

A novel helical copper complex: *catena*-poly[[[aquacopper(II)]- μ -*N*-(3-carboxy-2-oxidobenzylidene- κ O²)glycinato- κ^3 N,O':O'] monohydrate]

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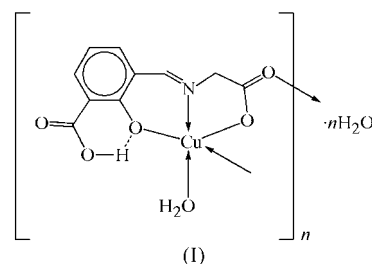
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In the polymeric title compound, $\{[\text{Cu}(\text{C}_{10}\text{H}_7\text{NO}_5)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$, the Cu atom adopts a square-based pyramidal coordination involving a *N,O,O'*-tridentate glycine dianionic ligand, a water O atom and an apical bridging carboxylate O atom from an adjacent ligand. The title compound also adopts a carboxylate-bridged chain structure. The molecular chain propagates in a helical fashion along the *b* axis of the monoclinic unit cell. Neighbouring chains are linked together to form a three-dimensional network *via* hydrogen-bonding interactions between coordinated and uncoordinated water molecules and O atoms of the bridging carboxylate groups.

Comment

Metal-organic frameworks (MOF), which consist of metal ions and organic molecules, have attracted considerable attention in recent decades due to their rich structural chemistry and potential applications. To date, a large number of architectures for MOFs have been reported, including helical, zigzag chain, honeycomb, square grid, ladder, brick wall and diamondoid (Peng *et al.*, 2003; Wang *et al.*, 2007). Among these architectures, helical structures have received extraordinary attention, because helicity is an essential feature of living systems and is also important in ligand exchange, asymmetric catalysis, chiral synthesis, nonlinear optical devices and magnetic materials (Cui *et al.*, 2003). Many single, double and higher-order stranded helical complexes have been synthesized by self-assembly processes (Chen & Liu, 2002; Qi *et al.*, 2003), in particular, metal ion-directed polynuclear helical complexes of well designed ligands. These facts have provided an important impetus for the creation of artificial helical structures.

Aminophenol-containing Schiff base ligands are a unique type of ligand showing flexible coordination modes and are well known as excellent building blocks for hydrogen-bonded networks. Some helical complexes with Schiff base ligands derived from amino acids have been reported (Ranford *et al.*, 1999; Erxleben, 2001). We therefore expected them to be good chiral building blocks for supramolecular assembly. Glycine Schiff base ligands are particularly fascinating, due to their extra β -carboxyl group possessing a bridging capability. They can connect metal ions in different directions, so are excellent candidates for the design and construction of chiral coordination polymers. We focused our attention on the assembly of transition metal ions with these flexible ligands. One helical structure of the ligand 3-carboxysalicylideneglycinate has been reported recently (Cai *et al.*, 2006). As an extension of our work on these complexes, we report here the preparation and crystal structure characterization of the title helical coordination polymer, (I).



In the crystal structure of complex (I), there is one Cu^{II} atom, one 3-carboxysalicylideneglycinate anion, one coordinated water molecule and one solvent water molecule in the asymmetric unit. Each Cu^{II} atom adopts a square-based pyramidal geometry. The four basal coordination sites are filled by the imine N atom, the phenolate O atom, one carboxylate O atom of the Schiff base ligand and one O atom of the coordinated water molecule, while the apical site is occupied by one carboxylate O atom from an adjacent ligand. Due to the Jahn–Teller effect, the pendant carboxylate O

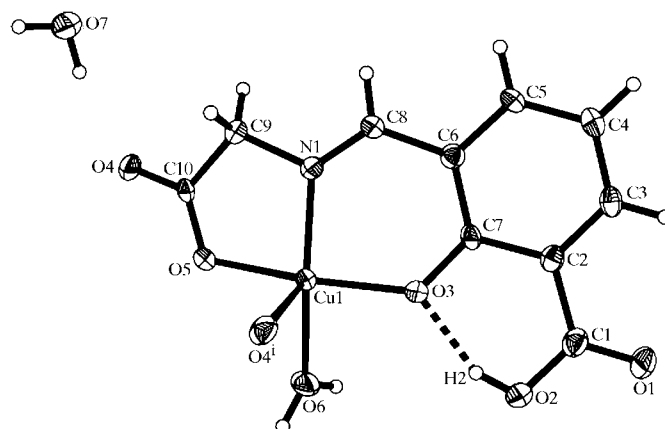


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line indicates the intramolecular hydrogen bond. [Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.]

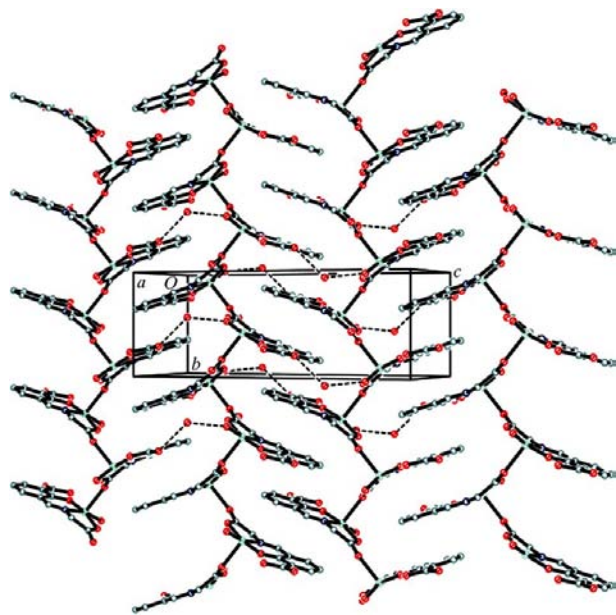


Figure 2
The crystal packing of the one-dimensional helical chains in (I). H atoms and cyclic fragments have been omitted for clarity. Hydrogen bonds are shown as dashed lines.

atoms have weak bonding interactions with the Cu^{II} atom [$\text{Cu1}-\text{O4}^{\text{i}} = 2.253(4) \text{ \AA}$; symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$]. However, this bond is somewhat shorter than that in the unsubstituted compound [$2.420(2) \text{ \AA}$; Butcher *et al.*, 2003]. The Cu–N and other Cu–O bond lengths (Table 1) are comparable with the corresponding values observed in other Schiff base–copper(II) complexes (Reddy *et al.*, 2000; Valent *et al.*, 2002). It is worthy of mention that the remaining protonated carboxyl group does not participate in coordination, but is involved in hydrogen bonding.

In complex (I), each pair of adjacent Cu^{II} atoms is bridged by the carboxylate group of the ligand to form a chiral helical chain running along a crystallographic 2_1 axis in the b direction, with a pitch of 6.968 \AA and decorated with the ligands alternately on two sides, while the benzene rings of the ligands on each side of the helix are arranged in a parallel fashion.

There are some intra- and intermolecular hydrogen bonds in (I). The acidic H atom forms a strong intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond with the phenolate O atom [$\text{O}\cdots\text{O} = 2.465(5) \text{ \AA}$]. Intermolecular hydrogen bonds are formed between the carboxylate and carboxyl O atoms (O4 and O1) of the ligand and the coordinated and uncoordinated O atoms of the water molecules, with distances of approximately $2.619(7)$ – $2.842(7) \text{ \AA}$ (Table 2). The chains are connected *via* these bonds to form a three-dimensional network.

Experimental

3-Carboxysalicylaldehyde (2 mmol, 0.336 g), glycine (2 mmol, 0.150 g) and potassium hydroxide (2 mmol, 0.112 g) were dissolved in 80% aqueous methanol (30 ml). To this clear yellow solution was added an aqueous solution (10 ml) of copper(II) sulfate pentahydrate (2 mmol, 0.50 g). The solution was kept at 323 K for 7 h and then

filtered. Green crystals of (I) were separated from the solution after two weeks in *ca* 46% yield. Elemental analysis found: C 37.46, H 3.47, N 4.36%; calculated for $\text{C}_{10}\text{H}_{11}\text{CuNO}_7$: C 37.45, H 3.46, N 4.37%.

Crystal data

$[\text{Cu}(\text{C}_{10}\text{H}_7\text{NO}_5)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$	$V = 1127.3(4) \text{ \AA}^3$
$M_r = 320.75$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 8.314(2) \text{ \AA}$	$\mu = 1.97 \text{ mm}^{-1}$
$b = 6.968(2) \text{ \AA}$	$T = 293(2) \text{ K}$
$c = 19.460(2) \text{ \AA}$	$0.40 \times 0.20 \times 0.15 \text{ mm}$
$\beta = 90.645(5)^\circ$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	5984 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2414 independent reflections
$T_{\text{min}} = 0.630, T_{\text{max}} = 0.744$	2057 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	H atoms refined by a mixture of independent and constrained refinement
$wR(F^2) = 0.134$	$\Delta\rho_{\text{max}} = 0.57 \text{ e \AA}^{-3}$
$S = 1.15$	$\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$
2414 reflections	
173 parameters	

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Cu1–N1	1.923(4)	Cu1–O5	1.959(3)
Cu1–O3	1.925(3)	Cu1–O6	1.968(4)
Cu1–O4 ⁱ	2.253(4)		
N1–Cu1–O3	92.17(14)	O3–Cu1–O5	167.97(14)
N1–Cu1–O4 ⁱ	106.14(14)	O3–Cu1–O6	88.10(15)
N1–Cu1–O5	84.49(14)	O5–Cu1–O4 ⁱ	96.59(15)
N1–Cu1–O6	164.82(16)	O5–Cu1–O6	92.12(15)
O3–Cu1–O4 ⁱ	95.43(15)	O6–Cu1–O4 ⁱ	88.93(15)

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

Table 2

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O2}-\text{H2}\cdots\text{O3}$	0.82	1.70	2.465(5)	153
$\text{O6}-\text{H6A}\cdots\text{O1}^{\text{ii}}$	0.84(6)	1.99(3)	2.803(6)	160(6)
$\text{O6}-\text{H6B}\cdots\text{O7}^{\text{iii}}$	0.84(5)	1.86(4)	2.619(7)	150(7)
$\text{O7}-\text{H7A}\cdots\text{O4}$	0.85(4)	1.92(2)	2.758(6)	167(8)
$\text{O7}-\text{H7B}\cdots\text{O1}^{\text{iv}}$	0.85(5)	2.15(7)	2.842(7)	138(9)

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

Water H atoms were located in a difference Fourier map and refined with $\text{O}-\text{H}$ distance restraints of $0.85(1) \text{ \AA}$, and with $U_{\text{iso}}(\text{H})$ values of $1.5U_{\text{eq}}(\text{O})$. The carboxyl H atom was placed in a calculated position, with $\text{O}-\text{H} = 0.82 \text{ \AA}$, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. All other H atoms were placed in calculated positions, with $\text{C}-\text{H} = 0.93$ – 0.97 \AA , and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3081). Services for accessing these data are described at the back of the journal.

References

- Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). *SMART* (Version 6.36a) and *SAINT* (Version 6.36a). Bruker AXS Inc., Madison, Wisconsin, USA.
- Butcher, R. J., Mockler, G. M. & McKern, O. (2003). *Acta Cryst.* **E59**, m1104–m1106.
- Cai, J.-H., Huang, Y.-H., Jiang, Y.-M. & Ng, S. W. (2006). *Acta Cryst.* **E62**, m2823–m2825.
- Chen, X. M. & Liu, G. F. (2002). *Chem. Eur. J.* **8**, 4811–4816.
- Cui, Y., Lee, S. J. & Lin, W. B. (2003). *J. Am. Chem. Soc.* **125**, 6014–6015.
- Erxleben, A. (2001). *Inorg. Chem.* **40**, 2928–2931.
- Peng, R., Wu, T. & Li, D. (2003). *CrystEngComm*, **7**, 595–598.
- Qi, Y. J., Wang, Y. H., Hu, C. W., Cao, M. H., Mao, L. & Wang, E. B. (2003). *Inorg. Chem.* **42**, 8519–8523.
- Ranford, J. D., Vittal, J. J., Wu, D. & Yang, X. (1999). *Angew. Chem. Int. Ed.* **23**, 3498–3501.
- Reddy, P. A. N., Datta, R. & Chakravaty, A. R. (2000). *Inorg. Chem. Commun.* **3**, 322–324.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Valent, A., Melnik, M., Hudcová, D., Dudová, B., Kivekas, R. & Sundberg, M. R. (2002). *Inorg. Chim. Acta*, **340**, 15–20.
- Wang, H. S., Ma, J. G., Zhai, B., Liu, Y. Y. & Cheng, P. (2007). *J. Mol. Struct.* **829**, 1–7.