

Jan Moncol,^{a*} Zuzana
Půčeková,^a Tadeusz Lis^b and
Dušan Valigura^a^aDepartment of Inorganic Chemistry, Slovak
Technical University, Radlinského 9, SK-812 37,
Bratislava, Slovakia, and ^bFaculty of Chemistry,
University of Wrocław, 14 Joliot-Curie St., 50-
383 Wrocław, Poland

Correspondence e-mail: jan.moncol@stuba.sk

Key indicators

Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.032
 wR factor = 0.083
Data-to-parameter ratio = 24.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.An enriched hydrogen-bond system in
trans-diaquabis(*N,N*-diethylnicotinamide- κN)-
bis(3-methoxysalicylato- κO)copper(II)
dihydrate

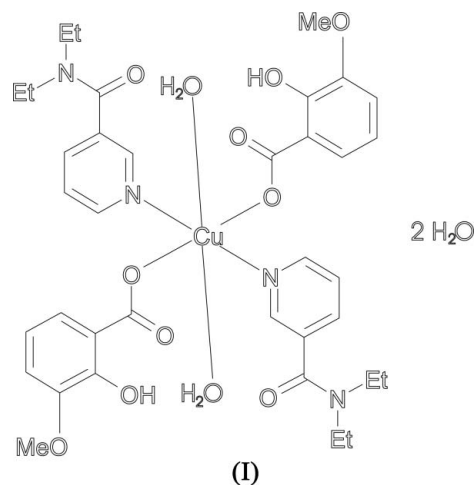
In the molecule of the title compound, $[\text{Cu}(\text{C}_8\text{H}_7\text{O}_4)_2(\text{C}_{10}\text{H}_{14}\text{N}_2\text{O})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, the Cu^{2+} cation lies on an inversion centre. It is coordinated by two pairs of O atoms of 3-methoxysalicylate anions and water molecules, and one pair of pyridine N atoms of *N,N*-diethylnicotinamide ligands, forming a tetragonal-bipyramidal coordination polyhedron. The two water molecules of solvation are linked to the complex molecule by $\text{O}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds. A $\pi-\pi$ stacking interaction is also observed between symmetry-related pyridine rings.

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Comment

The title compound, (I), was prepared as part of studies of the coordination chemistry of the *N,N*-diethylnicotinamide ligand. It exhibits a centre of symmetry and the coordination polyhedron around the Cu atom is an elongated tetragonal bipyramid (Fig. 1). The tetragonal plane is built up by a pair of monodentate 3-methoxysalicylate anions using carboxyl O atoms and by a pair of neutral *N,N*-diethylnicotinamide molecules using pyridine ring N atoms, in *trans* positions. The axial positions are occupied by water molecules (Table 1).



The coordinated water H atoms are linked to the uncoordinated carboxyl O4 atoms of the 3-methoxysalicylate anions by $\text{O1}-\text{H2O} \cdots \text{O4}$ intramolecular hydrogen bonds (Table 2), creating six-membered metallocyclic rings. $\text{O5}-\text{H5O} \cdots \text{O4}$ intramolecular hydrogen bonds, including hydroxyl H atoms and the uncoordinated carboxyl O4 atoms of the 3-methoxysalicylate anions (Table 2), likewise form six-membered rings, thus stabilizing the molecular structure.

The uncoordinated water molecules are linked to the $[\text{Cu}(3\text{-MeOsal})_2(\text{denia})_2(\text{H}_2\text{O})_2]$ molecule [where 3-MeOsal is the 3-

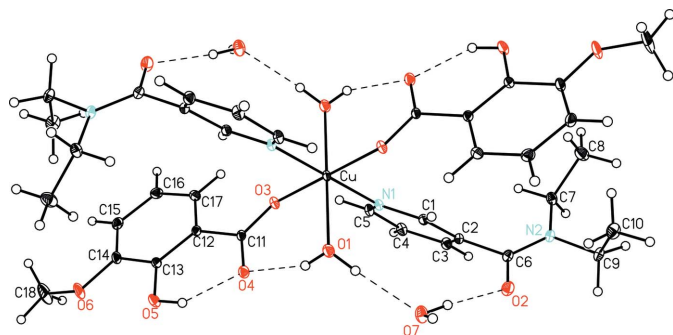


Figure 1

Perspective view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines.

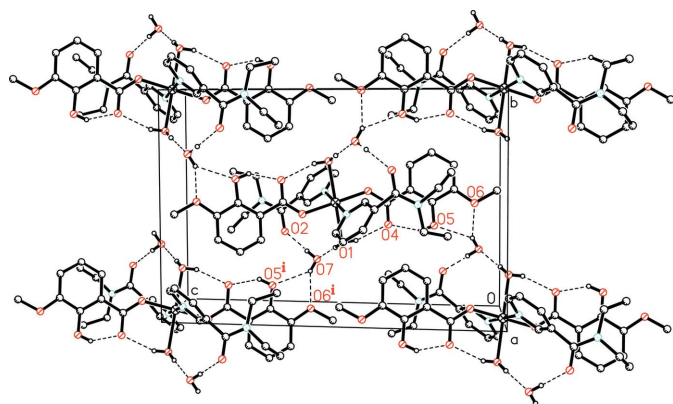


Figure 2

The crystal packing of (I), viewed along the *a* axis. Dashed lines indicate O—H...O hydrogen bonds. H atoms not involved in hydrogen bonds have been omitted.

methoxysalicylate anion ($C_8H_7O_4^-$) and denia is *N,N*-diethylnicotinamide ($C_{10}H_{14}N_2O$) by strong intermolecular hydrogen bonds (Table 2), which form two-dimensional sheets parallel to the (011) plane (Fig. 2). The H atoms of the coordinated water molecules are connected to O7 atoms of the uncoordinated water molecules by O1—H1O...O7 intermolecular hydrogen bonds (Table 2). One of the uncoordinated water H atom is linked to carboxamide atom O2 of the *N,N*-diethylnicotinamide by an O7—H3O...O2 intermolecular hydrogen bond (Table 2). The other uncoordinated water H atom is linked to hydroxyl atom O5¹ as well as to methoxy atom O6¹ of the 3-methoxysalicylate anion in the neighbouring structural unit [symmetry code: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$; Table 2]. The two-dimensional sheets are linked by very weak C3—H3...O4 and C4—H4...O7 intermolecular hydrogen bonds (Table 2). The additional interactions are π – π stacking interactions (Janiak, 2000) between the two symmetry-related adjacent pyridine rings, N1/C1–C5 (Φ) (at x, y, z and $2 - x, 1 - y, 1 - z$), of *N,N*-diethylnicotinamide molecules (Fig. 3) [centroid...centroid distance = 3.76 Å, distance between the two planes is 3.55 Å].

The structure of (I) can be compared with other complexes having the general formula $[CuX_2(\text{denia})_2(H_2O)_2]$, where *X* is mefenamate (Melník *et al.*, 1998), flufenamate (Melník *et al.*, 1996), 2-chloronicotinate (Moncol *et al.*, 2002) and 4-nitro-

benzoate (Hökelek *et al.*, 1997). This class of compounds displays monomeric structures with axially elongated tetragonal bipyramidal geometry about each Cu^{II} atom of the CuO_4N_2 chromophore, commensurate with Jahn–Teller distortion. The Cu—O_{eq} (O atom of carboxylate group), Cu—N_{eq} (N atom of pyridine ring of *N,N*-diethylnicotinamide) and Cu—O_{ax} (O atom of coordinated water) bonds are 1.936 (3), 2.027 (3) and 2.557 (3) Å for mefenamate; 1.961 (2), 2.001 (2) and 2.449 (4) Å for flufenamate; 1.965 (2), 2.015 (2) and 2.503 (2) Å for 2-chloronicotinate; and 1.959 (2), 2.019 (2) and 2.485 (2) Å for 4-nitrobenzoate. The corresponding bonds in (I) are consistent with these values.

The above-mentioned structures exhibit also a very similar hydrogen-bond system involving an intramolecular hydrogen bond of one water molecule H atom to a carboxylate O atom and an intermolecular bond of the other water molecule H atom to a neighbouring carboxamide O atom. Thus the uncoordinated water molecules within (I) have enriched the hydrogen-bond system.

Experimental

N,N-Diethylnicotinamide (2 mmol) was added to a stirred aqueous solution (20 ml) of copper(II) acetate (1 mmol). After several minutes, 3-methoxysalicylic acid (2 mmol) was added to the dark-blue solution. The reaction mixture was stirred for 5 d; after this time the light-green product was filtered off, washed with water and dried in air. Crystals of (I), suitable for X-ray analysis, were obtained from the mother liquor after slow room-temperature crystallization (yield 0.75 g, 91%; m.p. 357.6–358.6 K).

Crystal data

$[Cu(C_8H_7O_4)_2(C_{10}H_{14}N_2O)_2 \cdot (H_2O)_2] \cdot 2H_2O$
 $M_r = 826.35$
 Monoclinic, $P2_1/c$
 $a = 8.544$ (2) Å
 $b = 12.558$ (3) Å
 $c = 18.617$ (5) Å
 $\beta = 96.63$ (3)°
 $V = 1984.2$ (9) Å³
 $Z = 2$

$D_x = 1.383$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 22467 reflections
 $\theta = 2.9$ – 32.0°
 $\mu = 0.62$ mm⁻¹
 $T = 100$ (2) K
 Block, green
 $0.50 \times 0.45 \times 0.25$ mm

Data collection

Kuma KM-4 CCD diffractometer
 ω scans
 Absorption correction: analytical [CrysAlis RED (Oxford Diffraction, 2003); analytical numeric absorption using a multifaceted crystal model based on expressions derived by Clark & Reid (1995)]
 $T_{\min} = 0.756$, $T_{\max} = 0.867$

25778 measured reflections
 6589 independent reflections
 5512 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\max} = 32.0^\circ$
 $h = -12 \rightarrow 12$
 $k = -18 \rightarrow 17$
 $l = -23 \rightarrow 27$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.083$
 $S = 1.06$
 6589 reflections
 266 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 0.2889P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.45$ e Å⁻³
 $\Delta\rho_{\min} = -0.44$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu—O3	1.9821 (9)	Cu—O1	2.4169 (10)
Cu—N1	2.0191 (10)		
O3—Cu—N1	89.74 (4)	N1—Cu—O1	92.84 (3)
O3—Cu—O1	95.24 (3)		
C7—N2—C6—O2	−178.12 (10)	C6—N2—C7—C8	126.30 (12)
C1—C2—C6—O2	55.43 (14)	C9—N2—C7—C8	−53.54 (13)
C3—C2—C6—O2	−119.95 (12)	C18—O6—C14—C13	−167.14 (12)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H5O...O4	0.84	1.83	2.564 (1)	145
O1—H2O...O4	0.84 (1)	2.01 (2)	2.803 (1)	157 (2)
O1—H1O...O7	0.84 (1)	2.01 (2)	2.851 (1)	176 (2)
O7—H3O...O2	0.84 (2)	2.02 (1)	2.856 (1)	174 (2)
O7—H4O...O6 ⁱ	0.84 (1)	2.20 (1)	2.961 (1)	151 (2)
O7—H4O...O5 ⁱ	0.84 (1)	2.33 (2)	3.009 (1)	139 (2)
C3—H3...O4 ⁱⁱ	0.95	2.51	3.444 (2)	167
C4—H4...O7 ⁱⁱ	0.95	2.39	3.298 (2)	159

Symmetry codes: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $-x + 2, -y + 1, -z + 1$.

The water H atoms were located in a difference map and their positional parameters were refined, while their displacement parameters were fixed at 0.063 \AA^2 . The remaining H atoms were positioned with O—H = 0.84 Å for hydroxyl H atoms and C—H = 0.95, 0.98 and 0.99 Å for aromatic and methine, methyl, and methylene H atoms, respectively, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C}, \text{O})$, where $x = 1.5$ for methyl and hydroxyl H atoms, and $x = 1.2$ for all other H atoms.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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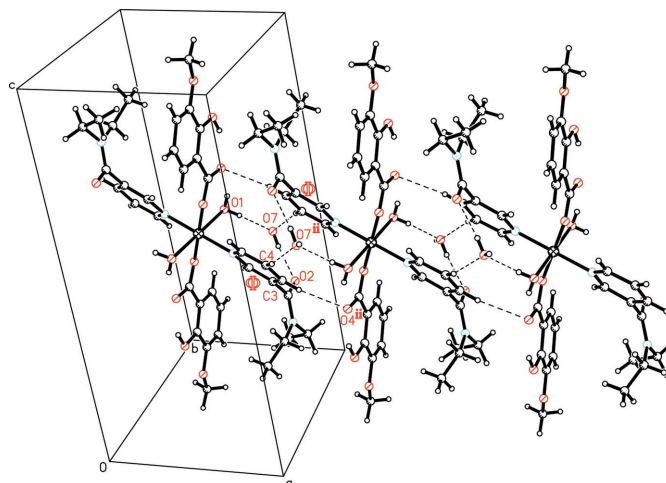


Figure 3

The hydrogen bonds (dashed lines) and π – π stacking interactions in the packing diagram of (I).

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