

catena-Poly[[diaquacobalt(II)]- μ -oxalato]

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Single crystals of the title compound, $[\text{Co}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2]_n$, have been prepared by hydrothermal methods and characterized by X-ray diffraction analysis. The crystal structure consists of infinite one-dimensional chains of diaquacobalt(II) units bridged by oxalate groups. These chains lie on twofold symmetry axes parallel to the *b* axis, and the $[\text{Co}(\text{C}_2\text{O}_4)]_n$ system is nearly planar within experimental error. The cobalt(II) coordination polyhedra are irregular octahedra, with oxalate O atoms at the equatorial positions and water molecules at the axial positions. The chains are linked by hydrogen bonds *via* the water molecules.

Comment

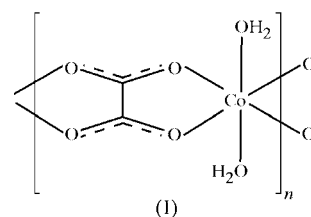
Polymeric divalent metal oxalates tend to form microcrystalline precipitates that are difficult to characterize by single-crystal X-ray diffraction. Rare prismatic crystals of whewellite $\{[\text{Ca}(\text{C}_2\text{O}_4)] \cdot \text{H}_2\text{O}\}$ up to 100 mm long have been discovered in Kladno, Czech Republic (Korbel & Novak, 1999), and diffraction quality crystals of humboldtine $\{[\text{Fe}(\text{C}_2\text{O}_4)] \cdot 2\text{H}_2\text{O}\}$ can be found as hydrothermal deposits in coal basins.

The mineral humboldtine crystallizes in the space group *C2/c* and consists of one-dimensional chains of $[\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2]$ units with bridging oxalate ions (Caric, 1959). One-dimensional coordination polymers are important for studying fundamental theoretical aspects of magnetism in the solid state.

Metal oxalates have also been subjected to detailed thermal analyses and the results used in establishing theoretical concepts applicable to solid-state reactions (see, for example, Coetzee *et al.*, 1994). Two different forms of ferrous oxalate dihydrate (α and β) have been characterized (Deyrieux & Peneloux, 1969), but the α form, humboldtine, is the more common. Powder diffraction patterns of the α -oxalates $[M(\text{C}_2\text{O}_4)] \cdot 2\text{H}_2\text{O}$ (with *M* = Mg, Mn, Fe, Co, Ni and Zn) have been indexed in the monoclinic space group *C2/c* with nearly identical cell parameters. The crystal structures of α -oxalates $[M(\text{C}_2\text{O}_4)] \cdot 2\text{H}_2\text{O}$ (with *M* = Mn, Co, Ni and Zn) have been

studied by Lagier *et al.* (1969) and Deyrieux *et al.* (1973) using powder diffraction.

The atomic coordinates of humboldtine have been used as starting values for a least-squares refinement based on fitting the calculated and observed intensity profiles of a powder diffraction pattern of microcrystalline $[\text{Mn}(\text{C}_2\text{O}_4)] \cdot 2\text{D}_2\text{O}$ (Śledzińska *et al.*, 1987). These results, and diffraction studies on single crystals of $[\text{Zn}(\text{C}_2\text{O}_4)] \cdot 2\text{H}_2\text{O}$ (Bacsa, 1995), confirm that these oxalates are isostructural and isomorphous. A new hydrated phase of cobalt oxalate crystallizes in the triclinic space group *P* $\bar{1}$ with similar cell parameters to the α -forms (Castillo *et al.*, 2004). We report here the crystal structure of the title compound, (I), prepared by hydrothermal methods.



The structure of (I) consists of infinite chains of $[\text{Co}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2]$ units which lie on twofold symmetry axes parallel to the *b* axis (Fig. 1). The neighbouring chains are parallel but displaced by 0.787 (1) Å relative to each other along the *b* axis. In this arrangement, the H atoms of the water molecules are in favourable positions for donating normal hydrogen bonds to oxalate O atoms (Fig. 2). This network of hydrogen bonds is in an up-down arrangement along these chains, *i.e.* when an oxalate O atom accepts a hydrogen bond above the $[\text{Co}(\text{C}_2\text{O}_4)]_n$ plane, the next O atom on the same side of the chain accepts a bond below the plane of the oxalate group. The separations of the Co^{II} atoms along the chains coincide with the repeat distance of the *b* axis. The closest interchain spacing is 4.9 Å, and the Co^{II} atoms are located on crystallographic planes with indices (200) and with a repeat distance of 5.853 (1) Å. The 200 reflection in the powder diffraction patterns of the α -oxalates is the most intense, and

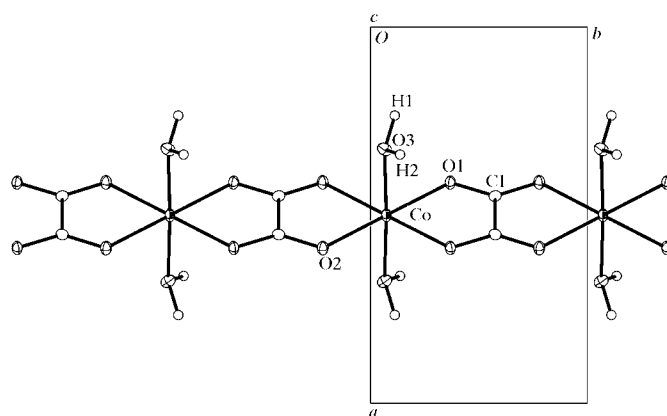


Figure 1

A view of one of the linear chains of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

studies (Masuda *et al.*, 1987) show that crystals of these oxalates have perfect cleavage planes parallel to the (100) plane.

The oxalate ions in (I) are bis-bidentate and bridge the Co atoms sideways rather than head-on, *i.e.* each oxalate ion forms two five-membered chelate rings rather than two four-membered rings. The O...O distance [2.700 (3) *versus* 2.239 (3) Å] in this arrangement is better for forming a stable octahedral coordination geometry about each Co^{II} atom with slight distortion.

The bridging oxalate ions and Co atoms are nearly planar within experimental error, and since the chains lie on twofold axes, the entire [Co(C₂O₄)]_n system is also planar. This planarity suggests the existence of delocalized bonding involving all the equatorial atoms. The C—C bond distance is slightly longer than that typically found in other oxalates (Cambridge Structural Database, Version 5.25; Allen, 2002). According to the bond-valence model (Brown, 2002), this should be an electron-pair bond and have a distance of 1.54 Å. Electron density that would be expected to be within this bond is likely to have been transferred to the C—O and Co—O bonds, resulting in a longer bond (Mak & Zhou, 1992).

The water molecule is tilted toward atom O1 and away from atom O2 (within each chain). The O—Co—O(H₂O) coordination angles are close to the ideal octahedral values, but the O—Co—O angles within the two unique chelate rings are acute, while the remaining unique angle is obtuse. The bond angle of the carboxylate O—C—O group is 126.5 (3)°. The ideal O—C—O angle in the oxalate ion is close to 120°. This bond angle widens to accommodate the Co atom. However, this angle is rigid and distorts to a lesser extent than the coordination angles. The two pairs of Co—O equatorial bonds are the same within experimental error. The axial Co—

O(H₂O) bond is almost exactly the same length as the equatorial bonds.

The structure of (I) is held together by an ordered network of coordination and hydrogen bonds. A disruption of any of these is likely to break the chains. Therefore, the crystals are small but diffract well, perhaps indicating an almost perfectly ordered structure.

Experimental

A solution of cobalt(II) chloride hexahydrate (1.2 g, 5.0 mmol) in water (10 ml) was added dropwise to an aqueous solution (10 ml) of potassium oxalate (1.2 g, 6.2 mmol). The resulting microcrystalline precipitate was transferred to a 23 ml Teflon-lined autoclave. The autoclave was sealed, transferred to an oven and heated to 483 K for 12 h. Small pink crystals of (I), as well as dark-blue soluble crystals of cobalt(II) chloride, were obtained on slowly cooling the mixture to room temperature.

Crystal data

[Co(C₂O₄)(H₂O)₂]
M_r = 182.98
 Monoclinic, *C*₂/*c*
a = 11.707 (2) Å
b = 5.4487 (10) Å
c = 9.6477 (19) Å
 β = 126.155 (8)°
V = 496.89 (17) Å³
Z = 4
D_x = 2.446 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 1356 reflections
 θ = 3.5–27.4°
 μ = 3.41 mm⁻¹
T = 298 (2) K
 Plate, pink
 0.11 × 0.08 × 0.03 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 ω and φ scans
 Absorption correction: multi-scan (SADABS; Bruker, 2003)
T_{min} = 0.708, *T_{max}* = 0.911
 1722 measured reflections
 565 independent reflections

542 reflections with *I* > 2σ(*I*)
R_{int} = 0.020
 θ_{\max} = 27.4°
h = -14 → 8
k = -5 → 7
l = -11 → 12

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.032
wR (*F*²) = 0.089
S = 1.15
 565 reflections
 50 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2 + 2.8955P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.83 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.72 \text{ e \AA}^{-3}$

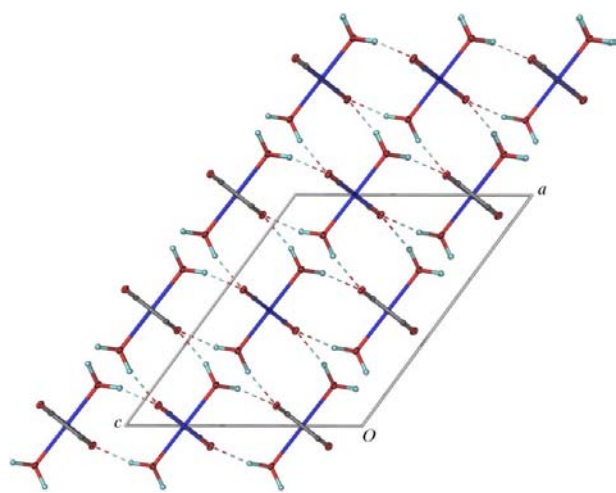


Figure 2

A view of part of the molecular packing of (I), projected onto the *ac* plane, showing how adjacent chains are linked by hydrogen bonds (dashed lines) between water molecules and oxalate O atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

Table 1

Selected geometric parameters (Å, °).

Co—O3	2.093 (2)	O1—C1	1.264 (4)
Co—O2 ⁱ	2.095 (2)	O2—C1	1.243 (4)
Co—O1	2.099 (2)	C1—C1 ⁱⁱ	1.571 (6)
O1 ⁱⁱ —Co—O1	80.07 (12)	O2 ^j —Co—O2 ⁱⁱⁱ	80.19 (12)
O2 ⁱ —Co—O1	99.87 (9)	O3—Co—O1	90.90 (9)
O3—Co—O3 ⁱⁱ	177.70 (13)	O3—Co—O1 ⁱⁱ	90.86 (9)
O3—Co—O2 ⁱ	88.96 (8)	O2 ⁱ —Co—O1	99.87 (9)
O3—Co—O2 ⁱⁱⁱ	89.28 (9)		
O1—C1—C1 ⁱⁱ —O1 ⁱⁱ	-1 (1)	Co—O1—C1—C1 ⁱⁱ	0.7 (4)
O1—C1—C1 ⁱⁱ —O2 ⁱⁱ	179.7 (2)	Co—O2 ⁱⁱⁱ —C1 ⁱⁱⁱ —C1 ⁱ	-0.2 (4)

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O3-H2\cdots O2^i$	0.98 (4)	1.80 (4)	2.751 (3)	164 (5)
$O3-H1\cdots O1^{ii}$	0.98 (4)	1.83 (4)	2.772 (3)	162 (5)

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

The two water H atoms were located from difference electron-density maps and refined isotropically with distances restrained [$O-H = 0.98$ (1) Å].

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1511). Services for accessing these data are described at the back of the journal.

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