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Polymeric (cyclopropane-1,1-dicarboxylato)copper(II)

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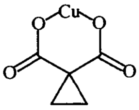
Abstract

The crystal structure of the polymeric title compound, $[Cu(C_5H_4O_4)]_n$, contains infinite chains of copper–carboxylate units in which the copper is coordinated in a planar manner by the O atoms. The chains are linked by –O—Cu—O– bridges resulting in a three-dimensional polymeric structure.

Comment

There is little information about the structures of compounds of transition metals with cyclopropane-1,1-dicarboxylic acid; only a few structures with platinum are known (Huang *et al.*, 1990). Recently, we reported the structure of hexaaquacobalt(II) bis(hydrogen cyclopropane-1,1-dicarboxylate) (Schwarz *et al.*, 1998), which is the only known structure of a first row transition metal complex with this acid.

In the title compound, (I), there are four identical $Cu[C_3H_4(COO)_2]$ formula units in the unit cell. Each copper ion is coordinated in a planar manner by four O atoms, with bonding angles of 96.18 (11) and 91.71 (11)°. Two atoms [O2^{i} and O2^{ii}; symmetry codes: (i) $y-\frac{1}{2}, \frac{1}{2}-x, z-\frac{1}{4}$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{4}-z$] belong to the same cyclopropane-1,1-dicarboxylate ligand, and the third and fourth O atoms to different ring systems in each case. This arrangement is illustrated in Fig. 1. The polymeric structure can be described as chains (formed by the fourfold screw axis) along **c**. Each chain includes four copper cations which will be denoted as Cu_A, Cu_B, Cu_C and Cu_D. The bridging O atoms which are not involved in the chelate bonding construct one string in the *c* direction with Cu_A and Cu_C. For Cu_B and Cu_D, they connect the chains in the *a* and *b* directions. The bond lengths range from 1.9243 (17) Å for Cu1—O2^{i} to 1.9464 (16) Å for Cu1—O1. The copper cation lies in the plane formed by the cyclopropane ring, C3^{i}—C2^{i}—C2^{ii}. Nevertheless, the point symmetry of the formula unit $Cu[C_3H_4(COO)_2]$ is not C_{2v}. The dihedral angle between the two carboxylate groups is found to be 77.81 (3)°, and between a carboxylate group and the cyclopropane ring is 52.15 (1)°. The average bond length within the ring is 1.518 Å, the individual bond lengths varying from 1.537 (4) (C2^{i}—C3^{i}) to 1.479 (6) Å (C2^{i}—C2^{ii}). Two bond angles are of major importance: on the one hand, the value for the angle C1^{i}—O2^{i}—Cu1 is 128.22 (16)°, while on the other hand, a value of 112.31 (15)° is found for the bridging angle Cu1—O1—C1. All other geometric parameters are in good agreement with other compounds which contain the cyclopropane-1,1-dicarboxylic acid moiety (Meester *et al.*, 1971; Bréhin *et al.*, 1992).



(I)

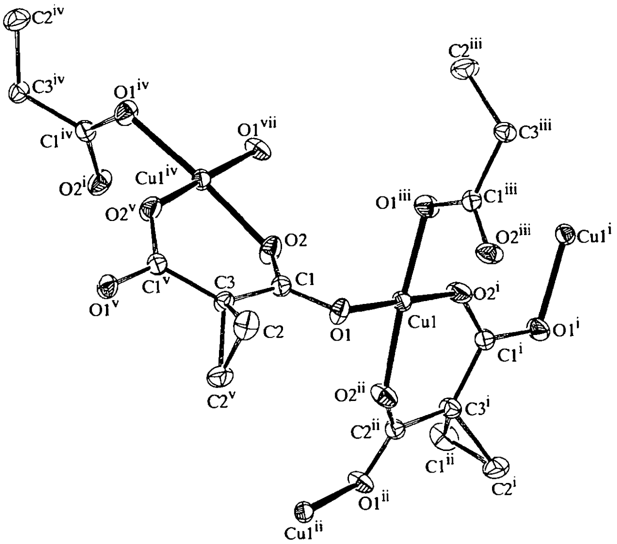


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme. Symmetry codes: (i) $-\frac{1}{2}+y, \frac{1}{2}-x, -\frac{1}{4}+z$; (ii) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{4}-z$; (iii) $y, x, -z$; (iv) $\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{4}+z$; (v) $1-y, 1-x, \frac{1}{2}-z$; (vii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z$.

Experimental

Single crystals suitable for X-ray analysis were grown in tetramethoxysilane gel (TMOS) (Arend & Connelly, 1982). A 0.1 mol l^{-1} copper nitrate solution with 10% TMOS was allowed to set in test tubes for four days. An aqueous solution of 0.2 mol l^{-1} cyclopropane-1,1-dicarboxylic acid (Singh & Danishefsky, 1975) was placed over the set gel. Well developed dark-blue crystals were obtained after three weeks at a growing temperature of 313 K.

Crystal data

$[Cu(C_5H_4O_4)]$	Mo $K\alpha$ radiation
$M_r = 191.62$	$\lambda = 0.71073$ Å

Tetragonal
$P4_12_12$
$a = 6.7940\,(5)$ Å
$c = 11.9557\,(11)$ Å
$V = 551.86\,(8)$ Å^3
$Z = 4$
$D_x = 2.306$ Mg m^{-3}
$D_m = 2.2$ Mg m^{-3}
D_m measured by pycnometry

Cell parameters from 616 reflections
$\theta = 1.65–26.05°$
$\mu = 3.892$ mm^{-1}
$T = 293\,(2)$ K
Bipyramidal
0.50 × 0.45 × 0.40 mm
Dark blue

Data collection

Stoe Imaging Plate Diffractometer System (IPDS)
Rotation scans
Absorption correction: numerical (*FACEIT*, *X-SHAPE* and *X-RED*; Stoe & Cie, 1995)
$T_{\rm min} = 0.163$, $T_{\rm max} = 0.211$

1070 measured reflections
358 independent reflections (plus 183 Friedel-related reflections)
522 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\rm max} = 25.99°$
$h = -5 \rightarrow 5$
$k = 0 \rightarrow 8$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.048$
$S = 1.095$
541 reflections
48 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0330P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.362$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.259$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.067 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.02 (3)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
Cu1	0.23094 (4)	0.23094 (4)	0	0.01612 (18)
O1	0.4727 (2)	0.2598 (3)	0.08576 (13)	0.0224 (4)
O2	0.2995 (3)	0.4824 (3)	0.17479 (13)	0.0244 (4)
C1	0.4541 (3)	0.3782 (3)	0.16531 (18)	0.0170 (5)
C2	0.8164 (4)	0.3071 (4)	0.2131 (2)	0.0264 (6)
C3	0.6144 (4)	0.3856 (4)	1/4	0.0171 (6)

Table 2. *Selected geometric parameters (Å, °)*

Cu1—O2$^{\rm i}$	1.9243 (17)	Cu1—O1	1.9464 (16)
O2$^{\rm i}$—Cu1—O2$^{\rm ii}$	91.71 (11)	O1—Cu1—O1$^{\rm iii}$	96.18 (11)

Symmetry codes: (i) $y - \frac{1}{2}, \frac{1}{2} - x, z - \frac{1}{4}$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{4} - z$; (iii) $y, x, -z$.

Two enantiomorphic space groups, $P4_12_12$ or $P4_32_12$, are possible for the investigated crystal. In order to determine the correct absolute structure, refinement was performed in both space groups. The Flack parameter (Flack, 1983) is helpful in solving the problem. It is almost zero [−0.02 (3)] for $P4_12_12$ and 1.00 (5) for $P4_32_12$, so it turns out that the first space group is correct.

Data collection: *IPDS Software* (Stoe & Cie, 1995). Cell refinement: *IPDS Software*. Data reduction: *IPDS Software*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *PLATON*92 (Spek, 1992). Software used to prepare material for publication: *PLATON*92.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1210). Services for accessing these data are described at the back of the journal.

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Tetraaqua(1,10-phenanthroline-*N*,*N*)-nickel(II) dinitrate monohydrate

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Abstract

The title compound, [Ni(C$_{12}$H$_8$N$_2$)(H$_2$O)$_4$](NO$_3$)$_2$·H$_2$O, consists of tetraaqua(1,10-phenanthroline)nickel(II) cations, nitrate anions and water molecules. The Ni$^{\rm II}$ ion is coordinated in a distorted octahedral arrangement by two water molecules and two tertiary N atoms from one phenanthroline ligand in equatorial positions, and by two O atoms of water in axial positions. The Ni—O bond lengths range from 2.053 (2) to 2.105 (2) Å and the two Ni—N bond lengths are 2.068 (2) and 2.070 (2) Å,