inorganic papers

Cadmium(II) diarsenate(V), Cd$_2$As$_2$O$_7$

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Cd$_2$As$_2$O$_7$ crystallizes in the thortveitite structure type and is isotypic with other M^{II}_2As$_2$O$_7$ diarsenates(V) (M = Mg, Mn, Co, Ni, Ca). The bridging O atom of the diarsenate group shows large thermal motion perpendicular to the As—O—As axis. No phase transition has been observed down to 193 K.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(As–O) = 0.002 Å
R factor = 0.036
wR factor = 0.086
Data-to-parameter ratio = 50.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

A first attempt to analyze the crystal structure of Cd$_2$As$_2$O$_7$ was performed by Calvo & Neelakantan (1970). The authors reported a close relationship between Cd$_2$As$_2$O$_7$, Zn$_2$As$_2$O$_7$ and Mg$_2$As$_2$O$_7$, but a reliable structure refinement was not possible for the cadmium and zinc compounds due to systematic twinning of the examined crystals.

Cd$_2$As$_2$O$_7$ crystallizes in the thortveitite-type structure (Zachariasen, 1930) and is isotypic with other divalent M_2As$_2$O$_7$ diarsenates(V), M = Mg (Calvo & Neelakantan, 1970), Mn (Buckley *et al.*, 1990; Aranda *et al.*, 1991), Co (Buckley *et al.*, 1990), Ni (Buckley *et al.*, 1990) and Ca (Pertlik, 1980). The main structural features are As$_2$O$_7$ groups with a linear As—O—As bridge showing large thermal motion of the bridging O atom perpendicular to the As—O—As axis (Fig. 1), and edge-sharing MO$_6$ octahedra, which form two-dimensionally infinite honeycomb sheets extending parallel to the *ac* plane. The As$_2$O$_7$ groups are situated below and above the vacant sites of the cationic layers (Fig. 2).

Since thortveitite-type structures are often dimorphous (having the thortveitite-type arrangement as the high-temperature modification), an examination of Cd$_2$As$_2$O$_7$ has also been performed at a temperature of 193 K (Weil, 2001). No phase transition was observed down to this temperature. Lattice parameters, bond lengths and angles calculated for both datasets are nearly the same. The mean distance $\overline{d}$(Cd—O) = 2.29 Å compares well with that of 2.31 Å calculated from the radii for six-coordinated Cd and three-coordinated O given by Shannon (1976). The conformation of the As$_2$O$_7$ anion is staggered with a longer distance d(As—O) to the bridging O atom as compared to the terminal atoms. The mean distance $\overline{d}$(As—O) = 1.676 Å is in good agreement with the mean $\overline{d}$(As—O) = 1.669 Å calculated for other M_2As$_2$O$_7$ diarsenates(V).

As well as the linear model, a so called split-atom model was introduced which describes a statistical disorder of the bridging O atom within X_2O$_7$ thortveitite-type groups (X = Si, P, V, As; Nord, 1984; Stefanidis & Nord, 1984). With respect to this model (space group $C2/m$, half occupation of the bridging O1 atom with fractional coordinates of x = 0, y = 0.0257 (13), z = 0) a bent diarsenate anion with an As—O—As angle of 164.5 (8)° and a slightly longer distance of d(As—O1) = 1.719 (2) Å results.
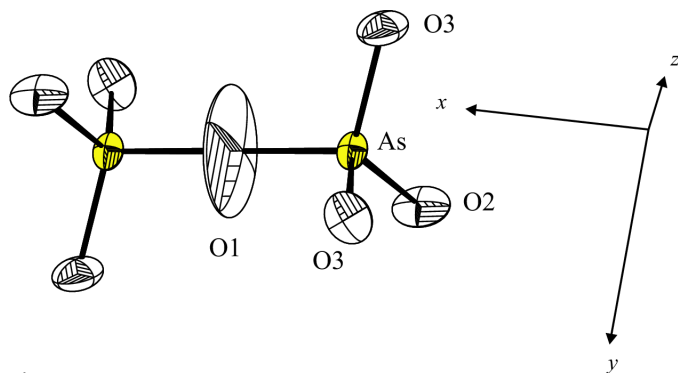
Figure 1
The As_2O_7 group (linear model) with anisotropic displacement ellipsoids drawn at the 90% probability level.

Experimental

Light-brown single crystals of $Cd_2As_2O_7$ up to 3 mm in length were prepared by chemical-transport reaction of microcrystalline material in evacuated and sealed silica tubes using $PtCl_2$ as the transport agent (temperature gradient $923 \rightarrow 873$ K, two weeks). Microcrystalline $Cd_2As_2O_7$ was synthesized by solid-state reaction of the binary oxides in closed silica ampoules at 873 K for 11 d.

Crystal data

|	
$Cd_2As_2O_7$	$D_x = 5.421$ Mg m^{-3}
$M_r = 486.64$	Mo $K\alpha$ radiation
Monoclinic, $C2/m$	Cell parameters from 24
$a = 6.9446$ (14) Å	reflections
$b = 9.0365$ (14) Å	$\theta = 8.2$–26.5°
$c = 4.8530$ (8) Å	$\mu = 18.13$ mm^{-1}
$\beta = 101.77$ (1)°	$T = 293$ (2) K
$V = 298.15$ (9) Å^3	Translucent plate, light brown
$Z = 2$	$0.28 \times 0.16 \times 0.06$ mm

Data collection

AED-2 (Siemens–Stoe) diffractometer	1550 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{int} = 0.035$
Absorption correction: numerical absorption correction on the basis of measured and indexed crystal faces	$\theta_{max} = 50.0°$
	$h = -14 \rightarrow 14$
	$k = -19 \rightarrow 19$
	$l = -10 \rightarrow 10$
$T_{min} = 0.040$, $T_{max} = 0.258$	3 standard reflections
6242 measured reflections	frequency: 120 min
1626 independent reflections	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$+ 3.2702P]$
$wR(F^2) = 0.086$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.23$	$(\Delta/\sigma)_{max} < 0.001$
1626 reflections	$\Delta\rho_{max} = 3.88$ e Å^{-3}
32 parameters	$\Delta\rho_{min} = -3.45$ e Å^{-3}
	Extinction correction: SHELXL97
	Extinction coefficient: 0.367 (11)
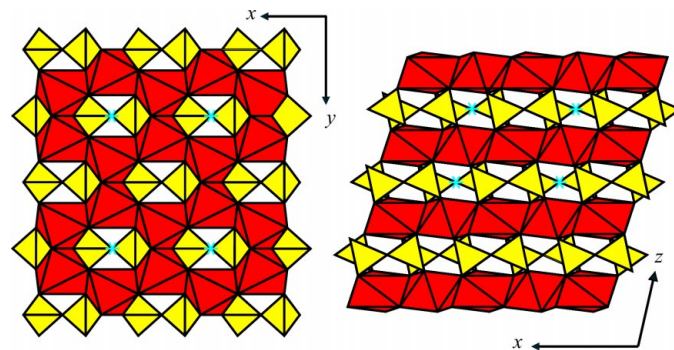
Figure 2
Projection of the structure along [001] (left) and [010] (right). CdO_6 octahedra are red, As_2O_7 groups are yellow. Unit-cell corners are marked with blue stars.

Table 1
Selected geometric parameters (Å, °).

Cd—O3^i	2.226 (2)	As—O3^{iv}	1.669 (2)
Cd—O2^{ii}	2.2819 (16)	As—O3	1.669 (2)
Cd—O3^{ii}	2.356 (2)	As—O1^{iii}	1.7036 (4)
As—O2^{iii}	1.663 (3)		
O2^{iii}—As—O3^{iv}	113.05 (10)	O3^{iv}—As—O1^{iii}	106.09 (7)
O2^{iii}—As—O3	113.05 (10)	O3—As—O1^{iii}	106.09 (7)
O3^{iv}—As—O3	113.14 (16)	As^v—O1—As^{vi}	180
O2^{iii}—As—O1^{iii}	104.51 (12)		

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

In the final electron density difference map the residual maximum of 3.9 e Å^{-1} and minimum of -3.5 e Å^{-1} (room temperature measurement) are located at a distance of 1.30 Å from As and 0.57 Å from Cd, respectively. They may be due to insufficient absorption correction caused by incorrect distance measurement of the crystal faces relative to the center of the crystal.

Data collection: STADI4 (Stoe & Cie, 1995); cell refinement: STADI4; data reduction: STADI4; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ATOMS (Dowty, 1995); software used to prepare material for publication: SHELXL97 (Sheldrick, 1997).

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