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Bis(nicotinamide-*N*)bis(salicylato-*O,O'*)-copper(II), the Monoclinic Form

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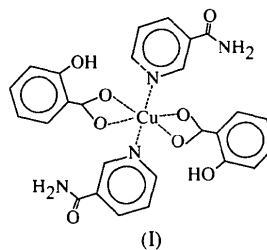
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Abstract

The monoclinic form of the title compound, [Cu(C₇H₅O₃)₂(C₆H₆N₂O)₂], was isolated during the systematic synthesis of copper salicylates. A distorted octahedral coordination around Cu^{II}, located on the centre of symmetry, is formed by four carboxylic O atoms from two salicylate ligands [Cu—O 1.928 (2) and 2.766 (2) Å] and by two N atoms from two nicotinamide groups [Cu—N 2.022 (2) Å]. Monomeric structural units are linked together *via* hydrogen bonds of the type N—H...O between the N and O atoms of the nicotinamide ligands.

Comment

The crystal structure of the orthorhombic form of the title compound, (I), [Cu(sal)₂(nia)₂] (where sal is salicylate, C₇H₅O₃[−], and nia is nicotinamide, C₆H₆N₂O), along with a survey of similar complexes have been reported previously by Hoang, Valach & Melnik (1993). The orthorhombic compound crystallizes in space group *Pbca* (No. 61) with four stoichiometric C₂₆H₂₂CuN₄O₈ moieties in the unit cell. The orthorhombic form was prepared from Cu(sal)₂·4H₂O and nicotinamide in methanol. The single crystals were obtained on cooling the mixture to 268 K for 24 h. However, monoclinic crystals precipitate from a mixture of acetonitrile and methanol solution of the same starting components at room temperature. The monoclinic crystals have a distinctly different powder-diffraction pattern compared with the orthorhombic crystals.



The monomeric monoclinic complex with the atomic numbering scheme and hydrogen bonding is depicted in Fig. 1. The distorted octahedral coordination around the Cu^{II} atom is formed by two O atoms from salicylate moieties and two pyridine N atoms of nicotinamide groups [at 1.928 (2) and 2.022 (2) Å, respectively] and by two O atoms from salicylate groups at a greater distance of 2.766 (2) Å. The overall coordination is nearly the same as found in the orthorhombic form (Hoang, Valach & Melnik, 1993) and is similar to that in bis(benzoato)bis(nicotinamide)copper(II) (Leban, Šegedin & Gruber, 1996). The corresponding values found in the orthorhombic form are: Cu—O1 1.935 (6), Cu—O2 2.609 (6) and Cu—N1 1.994 (7) Å. There exists significant elongation of the Cu—O2 bond lengths in the monoclinic form which could be attributed to the intramolecular hydrogen bond O2...H5—O3. However, in bis(benzoato)bis(nicotinamide)copper(II), the two Cu—O distances [2.180 (3) and 2.209 (3) Å] do not differ significantly.

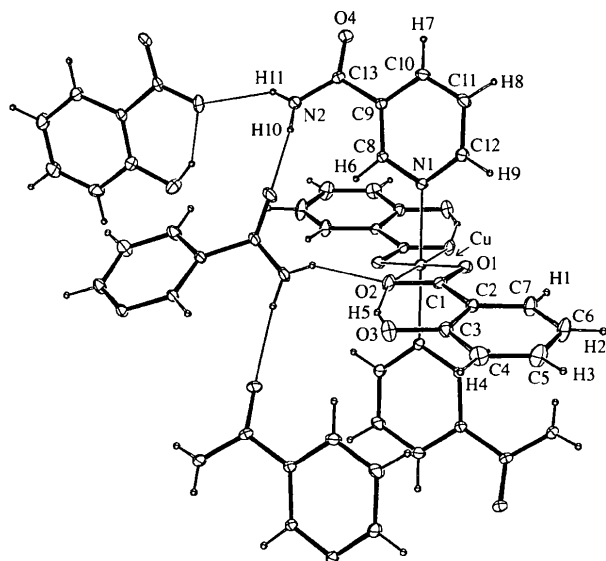


Fig. 1. ORTEP (Johnson, 1971) view of the molecular linking with the atomic numbering scheme. Anisotropic displacement ellipsoids for non-H atoms are drawn at the 20% probability level.

Although the packing mode of the centrosymmetric $[\text{Cu}(\text{sal})_2(\text{nia})_2]$ units in the monoclinic form is the same as in the orthorhombic form, there are subtle differences in the conformation of the complex molecule. The differences between the two forms were found to be particularly marked in the torsion angles: O1—Cu—N1—C8 27.8 (2), O2—Cu—N1—C8 80.0 (2), O1—C1—C2—C7 -1.8 (4), O2—C1—C2—C3 -2.4 (4) and C1—C2—C3—O3 3.5 (4)°, compared with the corresponding values of 36.8 (4), 92.1 (4), 4.6 (4), 5.5 (4) and -8.2 (4)°, respectively, found in the orthorhombic form. These values suggest a twist of the nicotinamide moi-

ety with respect to the $\text{Cu}(\text{sal})_2$ moiety and also a slight change in the interplanar angle between the planes defined by atoms O1, O2, C1, C2 (carboxylate group) and C2, C3, C4, C5, C6, C7 (benzene ring) is observed. The interplanar angle is 8.0 (3)° in the orthorhombic form and 4.7 (2)° in the monoclinic form.

Experimental

$\text{Cu}(\text{sal})_2 \cdot 4\text{H}_2\text{O}$ (0.80 g) was added to a mixture of 40 ml acetonitrile and methanol (5:1). The mixture was stirred for 15 min and filtered. The filtrate was added to a solution of nicotinamide (0.48 g) in 6 ml of the same solvent as above. Red-violet crystals were filtered after 6 d. Calculated for $[\text{Cu}(\text{sal})_2(\text{nia})_2]$: Cu 10.9, C 53.6, H 3.82, N 9.63%; found: Cu 11.2, C 53.3, H 3.40, N 9.43%. *d* spacings (Å), with relative intensities in parentheses (*I*/*I*₀): 8.7 (3), 7.6 (5), 7.4 (5), 7.15 (2), 5.88 (6), 4.40 (2), 4.35 (1), 4.22 (7), 3.73 (8), 3.68 (10). The powder pattern was obtained by Guinier de Wolf camera—II Enraf—Nonius (Cu *K*α radiation) (Kozlevčar, Fajfar, Petrič, Pohleven & Šegedin, 1996). The crystals were sealed in glass capillaries.

Crystal data

$[\text{Cu}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{C}_6\text{H}_6\text{N}_2\text{O})_2]$
 $M_r = 582.02$
 Monoclinic
 $P2_1/n$
 $a = 10.834$ (1) Å
 $b = 9.750$ (1) Å
 $c = 12.381$ (1) Å
 $\beta = 99.00$ (1)°
 $V = 1291.7$ (2) Å³
 $Z = 2$
 $D_x = 1.496$ Mg m⁻³
 $D_m = 1.49$ (5) Mg m⁻³
 D_m measured by flotation in hexane/ CCl_4

Mo *K*α radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 10$ –12°
 $\mu = 0.903$ mm⁻¹
 $T = 293$ (2) K
 Plate
 0.25 × 0.23 × 0.12 mm
 Red-violet

Data collection

Nonius CAD-4 diffractometer
 Variable rate $\theta/2\theta$ scans
 Absorption correction: none
 5720 measured reflections
 2337 independent reflections
 2003 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 26.25^\circ$
 $h = -13 \rightarrow 8$
 $k = -11 \rightarrow 11$
 $l = -14 \rightarrow 15$
 3 standard reflections
 frequency: 180 min
 intensity decay: 2.0%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.081$
 $S = 1.088$
 2337 reflections
 222 parameters
 All H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.0183P)^2 + 1.2159P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.272$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.244$ e Å⁻³
 Extinction correction: none
 Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U _{eq}
Cu	0	0	1/2	0.03582 (14)
O1	-0.1718 (2)	-0.0327 (2)	0.5160 (2)	0.0454 (5)
O2	-0.0870 (2)	-0.1477 (2)	0.6634 (2)	0.0567 (5)
O3	-0.2191 (2)	-0.3281 (3)	0.7476 (2)	0.0686 (7)
C1	-0.1792 (2)	-0.1181 (3)	0.5926 (2)	0.0410 (6)
C2	-0.3009 (2)	-0.1887 (3)	0.5925 (2)	0.0382 (6)
C3	-0.3136 (3)	-0.2918 (3)	0.6677 (2)	0.0455 (6)
C4	-0.4260 (3)	-0.3623 (4)	0.6614 (3)	0.0629 (9)
C5	-0.5240 (3)	-0.3293 (4)	0.5827 (3)	0.0741 (11)
C6	-0.5141 (3)	-0.2266 (5)	0.5084 (3)	0.0761 (12)
C7	-0.4025 (3)	-0.1582 (4)	0.5129 (3)	0.0556 (8)
O4	-0.2272 (2)	-0.5680 (2)	0.2826 (2)	0.0694 (7)
N1	0.0096 (2)	-0.1893 (2)	0.4352 (2)	0.0376 (5)
N2	-0.3092 (2)	-0.3592 (3)	0.2452 (2)	0.0556 (7)
C8	-0.0945 (2)	-0.2486 (2)	0.3817 (2)	0.0353 (6)
C9	-0.0969 (2)	-0.3783 (2)	0.3381 (2)	0.0375 (6)
C10	0.0139 (3)	-0.4515 (3)	0.3506 (3)	0.0554 (8)
C11	0.1216 (3)	-0.3913 (3)	0.4036 (3)	0.0615 (9)
C12	0.1156 (3)	-0.2616 (3)	0.4449 (3)	0.0488 (7)
C13	-0.2169 (3)	-0.4432 (3)	0.2852 (2)	0.0457 (7)

Table 2. Selected geometric parameters (Å, °)

Cu—O1	1.928 (2)	O3—C3	1.354 (3)
Cu—N1	2.022 (2)	C1—C2	1.487 (3)
Cu—O2	2.766 (2)	O4—C13	1.222 (3)
O1—C1	1.275 (3)	N2—C13	1.327 (4)
O2—C1	1.255 (3)	C9—C13	1.500 (3)
O1—Cu—N1	90.01 (8)	O3—C3—C4	117.8 (3)
O1—Cu—O2	52.72 (7)	O3—C3—C2	122.4 (3)
N1—Cu—O2	81.91 (7)	C8—C9—C13	121.4 (2)
O2—C1—O1	122.3 (2)	C10—C9—C13	120.6 (2)
O2—C1—C2	120.2 (3)	O4—C13—N2	122.9 (3)
O1—C1—C2	117.4 (2)	O4—C13—C9	120.1 (3)
C7—C2—C1	120.3 (2)	N2—C13—C9	117.0 (2)
C3—C2—C1	120.9 (2)		

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
N2—H10...O4 ⁱ	0.83 (3)	2.07 (3)	2.895 (3)	173 (3)
N2—H11...O2 ⁱⁱ	0.80 (3)	2.30 (3)	3.022 (3)	150 (3)
O3—H5...O2	0.87 (4)	1.79 (4)	2.588 (3)	151 (3)

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

The space group $P2_1/n$ was deduced from the systematic absences. All H atoms were found in the difference electron-density map and their positional and isotropic displacement parameters were fully refined. Final difference electron-density map revealed a maximum and minimum at 0.272 and $-0.244 \text{ e } \text{Å}^{-3}$, respectively. Calculations were performed on the standard PC 486/16MB.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1971) and *PLUTON* (Spek, 1991). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1233). Services for accessing these data are described at the back of the journal.

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Diaquabis(dimethyl 3-oxopentanedioato-O¹,O³)zinc(II)

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Abstract

The molecular structure of the title compound, [Zn(C₇H₉O₅)₂(H₂O)₂], shows the Zn atom coordinated by two monoanionic bidentate enolate ligands and two O atoms of water resulting in a pseudo-octahedral arrangement. The H atoms of the water molecules are oriented in such a way that one H atom forms an intramolecular hydrogen bond [H6B...O2(-x, -y, -z)], while the other H atom forms an intermolecular hydrogen bond [H6A...O3(1-x, -y, -z)]. The intermolecular contacts link the molecules into stacks.

Comment

We have shown that esters of 3-oxopentanedioic acid RCH₂COCH₂R, (2), react with carbonate complexes