted lines indicate O-H···O interactions. H atoms not involved in hydrogen bonding have been omitted. [Symmetry code: (i) *y*, -*x* + *y*, -*z* + 2]. (*b*) An *ab* projection of the crystal structure of (I), showing the [001] channels.

H atoms attached to C atoms were placed in geometrically idealized positions, with C-H = 0.93 Å, and refined with *U*<sub>iso</sub>(H) values of 1.2*U*<sub>eq</sub>(C). H atoms attached to O atoms were located from difference Fourier maps and refined as riding in their as-found positions, with *U*<sub>iso</sub>(H) values of 1.2*U*<sub>eq</sub>(O). The O-H distances are in the range 0.82–0.91 Å. Examination of the refined structure using *PLATON* (Spek, 2003) revealed the presence of voids, having a total volume of 1518.3 Å<sup>3</sup> per unit cell, arranged into three channels along the *c* axis with their centres at approximately (0, 0, 0), ( $\frac{1}{3}$ ,  $\frac{2}{3}$ ,  $\frac{4}{5}$ ) and ( $\frac{2}{3}$ ,  $\frac{1}{3}$ ,  $\frac{1}{2}$ ). No electron density greater than 0.63 e Å<sup>-3</sup> could be found in

**Table 1**

Selected geometric parameters (Å, °).

Cu1—O1	1.919 (4)	Cu2—O6	1.909 (4)
Cu1—N1	1.952 (4)	Cu2—N2	1.938 (5)
Cu1—O2	1.957 (4)	Cu2—O9	1.944 (4)
Cu1—O4	1.967 (4)	Cu2—O7	1.955 (4)
Cu1—O5	2.290 (4)	Cu2—O10	2.559 (5)
Cu1—Cu2	4.674 (1)		
O1—Cu1—N1	91.36 (18)	O6—Cu2—N2	91.10 (19)
O1—Cu1—O2	163.21 (18)	O6—Cu2—O9	87.79 (17)
N1—Cu1—O2	90.52 (18)	N2—Cu2—O9	174.2 (2)
O1—Cu1—O4	87.33 (18)	O6—Cu2—O7	166.71 (19)
N1—Cu1—O4	170.10 (19)	N2—Cu2—O7	91.97 (18)
O2—Cu1—O4	87.96 (17)	O9—Cu2—O7	87.86 (17)
O1—Cu1—O5	95.59 (17)	O6—Cu2—O10	95.44 (17)
N1—Cu1—O5	93.28 (18)	N2—Cu2—O10	88.08 (18)
O2—Cu1—O5	100.96 (16)	O9—Cu2—O10	97.68 (17)
O4—Cu1—O5	96.62 (17)	O7—Cu2—O10	97.59 (16)

**Table 2**

Hydrogen-bond geometry (Å, °).

Cg3 is the centroid of the C8—C13 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O10—H10B $\cdots$ O5	0.87	2.40	2.882 (7)	115
O10—H10A $\cdots$ O8 <sup>ii</sup>	0.82	1.93	2.727 (6)	163
O9—H9B $\cdots$ O2 <sup>iii</sup>	0.85	1.97	2.813 (5)	174
O9—H9A $\cdots$ O1	0.85	1.84	2.667 (6)	166
O5—H5A $\cdots$ O3 <sup>iii</sup>	0.90	2.37	2.842 (6)	112
O4—H4B $\cdots$ O7 <sup>ii</sup>	0.85	1.99	2.814 (6)	161
O4—H4A $\cdots$ O6	0.85	1.86	2.711 (6)	177
C23—H23 $\cdots$ Cg3 <sup>iv</sup>	0.93	2.87	3.618 (9)	139

 Symmetry codes: (ii)  $x, y, z + 1$ ; (iii)  $x, y, z - 1$ ; (iv)  $x - y, x, -z + 2$ .

the area of the void and so no definitive solvent molecule could be found. Since the electron count per void is 51 from SQUEEZE results (PLATON; Spek, 2003) and, considering the symmetry of the voids, six water molecules per void may be reasonable; these voids are certainly large enough.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL/PC (Sheldrick, 1999); software used to prepare material for publication: SHELXTL/PC.

The authors acknowledge the National Natural Science Foundation of China (grant No. 20471033) and the Natural Science Foundation of Shanxi Province of China (grant No. 20051013) for financial support. The authors also appreciate the help given by Dr Anthony Linden (Institute of Organic Chemistry, University of Zurich, Switzerland).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3011). Services for accessing these data are described at the back of the journal.

## References

- Asgedom, G., Sreedhara, A. J., Kivikoski, J. & Rao, C. P. (1997). *Polyhedron*, **16**, 643–651.
- Bruker (2000). SMART (Version 5.0) and SAINT (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.
- Clague, M. J., Keder, N. L. & Butler, A. (1993). *Inorg. Chem.* **32**, 4754–4761.
- Dey, D. K., Saha, M. K., Gielen, M., Kemmer, M., Biesemans, M., Willem, R., Gramlich, V. & Mitra, S. (1999). *J. Organomet. Chem.* **590**, 88–92.
- Gao, S., Shi, Z., Hua, J., Feng, S.-H., Xu, R.-R., Liu, S.-X., Huo, L.-H. & Chen, P.-G. (2000). *Chem. J. Chin. Univ.* **21**, 177–180.
- Li, S.-L., Liu, D.-X., Meng, F.-Q., Zhou, J.-H. & Yang, Z.-H. (1995). *Chin. J. Struct. Chem.* **14**, 55–60.
- Redshaw, C. & Elsegood, M. R. J. (2001). *Chem. Commun.* pp. 2016–2017.
- Rosair, G. M., Dey, D. K., Samanta, B. & Mitra, S. (2002). *Acta Cryst.* **C58**, m266–m267.
- Shan, X., Ellern, A., Guzei, I. A. & Espenson, J. H. (2003). *Inorg. Chem.* **42**, 2362–2367.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Sheldrick, G. M. (1999). SHELXTL/PC. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2000). SADABS. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.