

A one-dimensional carboxylate-bridged helical copper(II) complex containing (quinolin-8-yloxy)acetate

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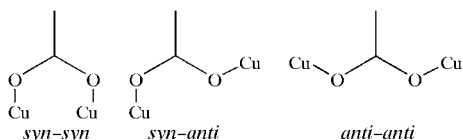
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The title compound, *catena*-poly[[bromocopper(II)]- μ -(quinolin-8-yloxy)acetato- $\kappa^4 N, O, O': O''$], $[\text{CuBr}(\text{C}_{11}\text{H}_8\text{NO}_3)]_n$, is a novel carboxylate-bridged one-dimensional helical copper(II) polymer. The metal ion exhibits an approximately square-pyramidal CuBrNO_3 coordination environment, with the three donor atoms of the ligand and the bromide ion occupying the basal positions, and an O atom belonging to the carboxylate group of an adjacent molecule in the apical site. Carboxylate groups are mutually *cis* oriented, and each *anti-anti* carboxylate group bridges two copper(II) ions *via* one apical and one basal position [$\text{Cu} \cdots \text{Cu} = 5.677(1) \text{ \AA}$], resulting in the formation of a helical chain along the crystallographic *b* axis.

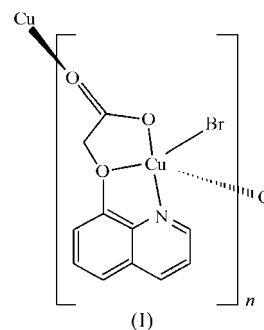
Comment

Self-assembly of supramolecules with helical structures by simple mixing of ligands and metal ions has been one of the targets of supermolecular chemistry (Pigué *et al.*, 1997), because helicity is an essential element of life and is also important in advanced materials, such as in the fields of optical devices and asymmetric catalysis (Albrecht, 2001; Erxleben, 2001; Jung *et al.*, 2000; Plasseraud *et al.*, 2001). It is well known that a carboxylate group can bridge two metal ions to give rise to a wide variety of polynuclear complexes, ranging from discrete entities to three-dimensional systems (Rettig *et al.*, 1999; Tangoluis *et al.*, 1996). In these complexes, a carboxylate group can assume many types of bridging conformations, the most important being triatomic *syn-syn*, *anti-anti* and *syn-*



anti, and monoatomic (Kato & Muto, 1988; Colacio *et al.*, 1999; Dey *et al.*, 2003; Yang *et al.*, 2003; see scheme above).

In our efforts to investigate the bonding nature of carboxylate-bridged copper(II) complexes, we succeeded in obtaining a new single-stranded helical coordination polymer, (I), by reacting quinolin-8-yloxyacetic acid with copper(II) bromide. Although a few similar helical chains with carboxylate-containing ligands have been reported (Colacio *et al.*, 1992, 2000; Yang *et al.*, 2003), to our knowledge, the title complex is the first helical carboxylate-bridged copper(II) polymer containing an aryloxyacetate ligand.



Complex (I) has a one-dimensional helical chain structure, which results from the fact that the copper(II) ions are bridged sequentially by *anti-anti* carboxylate groups (see below). A perspective view of the mononuclear fragment of (I) is given in Fig. 1, a view of the helical chain is shown in Fig. 2, and selected bond lengths and angles are listed in Table 1. The coordination geometry around the Cu atom may be described as that of a distorted square pyramid, the basal plane being defined by one N atom [$\text{Cu}-\text{N1} = 1.978(5) \text{ \AA}$], two O atoms [$\text{Cu}-\text{O1} = 2.017(4) \text{ \AA}$ and $\text{Cu}-\text{O3} = 1.936(4) \text{ \AA}$] from the quinolin-8-yloxyacetate ligand and one bromide anion [$\text{Cu}-\text{Br} = 2.3290(12) \text{ \AA}$]; the apical position is occupied by atom O2 from the carboxylate group of a neighbouring complex, this atom being coordinated at a longer distance [$\text{Cu}-\text{O2}^i = 2.294(4) \text{ \AA}$; symmetry code: (i) $-x, y - \frac{1}{2}, \frac{1}{2} - z$]. Atom O2

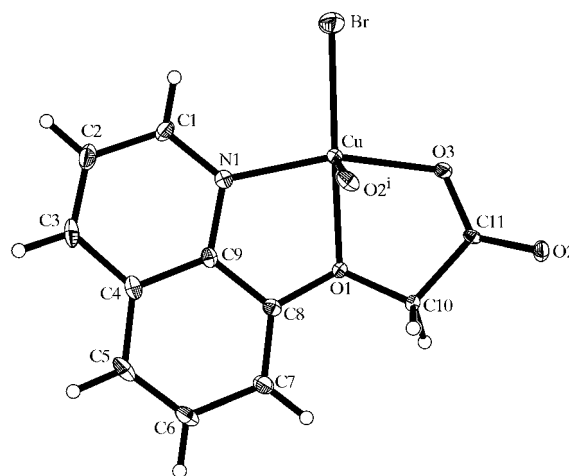


Figure 1

An ellipsoid plot of the mononuclear fragment of (I), which also shows atom O2 from a neighbouring complex. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $-x, y - \frac{1}{2}, \frac{1}{2} - z$].

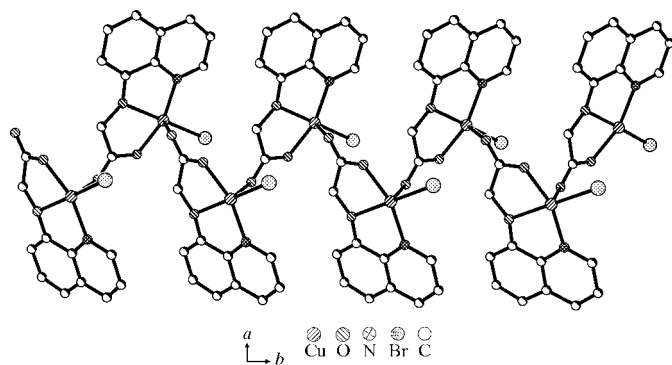


Figure 2
A view of the helical polymeric chain propagated along the crystallographic *b* axis.

thus forms a bridge between two Cu atoms. The inequivalence of the carboxylate C—O distances O3—C11 [1.290 (7) Å] and O2—C11 [1.206 (7) Å] may be correlated with their involvement in bonding with the Cu atoms. The other bond lengths and angles associated with the ligand and the Br[−] ion are as expected.

Atoms N1, O1, O3 and Br deviate by 0.0502 (1), −0.0633 (1), 0.0534 (1) and −0.0403 (1) Å, respectively, from the least-squares mean plane through these atoms, indicating a tetrahedral distortion from planarity. As expected, the Cu atom is displaced from this plane, by 0.1253 (1) Å towards the apical O2¹ atom. Each monodeprotonated ligand is tridentate with respect to one Cu centre but is, in fact, tetradentate when the bridge involving atom O2 is considered. Two considerably distorted five-membered chelate rings are formed with the metal atoms, the N1—Cu—O1 and O1—Cu—O3 chelate angles being 81.31 (19) and 79.32 (17)°, respectively. The five-membered chelate ring defined by atoms Cu, N1, C9, C8 and O1 is significantly non-planar [with a maximum atomic displacement of −0.1069 (1) Å], while the five-membered chelate ring defined by atoms Cu, O1, C10, C11 and O3 has a maximum atomic displacement of −0.1909 (1) Å. The two fused ring systems are also folded along the common Cu—O1 axis by 10.3 (1)°.

As noted above, each carboxylate group is in an *anti-anti* conformation with respect to the two copper centres that it bridges *via* two of its O atoms, and the copper ions deviate from the mean basal plane towards the axial O-atom donor. Because the three donor atoms of the ligands occupy the basal plane of the coordination sphere, the carboxylate bridges must be oriented in a mutually *cis* fashion and occupy basal and apical positions; the intrachain Cu···Cu distance is 5.677 (1) Å. Interestingly, both the *cis* orientations of the *anti-anti* carboxylate groups and the shifts of the copper(II) ions from the carboxylate mean planes contribute to helicity in the chains. The helix is generated by the operation of a 2₁ screw axis parallel to the *b* axis.

Experimental

The ligand quinolin-8-yloxyacetic acid was prepared according to the general procedure reported by Koelsch (1931). The title complex was

prepared by stirring together a solution of quinolin-8-yloxyacetic acid (0.0203 g, 0.1 mmol) in methanol (20 ml) and an aqueous solution (2 ml) of CuBr₂·2H₂O (0.027 g, 0.1 mmol) for 6 h. A solution of NaOH (0.004 g, 0.1 mmol) in methanol (10 ml) was then added. The resulting green solution was stirred for about 6 h at room temperature and then filtered. Slow evaporation from the filtrate yielded square prismatic green crystals suitable for X-ray analysis. Analysis found: C 38.69, H 2.11, N 4.07%; calculated for C₁₁H₈BrCuNO₃: C 38.22, H 2.33, N 4.00%.

Crystal data

[CuBr(C₁₁H₈NO₃)]
M_r = 345.63
Monoclinic, P2₁/c
a = 9.733 (5) Å
b = 6.725 (3) Å
c = 17.066 (9) Å
β = 102.922 (8)°
V = 1088.8 (9) Å³
Z = 4

D_x = 2.109 Mg m^{−3}
Mo Kα radiation
Cell parameters from 3148 reflections
θ = 3.0–27.5°
μ = 5.67 mm^{−1}
T = 193 (2) K
Square prism, green
0.40 × 0.20 × 0.15 mm

Data collection

Rigaku Mercury CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
T_{min} = 0.210, T_{max} = 0.484
8275 measured reflections

2490 independent reflections
2326 reflections with I > 2σ(I)
R_{int} = 0.040
θ_{max} = 27.5°
h = −12 → 12
k = −8 → 8
l = −18 → 22

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.063
wR(F²) = 0.154
S = 1.14
2490 reflections
154 parameters
H-atom parameters constrained

w = 1/[σ²(F_o²) + (0.057P)² + 11.343P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 1.38 e Å^{−3}
Δρ_{min} = −1.46 e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

Cu—Br	2.3290 (12)	O1—C8	1.388 (7)
Cu—N1	1.978 (5)	O1—C10	1.434 (7)
Cu—O1	2.017 (4)	O2—C11	1.206 (7)
Cu—O2 ¹	2.294 (4)	O3—C11	1.290 (7)
Cu—O3	1.936 (4)		
O3—Cu—N1	160.5 (2)	O1—Cu—O2 ¹	85.71 (16)
O3—Cu—O1	79.32 (17)	O3—Cu—Br	98.31 (13)
N1—Cu—O1	81.31 (19)	N1—Cu—Br	100.38 (15)
O3—Cu—O2 ¹	90.88 (17)	O1—Cu—Br	170.34 (13)
N1—Cu—O2 ¹	90.17 (18)	O2 ¹ —Cu—Br	103.75 (11)

Symmetry code: (i) −x, y − ½, ½ − z.

H atoms were included in calculated positions in the riding-model approximation, with C—H distances of 0.95 and 0.99 Å, and U_{iso}(H) values of 1.2U_{eq}(C).

Data collection: *CrystalClear* (Molecular Structure Corporation, 2000; Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MS & Rigaku, 2000–2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); 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: BM1576). Services for accessing these data are described at the back of the journal.

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