

The chiral helical structure of a copper(II) complex with a tridentate Schiff base ligand

Wen-Juan Shi

Jiangxi Key Laboratory of Surface Engineering, Jiangxi Science and Technology Normal University, Jiangxi 330013, People's Republic of China
Correspondence e-mail: swjuan2000@126.com

Received 8 June 2009

Accepted 2 July 2009

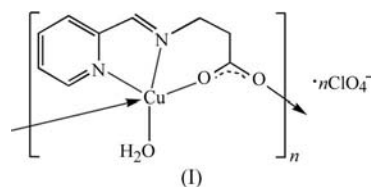
Online 9 July 2009

In the title salt, *catena*-poly[[[aquacopper(II)]- μ -3-(2-pyridylmethyleneamino)propanoato- $\kappa^4 N, N', O: O'$] perchlorate], $\{[\text{Cu}(\text{C}_9\text{H}_9\text{N}_2\text{O}_2)(\text{H}_2\text{O})]\text{ClO}_4\}_n$, the monomeric unit contains a square-based pyramidal Cu^{II} centre. The four basal positions are occupied by a tridentate anionic Schiff base ligand which furnishes an NNO-donor set, with the fourth basal position being occupied by an O-donor atom from the carboxylate group of an adjacent Schiff base ligand. The coordination sphere is completed by a water molecule at the apical position. Interestingly, each carboxylate group in the ligand forms a *syn-anti*-configured bridge between two Cu^{II} centres, leading to left-handed chiral helicity. The framework also exhibits $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonds involving the water molecules and an O atom of the perchlorate anion.

Comment

Well defined chiral metal complexes and metal-containing helical species have attracted much interest in coordination chemistry and materials science (Albrecht, 2001; Erxleben, 2001; Ezuhara *et al.*, 1999) due to their importance in biological systems, asymmetric catalysis, enantioselective separation and nonlinear optical material. The design and synthesis of chiral helical structures are challenging because the chirality must be achieved in the extended crystal structure (Coronado *et al.*, 2003; Imai *et al.*, 2004). In most cases, self-assembly of metal ions and multidentate ligands results in the formation of covalently bonded single-, double-, triple- and even quadruple-stranded metal helicates (Lehn, 1995; Piguet *et al.*, 1997; Williams, 1997), in which left- and right-handed helical chains alternate in the lattices, resulting in optically inactive racemic crystals. However, metal-containing chiral helical complexes derived from achiral ligands have received less attention (Biradha *et al.*, 1999; Colacio *et al.*, 1992; Studer *et al.*, 1989). We report here the preparation of a novel chiral single-stranded helical Cu^{II} coordination polymer, (I), using a tridentate Schiff base carboxylate-containing ligand derived

from the condensation of pyridine-2-carbaldehyde with β -alanine.



The structure of (I) consists of helical chains of $\{[\text{Cu}(\text{C}_9\text{H}_9\text{N}_2\text{O}_2)(\text{H}_2\text{O})]^+\}_n$ and of ClO_4^- anions, as shown in Fig. 1. The copper(II) complex exhibits a CuN_2O_3 square-based pyramidal coordination environment, with the three donor atoms of the ligand and one O atom belonging to the carboxylate group of an adjacent molecule occupying the four basal positions, while an O atom from a water molecule coordinates in the apical position. The Cu atom is displaced by 0.149 (2) Å from the mean basal plane towards the axial donor. Each carboxylate group bridges two Cu^{II} ions in a *syn-anti* fashion: the intrachain $\text{Cu} \cdots \text{Cu}$ distance is 4.938 (1) Å and left-handed chiral helices run parallel to the crystallographic *a* axis (Fig. 2). While the $\text{Cu1} \cdots \text{O1}$ distance of 1.959 (4) Å is comparable to the commonly observed bond lengths between bridging carboxylate O and Cu^{II} (Colacio *et al.*, 2000; Studer *et al.*, 1989), the $\text{Cu1} \cdots \text{O1W}$ distance is somewhat longer. The shortest $\text{Cu} \cdots \text{O}$ distance between Cu^{II} ions and ClO_4^- anions [$\text{Cu1} \cdots \text{O6} = 3.305$ (2) Å] indicates that such contacts are not significant. One water H atom (H1WB) participates in an intrachain $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bond with the carboxylate O1 atom [$\text{O1W} \cdots \text{O1} = 2.730$ (6) Å, $\text{H1WB} \cdots \text{O1} = 2.12$ Å and $\text{O1W} \cdots \text{H1WB} \cdots \text{O1} = 129^\circ$], but there are no significant hydrogen-bonding contacts between the helical chains due to the nearest interchain separation of 2.85 Å [$\text{H8B} \cdots \text{C3}^i$; symmetry code: (i) $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$]

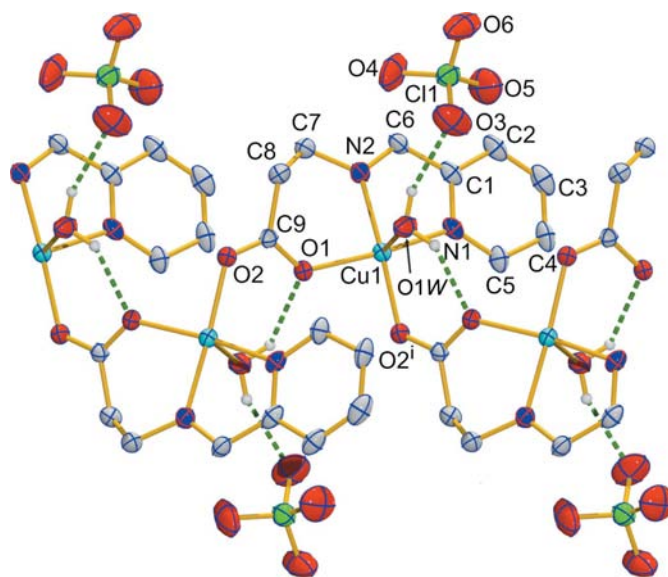
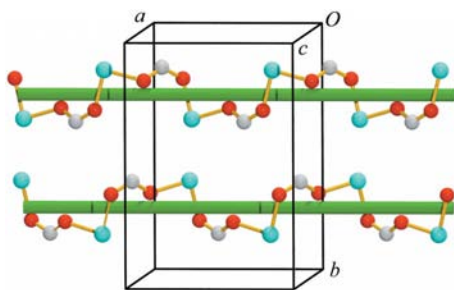


Figure 1
A view of the title salt showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 25% probability level and intra- and intermolecular hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 2$.]

**Figure 2**

A ball-and-stick diagram of two parallel neighbouring helical strands. Only the $-\text{Cu}-\text{OCO}-\text{Cu}-$ backbone is shown for clarity.

being somewhat longer. However, there are $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds between the water molecules and the O3 atoms of the perchlorate anions (Table 2 and Fig. 1).

Treatment of copper(II) perchlorate with an equimolar amount of the same ligand as in (I) in methanol/ H_2O (3:1 v/v) yields blue crystals of poly[[[μ -*N*-(2-pyridylmethylene)-2-carboxyethylamine]aquacopper(II)] perchlorate dihydrate], (II) (Colacio *et al.*, 2000), which has a similar structure to (I). Both complexes exhibit approximately square-based-pyramidal Cu^{II} ions which are bridged by *syn-anti* carboxylate groups to form helical chains. In the lattice of (II), however, left- and right-handed helical chains alternate, resulting in optically inactive racemic crystals. The structural differences between (I) and (II) suggest that the solvent molecules exert an influence on the spontaneous resolution of left- and right-handed helices; this opens up the possibility of controlling the formation of the chiral helical structures by varying the nature of the solvent used.

Experimental

To a solution of β -alanine (0.080 g, 1.0 mmol) in methanol (10 ml) containing KOH (0.050 g, 1.0 mmol) was added a solution of pyridine-2-carbaldehyde (0.100 g, 1.0 mmol) in methanol (10 ml). The resulting solution was refluxed with stirring for 2 h. To the cold filtered solution was added a solution of copper(II) perchlorate (0.350 g, 1.0 mmol) in dimethylformamide (5 ml) and the mixture was stirred for 2 h. After filtration, the filtrate was left to stand at room temperature for one month and blue block-like crystals of the title salt appeared in a yield of 0.11 g (22%).

Crystal data

$[\text{Cu}(\text{C}_9\text{H}_9\text{N}_2\text{O}_2)(\text{H}_2\text{O})]\text{ClO}_4$	$V = 1304.8 (4) \text{ \AA}^3$
$M_r = 358.19$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 7.9552 (13) \text{ \AA}$	$\mu = 1.91 \text{ mm}^{-1}$
$b = 11.6740 (19) \text{ \AA}$	$T = 295 \text{ K}$
$c = 14.050 (2) \text{ \AA}$	$0.14 \times 0.12 \times 0.10 \text{ mm}$

Data collection

Bruker SMART APEX CCD area-detector diffractometer	5173 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2457 independent reflections
$T_{\min} = 0.776$, $T_{\max} = 0.832$	2092 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$	H atoms treated by a mixture of restrained and constrained refinement
$wR(F^2) = 0.129$	$\Delta\rho_{\max} = 0.48 \text{ e \AA}^{-3}$
$S = 1.01$	$\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$
2457 reflections	Absolute structure: Flack (1983)
182 parameters	Flack parameter: $-0.02 (3)$

Table 1

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

$\text{Cu1}-\text{O1}$	1.959 (4)	$\text{O1}-\text{C9}$	1.268 (7)
$\text{Cu1}-\text{O2}^{\text{i}}$	1.957 (4)	$\text{O2}-\text{C9}$	1.240 (7)
$\text{Cu1}-\text{O1W}$	2.397 (4)	$\text{N2}-\text{C6}$	1.265 (8)
$\text{Cu1}-\text{N1}$	1.997 (5)	$\text{N2}-\text{C7}$	1.445 (8)
$\text{Cu1}-\text{N2}$	1.976 (5)		
$\text{O1}-\text{Cu1}-\text{O1W}$	91.26 (17)	$\text{O1W}-\text{Cu1}-\text{N2}$	91.1 (2)
$\text{O1}-\text{Cu1}-\text{N1}$	166.05 (18)	$\text{O1W}-\text{Cu1}-\text{O2}^{\text{i}}$	94.06 (17)
$\text{O1}-\text{Cu1}-\text{N2}$	91.13 (18)	$\text{N1}-\text{Cu1}-\text{N2}$	81.5 (2)
$\text{O1}-\text{Cu1}-\text{O2}^{\text{i}}$	87.57 (16)	$\text{O2}^{\text{i}}-\text{Cu1}-\text{N1}$	98.68 (18)
$\text{O1W}-\text{Cu1}-\text{N1}$	100.66 (17)	$\text{O2}^{\text{i}}-\text{Cu1}-\text{N2}$	174.7 (2)

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

Table 2

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1W}-\text{H1WB}\cdots\text{O1}^{\text{i}}$	0.85	2.12	2.730 (6)	129
$\text{O1W}-\text{H1WA}\cdots\text{O3}$	0.85	2.17	2.928 (9)	149

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

The water H atoms were located in a difference Fourier map and refined with $\text{O}-\text{H}$ distances restrained to 0.85 (1) \AA and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Other H atoms were placed at geometrically calculated positions ($\text{C}-\text{H} = 0.93$ or 0.97 \AA) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008) and DIAMOND (Brandenburg & Berndt, 2005); software used to prepare material for publication: SHELXTL.

The author thanks Jiangxi Science and Technology Normal University for supporting this study.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3081). Services for accessing these data are described at the back of the journal.

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