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Tricadmium bis(borate), $Cd_3(BO_3)_2$

Ying-Hua Zhao, Xue-An Chen,* Xin-An Chang, Jian-Long Zuo and Ming Li

College of Materials Science and Engineering, Beijing University of Technology, Ping Le Yuan 100, Beijing 100022, People's Republic of China

Correspondence e-mail:
xueanchen@bjut.edu.cn

The crystal structure of cadmium orthoborate, $Cd_3(BO_3)_2$, contains two crystallographically distinct Cd atoms in octahedral coordination with site symmetries $2/m$ and 2, and one unique B atom in triangular coordination with site symmetry m. The CdO_6 octahedra and BO_3 triangles share corners and edges to form a three-dimensional framework.

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Key indicators

Single-crystal X-ray study
T = 290 K
Mean σ(O–B) = 0.005 Å
R factor = 0.034
wR factor = 0.123
Data-to-parameter ratio = 18.8

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

Comment

Cadmium borates are of considerable interest because $Cd_2B_2O_5$ is an interesting host material for luminescent applications when doped with transition metal or rare earth ions. In the $CdO–B_2O_3$ system, at least three compounds have been proposed, including $Cd_3B_2O_6$ (Laureiro *et al.*, 1991), $Cd_2B_2O_5$ (Weil, 2003) and CdB_4O_7 (Ihara & Krogh-Moe, 1966), of which the latter two phases have been structurally well characterized by single-crystal X-ray diffraction. $Cd_2B_2O_5$ contains one-dimensional ribbons of edge-sharing CdO_6 octahedra that are bridged by B_2O_5 groups to form a three-dimensional network. CdB_4O_7 is characterized by a three-dimensional framework of corner-sharing B_4O_9 groups and tetrahedral Cd^{2+} centres. The crystal structure of $Cd_3B_2O_6$, or $Cd_3(BO_3)_2$, has previously been determined from powder X-ray data using the Rietveld method (Laureiro *et al.*, 1991). However, the reliability indices were large (R_{wp} = 0.221) and no standard uncertainties were given for the atomic coordinates and interatomic distances. While attempting to prepare novel lead cadmium borates, we unexpectedly obtained single crystals of $Cd_3B_2O_6$ and have redetermined its crystal structure.

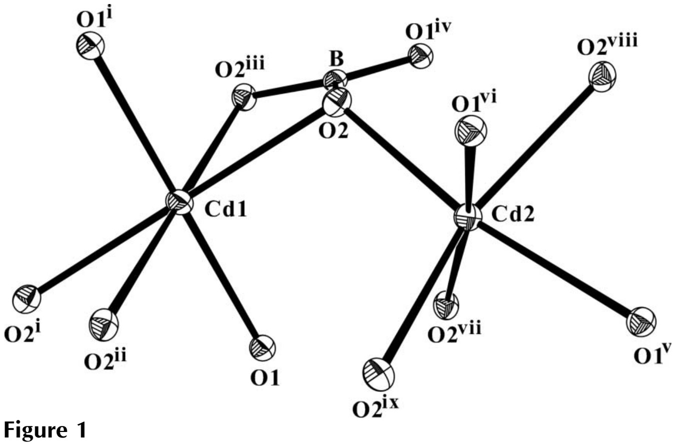

Figure 1
The local coordination geometries of Cd and B in $Cd_3B_2O_6$, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y, z$; (iii) $x, y, -z$; (iv) $-x, 1 - y, -z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vi) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (vii) $-x, 1 - y, z$; (viii) $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ix) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$.]

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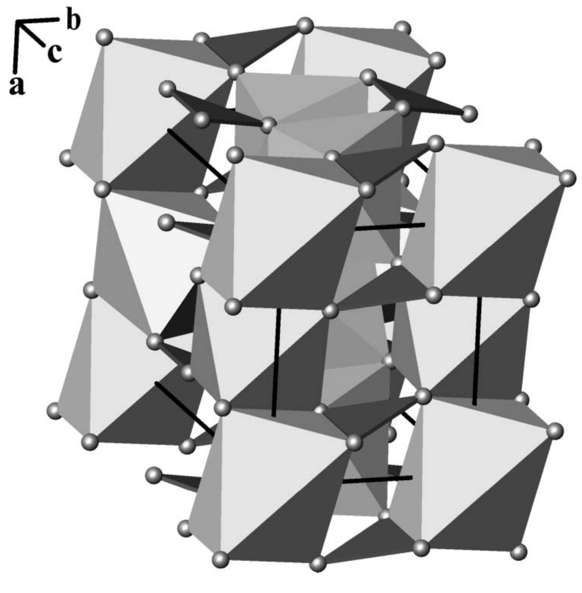

Figure 2
A drawing of the $Cd_3B_2O_6$ structure, illustrating the linkages between the CdO_6 octahedra and BO_3 triangles.

In this structure, the Cd atoms occupy two crystallographically distinct octahedral sites with site symmetries $2/m$ (Cd1) and 2 (Cd2) (Fig. 1 and Table 1). The mean Cd—O distances are 2.310 Å for Cd1 and 2.313 Å for Cd2, which are close to those in $Cd_2B_2O_5$ (2.303–2.334 Å; Weil, 2003). The unique B atom in the asymmetric unit lies on a mirror plane. The sum of the O—B—O angles is equal to 359.8°, indicating that the triangular coordination deviates only slightly from the ideal planar geometry. The average B—O distance is 1.393 Å, close to the values reported in other compounds having BO_3 groups, *e.g.* $PbZn_2(BO_3)_2$ (1.376 Å; Chen *et al.*, 2006). Of the two unique O atoms, O1 is on a mirror plane and O2 occupies a general position. Both O atoms are four-coordinated by three Cd atoms and one B atom in a distorted tetrahedral geometry. Bond-valence sum calculations (Brown & Altermatt, 1985) give values of 2.004–2.006 for Cd, 2.827 for B and 1.938–1.948 for O, consistent with their expected formal valences.

The CdO_6 octahedra are linked through common corners and edges to form a three-dimensional framework with one-dimensional channels running along the [100] direction (Fig. 2). The B atoms are incorporated into these channels and interact with the framework *via* B—O bonds to strengthen the structure. The BO_3 groups are aligned approximately parallel to the (100) plane [at an angle of 16.78 (8)°] and are stacked in a staggered arrangement along the *a* axis. Each BO_3 triangle shares one edge with one $Cd1O_6$ octahedron and its three vertices with seven other CdO_6 octahedra. This edge-sharing leads to a highly distorted $Cd1O_6$ coordination.

It is noteworthy that, although $Zn_3B_2O_6$ (Chen *et al.*, 2005) is related to $Cd_3B_2O_6$ in stoichiometry, the two structures are different. The Zn compound is characterized by a three-dimensional framework of corner- and edge-sharing ZnO_4 tetrahedra and BO_3 triangles.

Experimental

A powder mixture of PbO (0.1274 g, 0.5708 mmol), CdO (0.2924 g, 2.2773 mmol) and B_2O_3 (0.0794 g, 1.1405 mmol) was transferred to a small gold container. The sample was heated at 923 K for two weeks, cooled to 873 K at a rate of 0.5 K h^{-1}, and then cooled to room temperature at a rate of 30 K h^{-1}. Colourless block-like crystals of $Cd_3B_2O_6$ with dimensions of up to 0.3 × 0.3 × 0.2 mm^3 were recovered and mechanically separated from the reaction product. The powder X-ray diffraction pattern of the product revealed the existence of $Cd_3B_2O_6$ together with an unknown amorphous phase. The crystals were also checked by energy-dispersive X-ray analyses in a scanning electron microscope, which showed the presence of cadmium as the only heavy element. Although Pb was not incorporated into the final structure, lead borate possibly acted as a flux for the crystal growth.

The IR spectrum of $Cd_3B_2O_6$ exhibits three sets of bands characteristic of the planar triangular BO_3 group. They are the out-of-plane bending modes (ν_2) occurring at 711.9 cm^{-1}, the antisymmetric stretch (ν_3) in the range 1163.6–1230.5 cm^{-1}, and the in-plane mode (ν_4) between 576.9 and 612.8 cm^{-1}. These values correspond well with those reported in the literature (Thompson *et al.*, 1991).

Crystal data

$Cd_3(BO_3)_2$
$M_r = 454.82$
Orthorhombic, *Pnnm*
$a = 5.968$ (1) Å
$b = 4.786$ (1) Å
$c = 9.012$ (2) Å
$V = 257.41$ (9) Å^3
$Z = 2$
$D_x = 5.868$ Mg m$^{-3$}
Mo $K\alpha$ radiation
$\mu = 12.24$ mm^{-1}
$T = 290$ K
Prism, colourless
0.20 × 0.15 × 0.10 mm

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Kopfmann & Huber, 1968)
$T_{min} = 0.109$, $T_{max} = 0.289$
705 measured reflections
601 independent reflections
505 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 34.9°$
3 standard reflections every 150 reflections intensity decay: 1.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.123$
$S = 1.19$
601 reflections
32 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0703P)^2 + 1.0922P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.41$ e Å^{-3}
$\Delta\rho_{min} = -2.11$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.010 (2)

Table 1
Selected geometric parameters (Å, °).

Cd1—O1	2.269 (4)	Cd2—O1^{ii}	2.363 (3)
Cd1—O2	2.331 (3)	B—O1^{iii}	1.376 (7)
Cd2—O2	2.241 (3)	B—O2	1.402 (4)
Cd2—O2^{i}	2.336 (3)		
O1^{iii}—B—O2	121.8 (2)	O2^{iv}—B—O2	116.2 (5)

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

The highest residual electron-density peak is located 1.64 Å from atom Cd2 and the deepest hole is located 1.31 Å also from atom Cd2.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku, 1994); cell refinement: *Rigaku/AFC Diffractometer Control Software*; data reduction: *Rigaku/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL97*.

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