

β -CdC₂O₄

Erwann Jeanneau, Nathalie Audebrand* and Daniel Louër

Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR 6511 CNRS, Université de Rennes I, Institut de Chimie de Rennes, Avenue du Général Leclerc, 35042 Rennes CEDEX, France

Correspondence e-mail: nathalie.audebrand@univ-rennes1.fr

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 three-dimensional 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 MC₂O₄ (*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 single-crystal 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 β = 113.20 (2)°]. The structure displays a similar arrangement of the MO₆ 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 CdO₆ octahedra running along [110] and $[\bar{1}10]$. The corrugated sheets, parallel

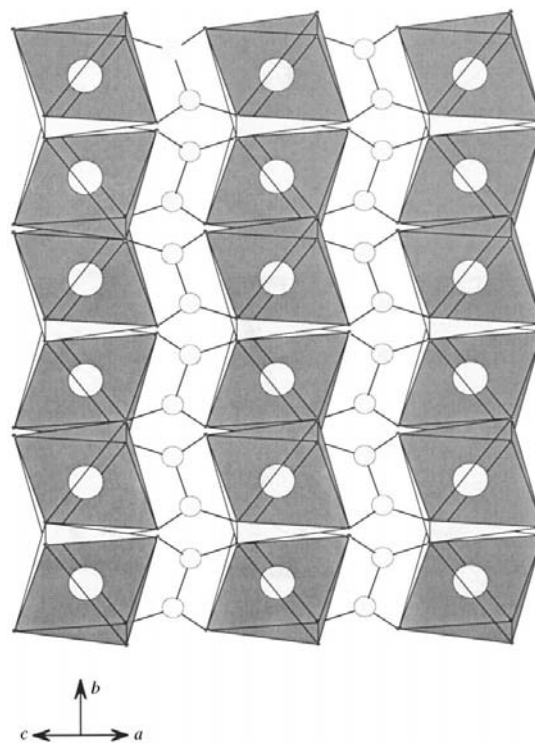


Figure 1

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

to (10 $\bar{1}$), are linked together *via* bidentate chelating oxalate groups lying in both the (110) and ($\bar{1}10$) 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 - MC_2O_4 and a precise description of the structural model is reported.

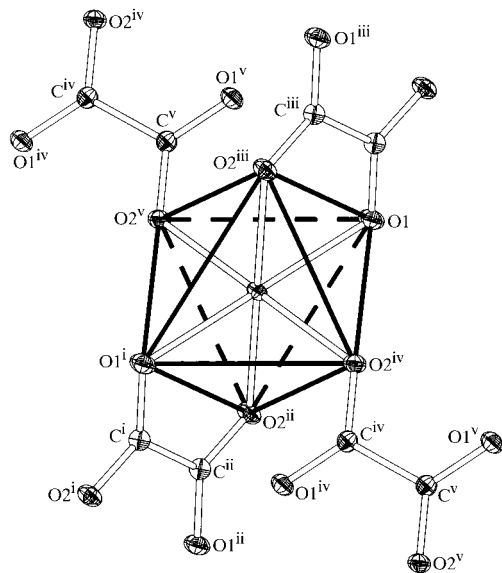


Figure 2
A view of the Cd environment in β - CdC_2O_4 , showing the atom-labelling scheme and 50% probability displacement ellipsoids [symmetry codes: (i) $-x, -y, -z$; (ii) $x, y, z - 1$; (iii) $-x, -y, 1 - z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (v) $-\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$].

Experimental

The synthesis of the title compound was carried out by hydrothermal reaction. $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.65 mmol), $\text{K}_2\text{C}_2\text{O}_4$ (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

| | |
|-------------------------------------|---|
| $[\text{Cd}(\text{C}_2\text{O}_4)]$ | $D_x = 4.079 \text{ Mg m}^{-3}$ |
| $M_r = 200.43$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/n$ | Cell parameters from 1867 reflections |
| $a = 5.8260$ (5) Å | $\theta = 1.0\text{--}35.0^\circ$ |
| $b = 5.2520$ (7) Å | $\mu = 6.54 \text{ mm}^{-1}$ |
| $c = 5.8320$ (7) Å | $T = 293$ (2) K |
| $\beta = 113.86$ (2)° | Lozenge, colourless |
| $V = 163.19$ (3) Å ³ | $0.08 \times 0.06 \times 0.03 \text{ mm}$ |
| $Z = 2$ | |

Data collection

| | |
|---|---------------------------------------|
| Nonius KappaCCD area-detector diffractometer | 721 independent reflections |
| $\theta/2\theta$ scans | 557 reflections with $I > 2\sigma(I)$ |
| Absorption correction: by integration (Coppens, 1970) | $R_{\text{int}} = 0.025$ |
| $T_{\text{min}} = 0.615, T_{\text{max}} = 0.841$ | $\theta_{\text{max}} = 34.9^\circ$ |
| 1314 measured reflections | $h = 0 \rightarrow 9$ |
| | $k = -8 \rightarrow 8$ |
| | $l = -9 \rightarrow 8$ |

Refinement

| | |
|---|--|
| Refinement on F^2 | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| $R[F^2 > 2\sigma(F^2)] = 0.022$ | $\Delta\rho_{\text{max}} = 1.30 \text{ e \AA}^{-3}$ |
| $wR(F^2) = 0.055$ | $\Delta\rho_{\text{min}} = -1.11 \text{ e \AA}^{-3}$ |
| $S = 1.10$ | Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997) |
| 721 reflections | Extinction coefficient: 0.047 (6) |
| 35 parameters | |
| $w = 1/[\sigma^2(F_o^2) + (0.0115P)^2 + 0.0246P]$ | |
| where $P = (F_o^2 + 2F_c^2)/3$ | |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|------------------------------------|-------------|-----------------------|-----------|
| Cd—O1 ($\times 2$) | 2.2417 (15) | C—O1 | 1.246 (2) |
| Cd—O2 ⁱⁱ ($\times 2$) | 2.3205 (15) | C—O2 | 1.264 (2) |
| Cd—O2 ^v ($\times 2$) | 2.3461 (15) | C—C ⁱⁱⁱ | 1.557 (4) |
| O1—C—O2 | 124.9 (2) | O2—C—C ⁱⁱⁱ | 116.8 (2) |
| O1—C—C ⁱⁱⁱ | 118.2 (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: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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.

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Bataille, T., Auffrédic, J. P. & Louër, D. (1999). *Chem. Mater.* **11**, 1559–1567.
- Boudaren, C., Auffrédic, J. P., Louër, M. & Louër, D. (2000). *Chem. Mater.* **12**, 2324–2333.
- Brandenburg, K. (1999). *DIAMOND*. Release 2.1c. Crystal Impact GbR, Bonn, Germany.
- Christensen, A. N., Cox, D. E. & Lehmann, M. S. (1988). *Acta Chem. Scand.* **43**, 19–25.
- Chung, K. H., Hong, E., Do, Y. & Moon, C. H. (1995). *J. Chem. Soc. Chem. Commun.* pp. 2333–2334.
- Coppens, P. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 255–270. Copenhagen: Munksgaard.
- Hahn, T. (1957). *Z. Anorg. Allg. Chem.* **109**, 438–466.
- Hanawalt, J. O., Rinn, H. W. & Frevel, L. K. (1938). *Anal. Chem.* **10**, 457–512.
- Jeanneau, E., Audebrand, N., Auffrédic, J. P. & Louër, D. (2001). *J. Mater. Chem.* In the press.
- Kondrashev, Y. D., Bogdanov, V. S., Golubev, S. N. & Pron, G. F. (1985). *Zh. Strukt. Khim.* **26**, 90–93.
- Naumov, D. Y., Podberezskaya, N. V., Boldyreva, E. V. & Virovets, A. V. (1996). *J. Struct. Chem.* **37**, 480–503.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
- Powder Diffraction File (2000). International Centre for Diffraction Data, Newtown Square, Pennsylvania, USA.
- Price, D. J., Powell, A. K. & Wood, P. T. (1999). *Polyhedron*, **18**, 2499–2503.
- Rao, C. N. R., Natarajan, S., Choudhury, A., Neeraj, S. & Vaidhyanathan, R. (2001). *Acta Cryst.* **B57**, 1–12.
- Schmittler, H. (1968). *Monatsber. Dtsch. Akad. Wiss. Berlin*, **10**, 581.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.