metal-organic compounds

Acta Crystallographica Section C Crystal Structure Communications

ISSN 0108-2701

β -CdC₂O₄

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Received 30 May 2001 Accepted 6 June 2001

Crystals of anhydrous cadmium oxalate, β -[Cd(C₂O₄)], have been synthesized hydrothermally and the crystal structure solved using single-crystal X-ray diffraction data. The Cd and oxalate ions lie about independent inversion centres. The structure consists of a three-dimensional framework built from sheets of cadmium octahedra linked together by oxalate groups.

Comment

The assembly of metal-organic frameworks is currently an intense research topic and many one-, two- and threedimensional structures have recently been characterized (Rao et al., 2001). Among the anions involved in the formation of such solids, the oxalate group, which possesses four donor O atoms, plays a major role. Indeed, it can act either as a monodentate or a bidentate chelating ligand and can thus bridge two or more metal atoms in a variety of arrangements, as recently shown with a number of compounds (Bataille et al., 1999; Boudaren et al., 2000). Recent studies reported the crystal structures of SrC₂O₄ (Price et al., 1999) and PbC₂O₄ (Christensen et al., 1988), both prepared by direct synthesis. Almost all known anhydrous metal oxalates MC_2O_4 (*M* is Mn, Ni, Zn, Sn, Fe, Co or Cu; Kondrashev et al., 1985) result from thermal decomposition of the related hydrates (Naumov et al., 1996). Two types of structures have been established for CuC₂O₄ (Schmittler, 1968), an α disordered structure and a suggested structural model for a β ordered phase. Among the microcrystalline β phases, β -ZnC₂O₄ showed the best crystallization and its crystal structure was solved from powder diffraction data using 62 Bragg reflections (Kondrashev et al., 1985). In the course of our study of cadmium oxalate-based compounds (Jeanneau et al., 2001), we have synthesized a new anhydrous cadmium oxalate, CdC₂O₄, which differs from the oxalate obtained by decomposition of the trihydrate [Hanawalt et al., 1938; Powder Diffraction File No. 14-0712 (2000)]. The structure of this compound has been solved from singlecrystal X-ray diffraction data and the results are presented here.

The title compound has a monoclinic unit cell with parameters close to those found for the β forms mentioned above [*e.g.* for M = Zn, a = 5.831 (2), b = 5.123 (2), c = 5.331 (2) Å and $\beta = 113.20$ (2)°]. The structure displays a similar arrangement of the MO_6 octahedra and oxalate anions. It can either be described as interlinked *M*-oxalate-*M* chains or as a layered material, as will be done here.

A cationic layer is built from corner-shared CdO_6 octahedra running along [110] and [$\overline{110}$]. The corrugated sheets, parallel



Figure 1

A polyhedral representation of the structure of β -CdC₂O₄ viewed along [101].

to $(10\overline{1})$, are linked together *via* bidentate chelating oxalate groups lying in both the (110) and ($\overline{110}$) planes (Fig. 1). The Cd environment consists of six O atoms, all belonging to an oxalate group (Fig. 2). The polyhedron is a nearly regular octahedron, with three of the Cd-O distances in agreement with the mean distance of 2.296 (4) Å reported by Chung et al. (1995) for six-coordinate Cd atoms. The mean distances and angles within the oxalate group are close to the values reported by Hahn (1957) for different oxalate compounds. Moreover, the oxalate group is nearly planar, with a mean atomic deviation of 0.002 Å from the plane. The oxalate group in the isostructural compound β -ZnC₂O₄ was found to be highly distorted, with a significant deviation from planarity (up to 0.11 Å) and unequal C–O bond lengths (1.40 and 1.15 Å), which can easily be explained by the difficulty of obtaining precise results from the small number of structure-factor amplitudes extracted from the powder diffraction pattern (Kondrashev et al., 1985).

The structure determination from single-crystal diffraction data described here shows that the title cadmium compound belongs to the isostructural family of anhydrous oxalates β -*M*C₂O₄ and a precise description of the structural model is reported.



Figure 2

A view of the Cd environment in β -CdC₂O₄, showing the atom-labelling scheme and 50% probability displacement ellipsoids [symmetry codes: (i) -x, -y, -z; (ii) x, y, z - 1; (iii) -x, -y, 1 - z; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (v) $-\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$].

Experimental

The synthesis of the title compound was carried out by hydrothermal reaction. $Cd(NO_3)_2$ ·4H₂O (0.65 mmol), $K_2C_2O_4$ (3.25 mmol) and water (8 ml) were placed in a Teflon-lined autoclave (Paar) at 423 K for 100 h. The mixture was then cooled to ambient temperature at a rate of 6 K h⁻¹, leading to the formation of colourless bipyramidal crystals. These were washed with water and then ethanol, and dried in air. Thermogravimetric analyses and temperature-dependent X-ray diffraction showed that the compound decomposes at about 523 K to yield cubic CdO.

Crystal data

$[Cd(C_2O_4)]$	$D_x = 4.079 \text{ Mg m}^{-3}$		
$M_r = 200.43$	Mo $K\alpha$ radiation		
Monoclinic, $P2_1/n$	Cell parameters from 1867		
a = 5.8260 (5) Å	reflections		
b = 5.2520(7) Å	$\theta = 1.0-35.0^{\circ}$		
c = 5.8320(7) Å	$\mu = 6.54 \text{ mm}^{-1}$		
$\beta = 113.86 \ (2)^{\circ}$	T = 293 (2) K		
$V = 163.19 (3) \text{ Å}^3$	Lozenge, colourless		
<i>Z</i> = 2	$0.08 \times 0.06 \times 0.03 \mbox{ mm}$		
Data collection			
Nonius KappaCCD area-detector	721 independent reflections		
diffractometer	557 reflections with $I > 2\sigma(I)$		
$\theta/2\theta$ scans	$R_{\rm int} = 0.025$		
Absorption correction: by integra-	$\theta_{\rm max} = 34.9^{\circ}$		
tion (Coppens, 1970)	$h = 0 \rightarrow 9$		
$T_{\min} = 0.615, \ T_{\max} = 0.841$	$k = -8 \rightarrow 8$		
1314 measured reflections	$l = -9 \rightarrow 8$		

Refinement

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Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.022$ $wR(F^2) = 0.055$ S = 1.10 721 reflections 35 parameters $w = 1/[\sigma^2(F_o^2) + (0.0115P)^2]$	$\begin{array}{l} (\Delta/\sigma)_{\rm max} < 0.001 \\ \Delta\rho_{\rm max} = 1.30 \ {\rm e} \ {\rm \AA}^{-3} \\ \Delta\rho_{\rm min} = -1.11 \ {\rm e} \ {\rm \AA}^{-3} \\ {\rm Extinction \ correction: \ SHELXL97} \\ ({\rm Sheldrick, \ 1997}) \\ {\rm Extinction \ coefficient: \ 0.047 \ (6)} \end{array}$
where $P = (F_o^2 + 2F_c^2)/3$ Table 1 Selected geometric parameters (Å, °).	

$Cd-O1 (\times 2)$	2.2417 (15)	C-01	1.246 (2)
$Cd-O2^{ii} (\times 2)$	2.3205 (15)	C-02	1.264 (2)
$Cd-O2^{v} (\times 2)$	2.3461 (15)	C-C ⁱⁱⁱ	1.557 (4)
01–C–O2 01–C–C ⁱⁱⁱ	124.9 (2) 118.2 (2)	O2-C-C ⁱⁱⁱ	116.8 (2)

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

The magnitude of the minimum and maximum residual electron densities correspond to the deepest hole, located 0.65 Å from the Cd atom, and to the highest peak, located 1.57 Å from atom O1.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1339). Services for accessing these data are described at the back of the journal.

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