μ-Pyrazine-N:N′-bis[aqua(N-salicylidene-glycinato-O,N,O′)copper(II)] Dihydrate

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(I)

Abstract

The title compound, $[Cu_2(C_9H_7NO_3)_2(\mu\text{-}C_4H_4N_2)(H_2O)_2]\cdot 2H_2O$, adopts a square-pyramidal copper(II) coordination with three donor atoms of the N-salicylideneglycinato Schiff base dianion and one N atom of the pyrazine ligand bound in the basal plane. The axial position is occupied by a water O atom at a distance of 2.436 (2) Å. The molecules are connected through the second N atom of the pyrazine to form binuclear copper units. The water molecules form a hydrogen-bonding network between the dicopper molecules.

Comment

Recently, we reported the polymeric structure of *catena*-poly[[(N-salicylideneglycinato)copper(II)-μ-pyrazine-(N-salicylideneglycinato)copper(II)]-μ-1,4-dioxane] (Warda, 1998), which crystallizes from a 1:2 dioxane–water mixture. The reaction also takes place in water, giving a new copper(II) complex of this series with an increased **g** value [electron paramagnetic resonance (EPR) result] compared with the **g** tensor of the dioxane compound. We present here the aqua product, μ-pyrazine-N:N′-bis[aqua(N-salicylideneglycinato-O,N,O′)copper(II)] dihydrate, (I).
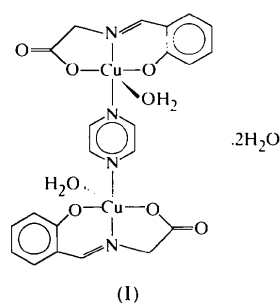
The Cu^{II} atoms adopt (4+1) square-pyramidal geometry, with three donor atoms of the tridentate (TSB-type) N-salicylideneglycinato dianion (ONO^{2-} chelator) and one N atom of the pyrazine (pzn) ligand in the basal plane. The apical coordination site is occupied by a water O atom at a distance of 2.436 (2) Å. The Cu atom is displaced from the basal plane by 0.120 (1) Å towards the apical ligand.

The pyrazine ring lies on an inversion centre and is inclined with respect to the basal plane (through atoms O1, O2, N1 and N2) at an angle of 11.1 (2)° (*PLATON*; Spek, 1994); it acts as a bidentate ligand joining two Cu–TSB–H$_2$O molecules to form pzn(H$_2$O–Cu–TSB)$_2$, with a Cu—N2 distance of 2.043 (2) Å (Fig. 1).

The water molecules (coordinated and uncoordinated) adapt the function of the dioxane ring in the structure mentioned above. The H atoms of two coordinated water molecules (H41—O4—H42) form an eight-membered ring (Fig. 2) across an inversion centre with two non-coordinated water molecules (O5) (see Table 2). These water rings are connected through atom H51 to the O3 atom of a neighbouring molecule (at $2-x, \frac{1}{2}+y, \frac{1}{2}-z$); a three-dimensional network results. Within the formula unit, there is an interaction between atoms H52 and O1.

The capacity for bonding of copper is essentially constant and is redistributed between equatorial and apical distances, as is nicely reflected by the aver-
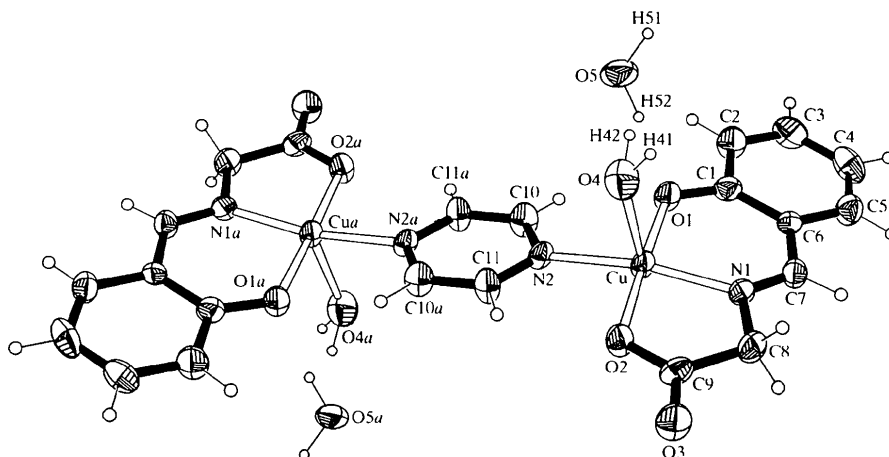

Fig. 1. The title compound with the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitary size. Atom labels appended by *a* are related by the symmetry operation $1-x, 1-y, -z$.
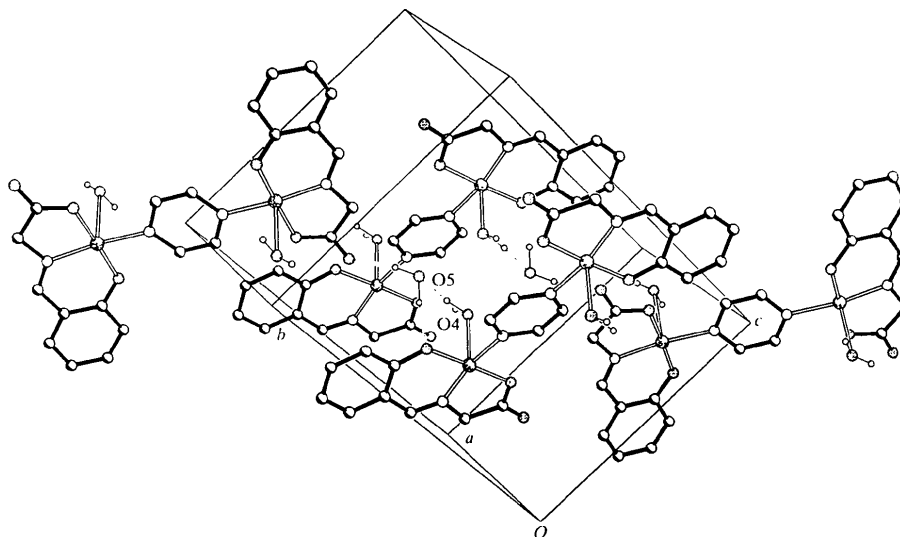
Fig. 2. Packing diagram of the title compound showing hydrogen bonds (narrow lines).

aged metal–ligand bond lengths [dioxane compound: 2.058 (2) Å, resulting from Cu—O1 1.892 (2), Cu—O2 1.936 (2), Cu—N1 1.920 (2), Cu—N2 2.032 (2) and Cu—O4 2.510 (2) Å; title compound: 2.054 (2) Å].

The difference between equatorial and apical bond lengths is also reflected by the EPR spectra; the averaged **g** tensor is significantly increased for the title compound compared with the dioxane compound, consistent with the significant shortening of the apical distance [2.436 (2) versus 2.510 (2) Å for the dioxane compound]. The **g** tensor of the title compound is coupled. The extended structure consists of parallel stacked copper(II) polyhedra, but the molecular axes, i.e. N1—Cu—N2 and O1—Cu—O2, are tilted at angles of 2ξ = 40.8 (5) and 35.5 (5)°, respectively, to those of another complex molecule at x, $\frac{3}{2} - y$, $-\frac{1}{2} + z$. The Cu···Cu distance between these magnetically inequivalent paramagnetic centres is 8.0523 (8) Å (PLATON; Spek, 1994), which is within the **g** tensor coupling range for these complexes (Warda, 1997).

Experimental

Compound (I) was synthesized from aqua(N-salicylideneglycinato)copper(II) hemihydrate according to the methods of Ueki et al. (1967) and Warda (1994), with pyrazine in water at 343 K. Dark-green crystals appeared within a few days.

Crystal data

[Cu$_2$(C$_9$H$_7$NO$_3$)$_2$(C$_4$H$_4$N$_2$)- (H$_2$O)$_2$].2H$_2$O
M_r = 633.54
Monoclinic
$P2_1/c$
a = 7.1135 (7) Å
b = 16.1388 (16) Å
c = 10.9876 (10) Å
β = 99.439 (11)°
V = 1244.3 (2) Å^3
Z = 2
D_x = 1.691 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 5000 reflections
θ = 2.26–25.96°
μ = 1.773 mm^{-1}
T = 240 (2) K
Prism
0.37 × 0.09 × 0.04 mm
Dark green

Data collection

Stoe IPDS diffractometer
Image plate scans
Absorption correction:
  by integration (XPREP in SHELXTL; Siemens, 1996b)
T_{min} = 0.545, T_{max} = 0.861
10 621 measured reflections
2410 independent reflections

1950 reflections with $I > 2\sigma(I)$
R_{int} = 0.089
θ_{max} = 25.96°
$h = -8 \rightarrow 8$
$k = -19 \rightarrow 19$
$l = -13 \rightarrow 13$
Intensity deacy: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.073
S = 0.972
2410 reflections
184 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.273 e Å^{-3}
$\Delta\rho_{min}$ = -0.451 e Å^{-3}
Extinction correction: none
Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu—O1	1.9117 (15)	Cu—N2	2.0425 (18)
Cu—N1	1.9197 (18)	Cu—O4	2.4361 (19)
Cu—O2	1.9593 (15)		
O1—Cu—N1	93.23 (7)	O2—Cu—N2	91.95 (7)
O1—Cu—O2	177.93 (7)	O1—Cu—O4	94.85 (7)

N1—Cu—O2	84.79 (7)	N1—Cu—O4	101.42 (7)
O1—Cu—N2	89.85 (7)	O2—Cu—O4	86.12 (7)
N1—Cu—N2	166.44 (7)	N2—Cu—O4	91.46 (7)

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H41···O5	0.89 (3)	2.04 (3)	2.855 (3)	153 (3)
O4—H42···O5ⁱ	0.89 (3)	1.94 (3)	2.821 (3)	167 (3)
O5—H51···O3ⁱⁱ	0.89 (3)	1.85 (3)	2.733 (3)	171 (3)
O5—H52···O1	0.89 (3)	1.89 (3)	2.757 (3)	165 (3)

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

All H atoms, except water H atoms, were included at calculated positions using *SHELXL97* (Sheldrick, 1997a) and were refined using a riding model. The U_{iso} value for H atoms of CH and CH₂ groups were taken as $1.2U_{eq}$ of the parent atoms. Atoms H41, H42, H51 and H52 were found from difference Fourier syntheses and refined with $U_{iso} = 1.2U_{eq}$ of the water O atom; O—H distances were restrained equal. An analytical absorption correction based on face indexing was carried out with the following faces and distances (mm): 0$\bar{1}$0 0.0385, 010 0.0385, 0$\bar{1}$1 0.3465, 01$\bar{1}$ 0.3850, $\bar{1}$00 0.0192 and 100 0.1540. The fraction of unique reflections measured to the 2θ value of 51° was 99.0%.

Data collection: *EXPOSE* (Stoe, 1997b). Cell refinement: *CELL* (Stoe, 1997a). Data reduction: *INTEGRATE* (Stoe, 1997c). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *XP* in *SHELXTL* (Siemens, 1996a). Software used to prepare material for publication: *SHELXL97*.

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References

Sheldrick, G. M. (1997a). *SHELXL97. Release 97-2. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1997b). *SHELXS97. Release 97-1. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Siemens (1996a). *XP* in *SHELXTL. Molecular Graphics Program*. Version 5.06. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996b). *XPREP* in *SHELXTL. Program for Data Preparation and Reciprocal Space Exploration*. Version 5.05. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (1994). *PLATON. Molecular Geometry Program*. University of Utrecht, The Netherlands.
Stoe (1997a). *CELL. Program for Cell Refinement*. Version 2.79. Stoe IPDS, Darmstadt, Germany.
Stoe (1997b). *EXPOSE. Stoe IPDS Software for Data Collection*. Version 2.79. Stoe IPDS, Darmstadt, Germany.
Stoe (1997c). *INTEGRATE. Program for Reduction of IPDS Data*. Version 2.79. Stoe IPDS, Darmstadt, Germany.
Ueki, T., Ashida, T., Sasada, Y. & Kakudo, M. (1967). *Acta Cryst.* **22**, 870–878.
Warda, S. A. (1994). In *Bioanorganische Kupfer(II) Komplexe mit dreizähnigen O,N,O-Chelat-Dianionen und additiven einzähnigen Donorliganden*. Aachen: Verlag Shaker.
Warda, S. A. (1997). *Acta Cryst.* **C53**, 1590–1593.
Warda, S. A. (1998). *Acta Cryst.* **C54**, 189–191.

Magnesium Sulfate Hexaurea Hemihydrate

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Abstract

The structure of the title compound, hexakis(urea-O)magnesium sulfate hemihydrate, [Mg(CH₄N₂O)₆]SO₄.0.5H₂O, consists of a regular arrangement of [Mg(CH₄N₂O)₆]²⁺ cations, SO₄²⁻ anions and water molecules, held together by an extensive network of hydrogen bonds. The Mg atoms are octahedrally coordinated by urea O atoms. The N1—C—O—Mg torsion angles are between −5.1 (5) and −30.5 (5)°.

Comment

Recently, the preparation and crystal structure of a new urea adduct of magnesium sulfate, MgSO₄.4CH₄N₂O.H₂O, were reported by Todorov et al. (1998a). We have now established an adduct of higher urea content, MgSO₄.6CH₄N₂O.0.5H₂O, (I). Formally, these are compounds from the ternary system MgSO₄–urea–H₂O. Sulaimankoulov (1971) has studied the solubility diagram of this system and reported only the compound MgSO₄.CH₄N₂.3H₂O. Numerous attempts to isolate this latter compound, as well as adducts with other sulfate–urea ratios, have been unsuccessful.

(I)
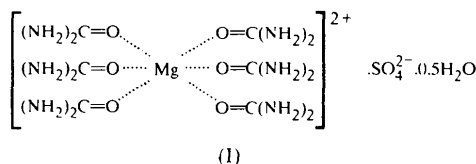
Our interest in adducts from the MgSO₄–urea–H₂O system was prompted by their presence as by-products during the development of a novel method for the