Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Di-μ-salicylato-$\kappa^4O:O'$-bis[(2,2′-bipyridine-κ^2N,N')-copper(II)] bis(salicylic acid)

Yue Wang[a] and Nobuo Okabe[b]*

[a]Laboratory of Inorganic Chemistry, China Pharmaceutical University, Nanjing 210009, China, and [b]Faculty of Pharmaceutical Sciences, Kinki University, Kowakae 3-4-1, Higashiosaka, Osaka 577-8502, Japan

Correspondence e-mail: okabe@phar.kindai.ac.jp

Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.005 Å
R factor = 0.044
wR factor = 0.131
Data-to-parameter ratio = 15.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 27 August 2004
Accepted 10 September 2004
Online 18 September 2004

The title complex, $[Cu_2(C_7H_4O_3)_2(C_{10}H_8N_2)_2]\cdot 2C_7H_6O_3$, crystallizes as a centrosymmetric dimer containing two Cu^{II} atoms bridged by two phenolato O atoms from salicylate ligands. Each Cu^{II} atom lies in an approximate square planar environment and is bonded to two N atoms of a 2,2′-bipyridine ligand, the phenolato O and the carboxylato O atoms of a salicylate ligand. The coordination of Cu^{II} is completed by bonding to a phenolato O atom in the axial direction, giving square pyramidal geometry. The dimer is stabilized by a strong intermolecular π–π interaction involving pairs of bipyridine ligands and a salicylate ring. The crystal structure is stabilized by π–π interactions and hydrogen bonds.

Comment

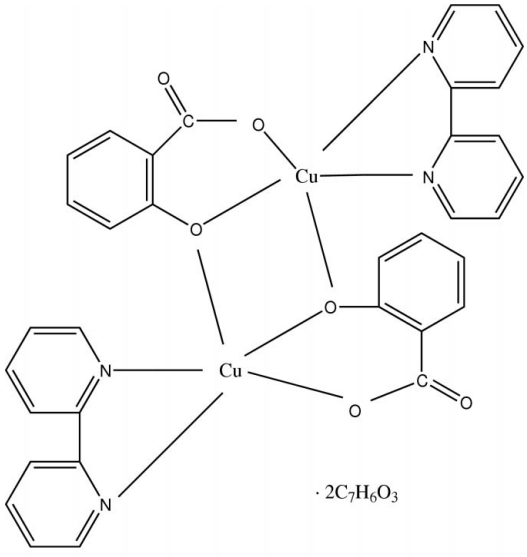
The biological activity of a wide variety of organic ligands is enhanced on coordination to copper (Mohindru *et al.*, 1983). It has been reported that the copper(II) complex of aspirin is more active as an anti-inflammatory agent than the free ligand (Korolkiewicz *et al.*, 1989). The pyridine adduct $[Cu_2(asp)_4(py)_2]$ (asp = aspirin) has been found to be an effective anti-inflammatory, anticancer and anticonvulsant agent (Brown *et al.*, 1980). In particular, copper complexes with salicylic acid or its derivatives show very important biological activities in addition to their role as an active ligands applied for the designed synthesis of bridged complexes. Bis(salicylato)copper(II) is an analgesic and anti-inflammatory agent (Jacka *et al.*, 1983); the complex of 3,5-diisopropylsalicylic acid also shows anti-inflammatory, antineoplastic and anticonvulsant activities (Sorenson, 1978). Many cytotoxicity and antiviral activities of salicylato–copper complexes have been summarized (Ranford *et al.*, 1993). A series of copper(II) complexes of salicylic acid and 4,4′-bipyridine in different solvent systems has been reported (Zhu *et al.*, 2003). It is well known that bipyridine has an important role in constructing various structural motifs. Different isomeric bipyridine molecules have different coordination properties, and we have chosen 2,2′-bipyridine combined with salicylic acid to prepare the dinuclear title copper(II) complex, (I).

The structure of complex (I) is shown in Fig. 1. Each copper(II) atom is coordinated by two N atoms from one 2,2′-bipyridine molecule, and by one carboxylate O atom and one phenolato O atom from one salicylate anion. Atoms N1, N2, O1 and O3 are nearly in a square planar arrangement, surrounding the central Cu^{II} atom. Selected geometric parameters are shown in Table 1. The phenolato O atom bridges to another Cu atom in an axial direction with a longer Cu—O bond [2.536 (2) Å], which may be explained by the well known Jahn–Teller effect. With this bridging phenolato O

atom, linking to a second [Cu(sal)(bipy)] unit of the dimer, the square pyramidal coordination of copper is completed, with the formation of a Cu_2O_2 parallelogram. The dimeric cation is centrosymmetric.

In the structure of (I), because of the proximity of the two N atoms in 2,2′-bipyridine, both of these are bonded to one Cu^{II}, with a slightly stronger interaction compared with that reported [Cu—N 2.133 (3) Å] in the related copper complex with 4,4′-bipyridine (Zhu *et al.*, 2003). In the latter, the two well separated N atoms are coordinated to two different Cu atoms and this generates a polymer; the carboxylate O atoms are also coordinated to copper, leaving the phenolato O atom uncoordinated, unlike the situation in (I). The two rings in the 2,2′-bipyridine ligand are a little twisted relative to each other, with a dihedral angle N1—C1—C6—N2 of −2.0 (4)°.

The title compound contains no solvent molecules, but an uncoordinated salicylic acid molecule is present in the asymmetric unit. A solvated form of the compound is also known, $[Cu_2(sal)_2(bipy)_2]\cdot 2C_2H_5OH\cdot 2H_2O$ (Geraghty *et al.*, 1999), in which the dimeric complex has a similar geometry.



(I)

One intermolecular hydrogen bond links the independent salicylic acid molecule to the neighbouring dimer, and there is also one intramolecular hydrogen bond (Table 2). The dimer is stabilized by a π–π interaction involving two 2,2′-bipyridines and one salicylate ligand, with an interplanar distance of 3.489 (8) Å. As shown in Fig. 2, the free salicylic acid ring also interacts with the (bipy)Cu chelate ring of the complex, with an interplanar distance of 3.322 (4) Å. The overall crystal packing is stabilized by these π–π interactions and the hydrogen bonds.

Experimental

Thin blue plate-shaped crystals of (I) were obtained by slow evaporation of an aqueous solution, containing a very small amount of methanol, of a mixture of salicylic acid, 2,2′-bipyridine and $CuCl_2\cdot 2H_2O$ (molar ratio 4:4:1) at room temperature.

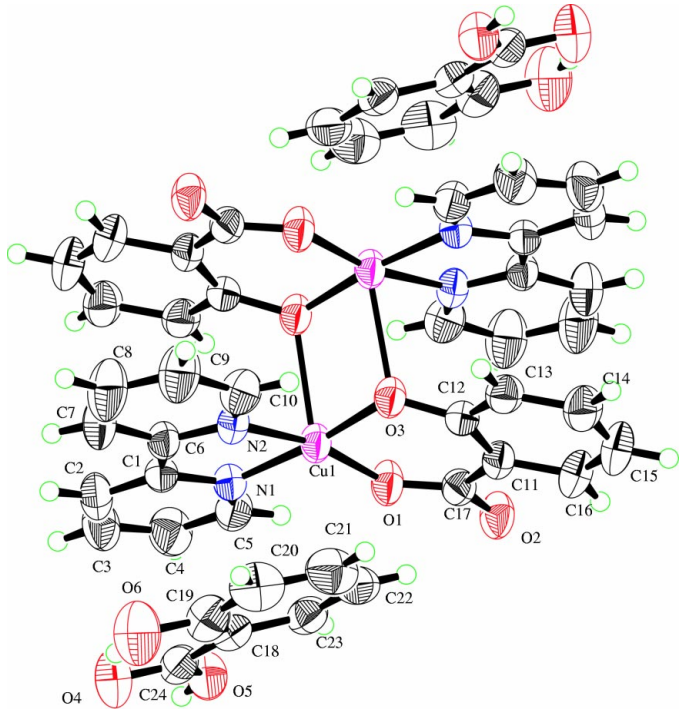


Figure 1
*ORTEP*3 (Farrugia, 1997) drawing of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

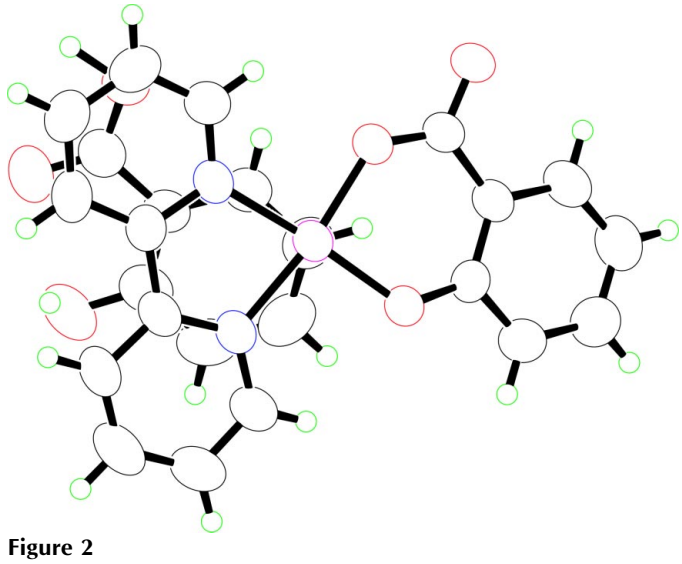


Figure 2
The overlap of stacked rings.

Crystal data

$[Cu_2(C_7H_4O_3)_2(C_{10}H_8N_2)_2]\cdot 2C_7H_6O_3$
M_r = 987.91
Monoclinic, $P2_1/a$
a = 10.46 (1) Å
b = 17.79 (2) Å
c = 12.04 (1) Å
β = 109.25 (4)°
V = 2115 (4) Å^3
Z = 2
D_x = 1.550 Mg m^{-3}
Mo Kα radiation
Cell parameters from 13777 reflections
θ = 3.1–27.4°
μ = 1.08 mm^{-1}
T = 296.1 K
Lath, blue
0.50 × 0.10 × 0.05 mm

Data collection

Rigaku R-AXIS RAPID diffractometer	4824 independent reflections
ω scans	2392 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$R_{int} = 0.034$
$T_{min} = 0.534$, $T_{max} = 0.948$	$\theta_{max} = 27.5^\circ$
20430 measured reflections	$h = -13 \rightarrow 13$
	$k = -23 \rightarrow 22$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + (0.0917P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.131$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.85$	$\Delta\rho_{max} = 1.08$ e Å^{-3}
4824 reflections	$\Delta\rho_{min} = -0.46$ e Å^{-3}
304 parameters	

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.906 (2)	Cu1—N2	2.002 (3)
Cu1—O3	1.882 (2)	Cu1—O3^{i}	2.536 (3)
Cu1—N1	1.991 (2)		
O1—Cu1—O3	93.27 (9)	O3—Cu1—N1	174.0 (1)
O1—Cu1—N1	91.8 (1)	O3—Cu1—N2	93.83 (9)
O1—Cu1—N2	167.8 (1)	N1—Cu1—N2	81.8 (1)

Symmetry code: (i) $2 - x, -y, 2 - z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H17···O4	0.80	1.86	2.574 (4)	149
O5—H18···O2^{ii}	0.84	1.69	2.514 (3)	165

Symmetry code: (ii) $1 - x, -y, 2 - z$.

The low precision of the cell parameters is due to poor crystal quality.

All H atoms were found in difference Fourier maps; all except those on OH groups were then adjusted to ideal geometry. They were refined with a riding model, with C—H = 0.93 Å and with U(H) = 1.2 times U_{eq} of the carrier atom.

The largest residual electron density lies close to the Cu atom.

Data collection: *CrystalStructure* (Rigaku & Rigaku/MSC, 2000–2004); cell refinement: *CrystalStructure*; data reduction: *CrystalStructure*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999) and *DIRDIF* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Beurskens, P. T., Beurskens, G., de Gelder, R., García-Granda, S., Gould, R. O., Israel, R. & Smits, J. M. M. (1999). *The DIRDIF-99 Program System*. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

Brown, D. H., Smith, W. E., Teape, J. W. & Lewis, A. J. (1980). *J. Med. Chem*, **23**, 729–734.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Geraghty, M., Sheridan, V., McCann, M., Devereux, M. & McKee, V. (1999). *Polyhedron*, **18**, 2931–2939.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Jacka, T., Bernard, C. C. A. & Singer, G. (1983). *Life Sci.* **32**, 1023–1030.

Korolkiewicz, Z., Hac, E., Gagalo, I., Gorczyca, P. & Lodzinska, A. (1989). *Agent Actions*, **26**, 355–359.

Mohindru, A., Fisher, J. M. & Rabinovitz, M. (1983). *Nature* (*London*), 303, 64–65.

Ranford, J. D., Sadler, P. J. & Tocher, D. A. (1993). *J. Chem. Soc. Dalton Trans*, pp. 3393–3399.

Rigaku & Rigaku/MSC (2000–2004). *CrystalStructure*. Version 3.6.0. Rigaku & Rigaku/MSC, 9009 New Trails Drive, Woodlands, Texas 77381, USA.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Sorenson, J. R. J. (1978). *Prog. Med. Chem*, **15**, 211–260.

Zhu, L. G., Kitagawa, S., Miyasaka, H. & Chang, H. C. (2003). *Inorg. Chim. Acta*, **355**, 121–126.