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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{O}-\text{B}) = 0.002\text{ \AA}$

R factor = 0.022

w R factor = 0.056

Data-to-parameter ratio = 31.1

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

Re-investigation of $\text{Cd}_2\text{B}_2\text{O}_5$: evidence of a centre of symmetry

The previously determined structure of cadmium diborate, $\text{Cd}_2\text{B}_2\text{O}_5$, has been re-investigated and a change in space-group symmetry from $P1$ to $P\bar{1}$ evidenced. $\text{Cd}_2\text{B}_2\text{O}_5$ crystallizes isotypically with other triclinic members of the $M_2\text{B}_2\text{O}_5$ ($M = \text{Mg}, \text{Mn}, \text{Co}, \text{Fe}$) family and is composed of slightly distorted $[\text{CdO}_6]$ octahedra, forming ribbons built of four condensed single-chains and diborate anions, $\text{B}_2\text{O}_5^{2-}$, which are composed of corner-sharing BO_3 triangles and which interconnect adjacent ribbons.

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Comment

$\text{Cd}_2\text{B}_2\text{O}_5$ is an interesting host material for luminescent applications when doped with transition metal or rare earth ions. Its structure has been determined by Sokolova *et al.* (1979) and was described in space group $P1$. Comparison of the symmetry and lattice parameters of other $M_2\text{B}_2\text{O}_5$ members [$M = \text{Co}$ (Berger, 1950), $\text{Mg}, \text{Fe}, \text{Mn}$ (Block *et al.*, 1959), Mg (Guo, Cheng, Chen, Huang & Zhang, 1995)] and solid solutions $MM'\text{B}_2\text{O}_5$ [$M = \text{Mn}, M' = \text{Mg}, \text{Co}$ (Utzolino & Bluhm, 1996); $M = \text{Zn}, M' = \text{Co}, \text{Ni}$ (Busche & Bluhm, 1995)], which all crystallize with similar lattice parameters in the centrosymmetric space group $P\bar{1}$, suggested a possible change in the space-group symmetry. Therefore the published atomic coordinates (Sokolova *et al.*, 1979) were checked with the *PLATON* program (Spek, 2003) which, in fact, indicated a centre of symmetry within the default tolerances of the program. For experimental proof, single crystals of $\text{Cd}_2\text{B}_2\text{O}_5$ were grown and the structure was redetermined in space group $P\bar{1}$.

$\text{Cd}_2\text{B}_2\text{O}_5$ crystallizes isotypically with the triclinic representatives of the $M_2\text{B}_2\text{O}_5$ family mentioned above. For all these structures, two angles close to 90° are observed, indi-

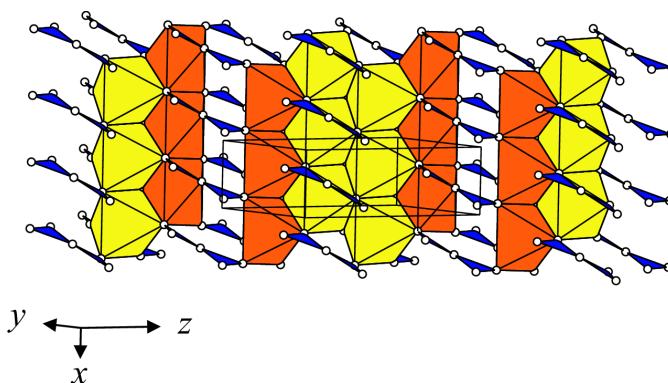


Figure 1

Slice through the structure, approximately parallel to (011). The structure is plotted in polyhedral representation; $[\text{Cd1O}_6]$ octahedra are orange, $[\text{Cd2O}_6]$ octahedra are yellow and B_2O_5 groups are blue.

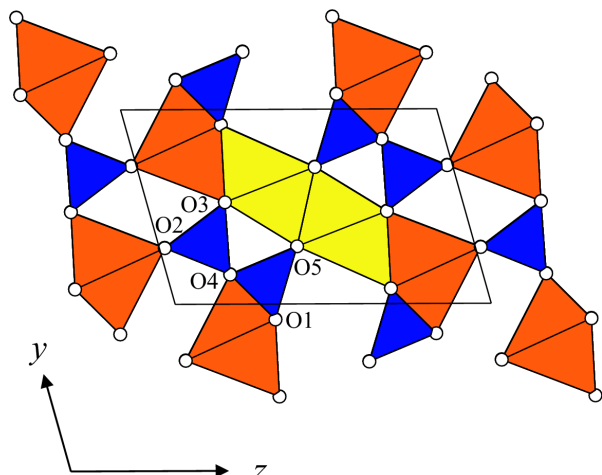


Figure 2
Projection of the crystal structure in polyhedral representation, viewed along [100]. [Cd1O₆] octahedra are orange, [Cd2O₆] octahedra are yellow and B₂O₅ groups are blue.

cating a possible phase transition to the monoclinic crystal system. At least for Mg₂B₂O₅, a synthetic monoclinic polymorph is described (Guo, Cheng, Chen, Zhuang *et al.* 1995), which is identical to the mineral Suanite (Takéuchi, 1952).

The crystal structure is composed of two crystallographically independent and distorted [CdO₆] octahedra, and B₂O₅ groups as the main building units. The [CdO₆] octahedra have mean Cd–O distances of 2.303 Å (Cd1) and 2.334 Å (Cd2) and build chains running parallel to the [100] direction by edge-sharing (Fig. 1). Four of these chains are connected to form ribbons along the [011] direction (Fig. 2). Adjacent ribbons are held together by the interstitial B₂O₅ anions.

As in other diborate structures with two condensed BO₃ triangles, the corresponding polyhedra are substantially distorted. The distances from B to the bridging atom O4 are considerably longer than to the terminal atoms O1, O2, O3 and O5 (see Table 1). The B–O distances for the two independent BO₃ triangles are very similar, and the average B–O distances [*d*(B1–O) = 1.377 and *d*(B2–O) = 1.381 Å] are in good agreement with the data for many other borate structures with BO₃ groups (Zobetz, 1982). The B₂O₅ anion (Fig. 3) deviates significantly from coplanarity; the dihedral angle between the two slanting BO₃ triangles is 13.1 (1)°.

The O atoms O1, O3 and O5 exhibit coordination number 4 and are each surrounded by three Cd and one B atom. O2 has three coordination partners (two Cd and one B) with two short Cd–O distances and a short B–O distance. O4 is the bridging atom of the diborate group and has an additional Cd atom with a long Cd–O distance in its coordination environment.

Experimental

Stoichiometric amounts of CdCO₃ (Merck, p. A.) and H₃BO₃ (10% excess, Merck, p. A.) were ground together finely in an agate mortar and charged in a platinum crucible which was heated to 1353 K over

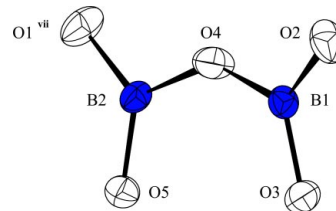


Figure 3
The diborate anion, with anisotropic displacement ellipsoids drawn at the 90% probability level.

the course of 5 h, kept at that temperature for 1 h and cooled to 973 K over 4 d. The furnace was then shut off. After leaching with boiling demineralized water, colourless single crystals of Cd₂B₂O₅, with mainly plate-like habit and an edge-length of up to 2 mm, were isolated.

Crystal data

Cd ₂ (B ₂ O ₅)	<i>Z</i> = 2
<i>M_r</i> = 326.42	<i>D_x</i> = 5.157 Mg m ⁻³
Triclinic, <i>P</i> 1	Mo <i>K</i> α radiation
<i>a</i> = 3.4490 (2) Å	Cell parameters from 25 reflections
<i>b</i> = 6.3603 (5) Å	<i>θ</i> = 12.4–14.9°
<i>c</i> = 9.9502 (8) Å	<i>μ</i> = 10.02 mm ⁻¹
<i>α</i> = 105.441 (8)°	<i>T</i> = 293 (2) K
<i>β</i> = 90.807 (6)°	Plate, colourless
<i>γ</i> = 91.933 (6)°	0.22 × 0.14 × 0.07 mm
<i>V</i> = 210.22 (3) Å ³	

Data collection

Enraf–Nonius CAD-4 diffractometer	2464 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>ω</i> / <i>θ</i> scans	<i>R</i> _{int} = 0.018
Absorption correction: numerical (<i>HABITUS</i> ; Herrendorf, 1993–1997)	<i>θ</i> _{max} = 39.9°
<i>T</i> _{min} = 0.267, <i>T</i> _{max} = 0.473	<i>h</i> = –6 → 6
5166 measured reflections	<i>k</i> = –11 → 11
2584 independent reflections	<i>l</i> = –17 → 17
	3 standard reflections
	frequency: 500 min
	intensity decay: none

Refinement

Refinement on <i>F</i> ²	(Δ/σ) _{max} = 0.001
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.022	Δ <i>ρ</i> _{max} = 2.33 e Å ⁻³
<i>wR</i> (<i>F</i> ²) = 0.056	Δ <i>ρ</i> _{min} = –2.03 e Å ⁻³
<i>S</i> = 1.13	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
2584 reflections	Extinction coefficient: 0.238 (4)
83 parameters	
<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0307 <i>P</i>) ² + 0.3225 <i>P</i>]	
where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3	

Table 1

Selected geometric parameters (Å, °).

Cd1–O1	2.2152 (15)	Cd2–O1 ⁱⁱⁱ	2.3787 (16)
Cd1–O5 ⁱ	2.2544 (15)	Cd2–O4 ^{vi}	2.4004 (15)
Cd1–O3 ⁱⁱ	2.2993 (15)	Cd2–O1 ⁱⁱ	2.5603 (18)
Cd1–O5	2.3162 (15)	B1–O2	1.356 (3)
Cd1–O5 ⁱⁱ	2.3631 (15)	B1–O3	1.364 (2)
Cd1–O3 ⁱⁱⁱ	2.3722 (15)	B1–O4	1.411 (3)
Cd2–O2 ^{iv}	2.1853 (16)	B2–O1 ^{vii}	1.357 (2)
Cd2–O2 ^v	2.2071 (16)	B2–O5	1.364 (3)
Cd2–O3	2.2742 (15)	B2–O4	1.421 (3)
O2–B1–O3	122.46 (17)	O1 ^{vii} –B2–O4	112.94 (16)
O2–B1–O4	116.53 (17)	O5–B2–O4	120.70 (17)
O3–B1–O4	120.97 (17)	B1–O4–B2	136.82 (16)
O1 ^{vii} –B2–O5	126.35 (18)		

Symmetry codes: (i) *x* – 1, *y*, *z*; (ii) 1 – *x*, 1 – *y*, 1 – *z*; (iii) –*x*, 1 – *y*, 1 – *z*; (iv) –*x*, 1 – *y*, –*z*; (v) 1 – *x*, 1 – *y*, –*z*; (vi) *x*, 1 + *y*, *z*; (vii) 1 – *x*, –*y*, 1 – *z*.

The structure was refined with the atomic coordinates of the isomorphous solid solution MnMgB_2O_5 (Utzolino & Bluhm, 1996) as starting parameters. The refined positional parameters were afterwards standardized using the program *STRUCTURE-TIDY* (Gelato & Parthé, 1987). The highest difference peak is located at a distance of 0.59 Å from Cd1, and the deepest hole 0.63 Å from this atom.

Data collection: *CAD-4 Software* (Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELENA* implemented in *PLATON* (Spek, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *SHELXL97*.

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