

S1—Cd1—S3	109.98 (4)	S3—Cd1—S2	153.93 (3)
S4—Cd1—S3	69.97 (3)	Cd1 ¹ —S2—Cd1	83.33 (3)
S2 ¹ —Cd1—S3	109.16 (4)		

Symmetry code: (i) 1 - x, 1 - y, -z.

All H atoms were located from a difference Fourier map and were refined isotropically.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXL93 and PARST (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1201). Services for accessing these data are described at the back of the journal.

References

- Casas, J. S., Sanchez, A., Bravo, J., Garcia-Fontan, S., Castellano, E. E. & Jones, M. M. (1989). *Inorg. Chim. Acta*, **158**, 119–126.
 Cherian, M. G. & Goyet, R. A. (1978). *Life Sci.* **23**, 1–9.
 Gale, G. R., Atkins, L. M., Walker, E. M., Smith, A. B. & Jones, M. M. (1984). *Ann. Clin. Lab. Sci.* **14**, 137–145.
 Iwasaki, H. & Kobayashi, K. (1980). *Acta Cryst.* **B36**, 1655–1657.
 Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
 Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
 Shinobu, L. A., Jones, S. G. & Jones, M. M. (1984). *Acta Pharmacol. Toxicol.* **54**, 189–194.
 Siemens (1994). *XSCANS User's Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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trans-Diaquabis(nicotinamide-*N*)bis(salicylate-*O*)copper(II)

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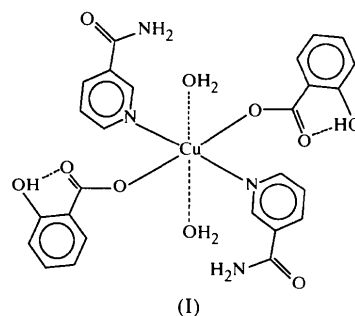
Abstract

The Cu^{II} atom in [Cu(C₇H₅O₃)₂(C₆H₆N₂O)₂(H₂O)₂] is octahedrally coordinated by N atoms from two nicotinamide ligands [at 2.018(2) and 2.019(2) Å], by O

atoms of two salicylate ligands [at 1.9656(19) and 1.9762(19) Å], and by *trans* water molecules at considerably different distances [2.373(3) and 2.894(4) Å]. Neutral monomeric units are held together by hydrogen bonds through water molecules and N and O atoms of the CONH₂ group of nicotinamide and carboxylate groups.

Comment

Crystals of the title compound, [Cu(sal)₂(nia)₂(H₂O)₂], (I), where sal is salicylate (2-hydroxybenzoate, C₇H₅O₃⁻) and nia is nicotinamide (C₆H₆N₂O), were isolated during systematic work on copper salicylates in our laboratory. The anhydrous form of [Cu(sal)₂(nia)₂] exists in both an orthorhombic (Hoang *et al.*, 1993) and a monoclinic form (Leban *et al.*, 1997). Recently, the crystal structure of *trans*-diaquabis(4-hydroxybenzoato-*O*)bis(nicotinamide-*N*)copper(II), with a short account of the structural chemistry and biological activity of these compounds, was also reported (Hökelek *et al.*, 1998). This compound is a crystallographically centrosymmetric complex in which two *trans* water molecules are located at 2.575(2) Å from the Cu^{II} atom.



In the majority of monomeric *trans*-diaquacopper(II) complexes, the Cu atom is located either at a centre of symmetry or on a twofold axis, so that the Cu—O distances are the same [a survey of the Cambridge Structural Database (Allen & Kennard, 1993) gave 29 hits]. There are only a few examples where the copper octahedral complex is not centrosymmetric and the water molecules are coordinated either at different distances [e.g. IMDZNB (Kozhemyak *et al.*, 1980) and VANCAO (Biagini Cingi *et al.*, 1989)] or the Cu—O distances are essentially the same [e.g. HEWVAG (Castro *et al.*, 1994) and YUDNAM (Schindler & Szalda, 1995)].

Whereas the complex *trans*-diaquabis(4-hydroxybenzoato-*O*)bis(nicotinamide-*N*)copper(II) is centrosymmetric, the title complex (Fig. 1) crystallizes in the non-centrosymmetric space group *P*2₁ and the distances Cu—OW1 [2.373(3) Å] and Cu—OW2 [2.894(4) Å] are significantly different. This is in accord with previous thermogravimetric data (Kozlevčar *et al.*, 1996),

where the weight loss at 453 K indicated the presence of only one loosely bound water molecule and the formula of the compound was erroneously given as $[\text{Cu}(\text{sal})_2(\text{nia})_2(\text{H}_2\text{O})]$. The elongation of the Cu—OW2 distance can be explained by the hydrogen-bonding scheme (Table 2). The water molecule OW1 is only involved in two weak intermolecular hydrogen bonds, but the water molecule OW2 is linked through three hydrogen bonds. Moreover, the overall coordination around copper is similar to that found in IMDZNB (Kozhemyak *et al.*, 1980), where the *trans* water molecules are coordinated to the Cu atom at distances of 2.295 and 2.612 Å.

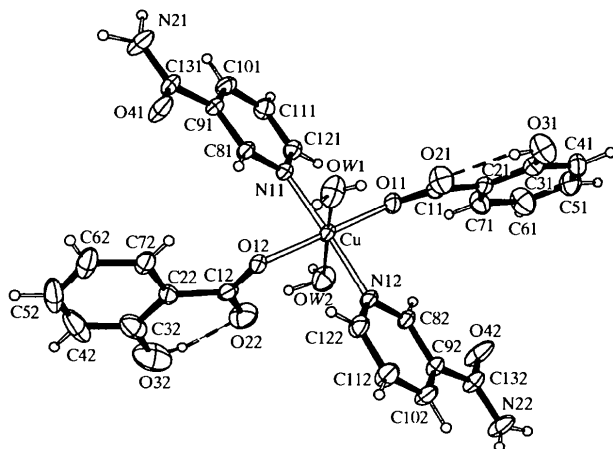


Fig. 1. The molecular structure of the title compound with the atomic numbering. Ellipsoids are drawn at the 30% probability level.

The geometries of the salicylate and nicotinamide ligands are normal and in agreement with the values found in the orthorhombic and monoclinic forms of bis(salicylate)bis(nicotinamide)copper(II), $[\text{Cu}(\text{sal})_2(\text{nia})_2]$ (Hoang *et al.*, 1993; Leban *et al.*, 1997). The interplanar angles between the carboxylate groups and benzene rings in salicylate are 5.8 (2) and 8.6 (2)°. The corresponding angles between the amide and pyridine parts of nicotinamide are 3.1 (3) and 2.4 (3)°, respectively. Whilst the two *trans* nicotinamide moieties are nearly parallel [interplanar angle 3.6 (2)°], there is a twist of 25.1 (1)° of one salicylate with respect to the other.

The neutral monomeric copper complex molecules of the title compound are linked together by hydrogen bonds (Table 2) through water molecules, and N and O atoms of CONH₂ of nicotinamide and carboxylate groups, forming sheets perpendicular to the *b* axis.

Experimental

$\text{Cu}(\text{sal})_2 \cdot 4\text{H}_2\text{O}$ (0.037 g, 0.09 mol) was dissolved in 15 ml of water with heating and stirring. This solution was added to

nicotinamide (0.022 g, 0.18 mol) dissolved in 2.5 ml of water. Deep-blue crystals were filtered off after a day at 279 K.

Crystal data

$[\text{Cu}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{C}_6\text{H}_6\text{N}_2\text{O})_2 \cdot (\text{H}_2\text{O})_2]$
 $M_r = 618.05$
 Monoclinic
 $P2_1$
 $a = 7.442$ (1) Å
 $b = 18.290$ (1) Å
 $c = 10.284$ (1) Å
 $\beta = 104.74$ (1)°
 $V = 1353.7$ (2) Å³
 $Z = 2$
 $D_x = 1.516$ Mg m⁻³
 $D_m = 1.52$ (5) Mg m⁻³
 D_m measured by flotation in chlorobenzene/ CCl_4

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 96 reflections
 $\theta = 10\text{--}17^\circ$
 $\mu = 0.871$ mm⁻¹
 $T = 293$ (2) K
 Plate
 $0.26 \times 0.13 \times 0.12$ mm
 Deep blue

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: by integration (ABSORP in NRCVAX; Gabe *et al.*, 1989)
 $T_{\min} = 0.637$, $T_{\max} = 0.812$
 12 907 measured reflections
 6468 independent reflections

5060 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$
 $\theta_{\max} = 27.90^\circ$
 $h = -9 \rightarrow 9$
 $k = -24 \rightarrow 24$
 $l = -13 \rightarrow 13$
 3 standard reflections every 600 reflections
 intensity decay: 2.5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.097$
 $S = 1.034$
 6468 reflections
 404 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0599P)^2 + 0.1633P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.076$
 $\Delta\rho_{\max} = 0.807$ e Å⁻³
 $\Delta\rho_{\min} = -0.662$ e Å⁻³

Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.0051 (13)
 Scattering factors from *International Tables for Crystallography* (Vol. C)
 Absolute structure: Flack (1983)
 Flack parameter = 0.45 (1)

Table 1. Selected geometric parameters (Å, °)

Cu—O11	1.9656 (19)	Cu—N11	2.019 (2)
Cu—O12	1.9762 (19)	Cu—OW1	2.373 (3)
Cu—N12	2.018 (2)	Cu—OW2	2.894 (4)
O11—Cu—O12	175.84 (10)	N12—Cu—OW1	93.71 (10)
O11—Cu—N12	90.87 (8)	N11—Cu—OW1	90.60 (10)
O12—Cu—N12	90.85 (8)	O11—Cu—OW2	80.70 (9)
O11—Cu—N11	90.45 (8)	O12—Cu—OW2	95.69 (10)
O12—Cu—N11	87.53 (8)	N12—Cu—OW2	84.99 (9)
N12—Cu—N11	175.25 (10)	N11—Cu—OW2	90.73 (9)
O11—Cu—OW1	98.73 (11)	OW1—Cu—OW2	178.56 (10)
O12—Cu—OW1	84.94 (11)		

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

D—H...A	D—H	H...A	D...A	D—H...A
OW1—H1...O21	0.75 (4)	2.37 (4)	2.836 (5)	122 (4)
OW1—H2...OW2 ⁱ	0.82 (5)	2.46 (6)	3.007 (5)	125 (5)
OW2—H3...O22	0.91 (4)	1.88 (4)	2.741 (5)	156 (4)
OW2—H4...O41 ⁱⁱ	0.81 (4)	2.13 (4)	2.895 (4)	157 (5)
O31—H31...O21	0.82	1.846	2.570 (4)	146.4
O32—H32...O22	0.82	1.848	2.559 (5)	144.2
N21—H211...O42 ⁱⁱⁱ	1.08 (5)	1.78 (5)	2.850 (5)	171 (4)
N21—H212...O21 ^{iv}	0.80 (3)	2.42 (4)	2.971 (4)	127 (4)
N22—H221...O41 ^v	0.94 (5)	2.04 (4)	2.974 (5)	173 (4)

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

Phenyl H atoms were made to ride on C atoms with $U(H) = 1.5U_{eq}(C)$. Hydroxy H atoms were also riding, but U_{iso} for these was refined freely as were coordinates and U_{iso} for amide and water H atoms. The absolute structure parameter indicates racemic twinning of the crystal.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1994). Cell refinement: *PARAM* in *XRAY76* (Stewart *et al.*, 1976). Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPII* (Johnson, 1971). Software used to prepare material for publication: *SHELX97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1276). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
- Biagini Cingi, M., Lanfredi, M. M., Tiripicchio, A., Haasnoot, J. G. & Reedijk, J. (1989). *Acta Cryst.* **C45**, 601–604.
- Castro, I., Sletten, J., Glaerum, L. K., Lloret, F., Faus, J. & Julve, M. (1994). *J. Chem. Soc. Dalton Trans.* pp. 2777–2782.
- Enraf-Nonius (1994). *CAD-4 Software*. Version 5.1. Enraf-Nonius, Delft, The Netherlands.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Hoang, N. N., Valach, F. & Melnik, M. (1993). *Z. Kristallogr.* **208**, 27–33.
- Hökelek, T., Budak, K., Şendil, K. & Necefoğlu, H. (1998). *Acta Cryst.* **C54**, 347–348.
- Johnson, C. K. (1971). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
- Kozhemyak, N. V., Podberezskaya, N. V. & Bakakin, V. V. (1980). *Zh. Strukt. Khim.* **21**, 124–128.
- Kozlevčar, B., Fajfar, S., Petrič, M., Pohleven, F. & Šegedin, P. (1996). *Acta Chim. Slov.* **43**, 385–395.
- Leban, I., Kozlevčar, B., Sieler, J. & Šegedin, P. (1997). *Acta Cryst.* **C53**, 1420–1422.
- Schindler, S. & Szalda, D. J. (1995). *Inorg. Chim. Acta*, **228**, 93–101.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). *The XRAY76 System*. Technical Report TR-446. Computer Science Center, University of Maryland, College Park, Maryland, USA.

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Pentaaqua(chelidonato-*O*⁴)copper(II) monohydrate

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Abstract

In crystals of pentaaqua(4-oxo-4*H*-pyran-2,6-dicarboxylato-*O*⁴)copper(II) hydrate, [Cu(C₇H₂O₆)(H₂O)₅].H₂O, the Cu^{II} cation is surrounded by an elongated O₆ octahedron. The chelidonate anion {chel, [C₅H₂O₂(COO)₂]²⁻} binds to the metal centre through the carbonyl rather than a carboxylate oxygen, and forms a long axial Cu—O bond [2.6746 (16) Å]. The axial Cu—O_{aq} bond is also relatively long [2.3763 (15) Å]. The molecular assembly in the crystal is stabilized by a complex three-dimensional network of intermolecular O—H...O bonds [O...O 2.597 (2)–2.851 (2) Å], the water molecules providing the donors, and the carboxylate and carbonyl groups of the chel ligand most of the acceptors, of the hydrogen bonding.

Comment

Dihydrodipicolinate synthase, a key enzyme in the biosynthesis of lysine *via* the diaminopimelate pathway (Borthwick *et al.*, 1995), can be inhibited by chelidonic acid [(I); 4-oxo-4*H*-pyran-2,6-dicarboxylic acid]. Our interest in interactions of this acid and its derivatives with water, which has led us to determine the crystal structure of the title compound, (II), stems from the mediating role of water in molecular recognition of enzymes and small-molecule inhibitors.

