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The centrosymmetric metal metaborate $KCdB_3O_6$

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The title compound, potassium cadmium metaborate, crystallizes in a monoclinic cell, featuring infinite one-dimensional CdO_5 chains and trigonal planar B atoms in hexagonal B_3O_6 metaborate ions. The trigonal bipyramidal CdO_5 chains and metaborate ions are interlinked to form a three-dimensional framework, creating channels running parallel to the $[10\overline{1}]$ direction in which the potassium ions reside.

Comment

Metal borates are rich in structure owing to the flexibility of the trigonal or tetrahedral borate–oxygen coordination. Therefore, the crystallography of metal borates has been a focus of research for several decades (Rowsell *et al.*, 2002), leading to new luminescent (Keszler, 1999) and nonlinear optical materials (Becker, 1998). The present work originates from our ongoing interest in the optical and electrical properties of borates consisting of highly disordered alkali–oxygen polyhedrons and B–O groups (Wu *et al.*, 2005, 2006, 2007). Considering the highly flexible coordination nature of B, Cd and K atoms and the increasing interest in metal borates, we investigated the $K_2O–CdO–B_2O_3$ system, with the title compound, (I), being the first identified compound.

The title compound crystallizes in the monoclinic space group *C*2/*c*, with 11 crystallographically independent atoms: one K, one Cd, three B and six O, all of which reside on general positions. Fig. 1 illustrates a selected unit of the compound, which highlights that the Cd atom is five-coordinated by O atoms in a distorted trigonal bipyramidal geometry. The trigonal planar BO_3 groups form the metaborate ion, with each of the three B atoms bonded to two bridging O atoms, forming a planar six-membered ring, and one acyclic O atom. The cadmium-centered trigonal bipyramids are connected by sharing the $O4^{ii}\cdots O4^{iv}$ and $O6^{i}\cdots O6^{iii}$ edges alternately (see Table 1 for symmetry codes), forming a one-dimensional CdO_5 chain along the *c* axis (see Fig. 2*a*). The B_3O_6 groups are attached to each O vertex of the bipyramids, with the B–O planes almost perpendicular to the chain. Three adjacent CdO_5 chains are interlinked by B_3O_6 units, forming a three-dimensional $[CdB_3O_6]$ framework structure. The framework also affords one-dimensional open channels running parallel to the $[10\overline{1}]$ direction, bounded by the edges of three CdO_5 and three B_3O_6 units. Potassium ions are located in the channels.

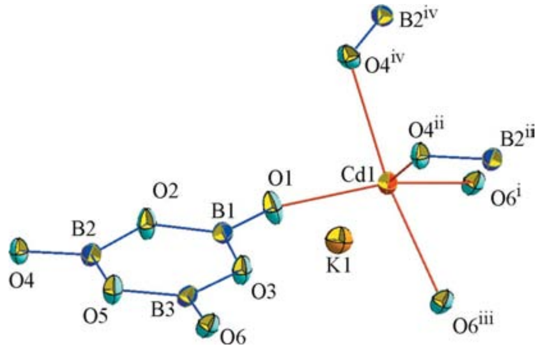

Figure 1
A fragment of the structure of $KCdB_3O_6$. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (ii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (iv) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.]

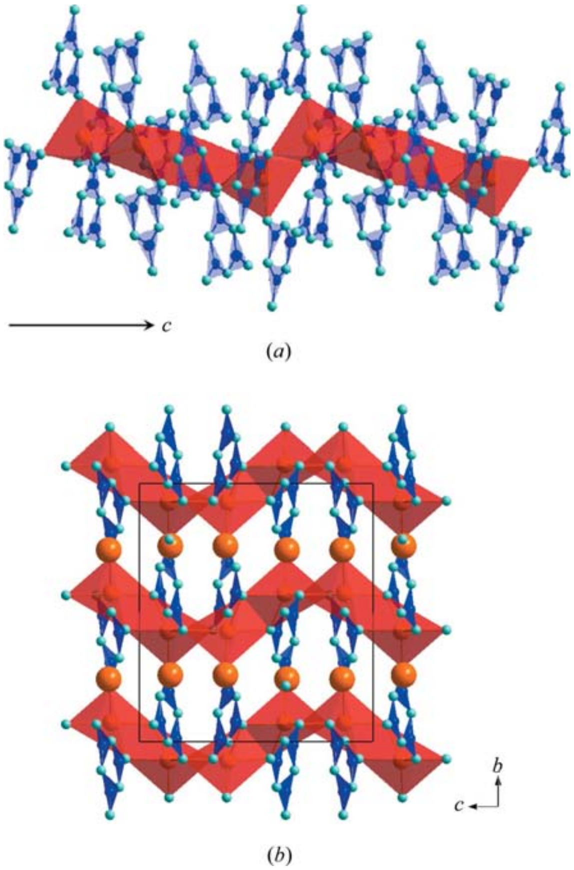

Figure 2
(*a*) The one-dimensional CdO_5 trigonal bipyramidal chain and the linkage to the B_3O_6 borate groups in $KCdB_3O_6$ (key in the electronic version of the paper: CdO_5 are red polyhedra, BO_3 are dark-blue triangles, O atoms are small cyan balls and K atoms are large orange balls). (*b*) A projection of the structure along the *a* axis.

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The bond distances and angles of the B–O units are regular (Table 1). The mean value (m.v.) of the B—O bond lengths is 1.372 Å, with a standard deviation (s.d.) of 0.036 Å, very close to the statistically averaged value for three-coordinate boron (1.370 Å). However, individually the B—O bonds can be divided into two groups. The three bonds connected with CdO_5 chains are quite short, ranging from 1.312 (4) to 1.333 (4) Å (m.v. = 1.326 Å and s.d. = 0.012 Å), while the bonds within the B_3O_3 rings are much longer, in the range 1.388 (4)–1.402 (4) Å (m.v. = 1.395 Å and s.d. = 0.005 Å). This phenomenon is quite similar to the bond-length variations when BO_3 and BO_4 groups are linked together (Filatov & Bubnova, 2000). The O—B—O bond angles range from 117.2 (2) to 123.0 (3)° (m.v. = 120.0° and s.d. = 2.0°). The Cd—O bond lengths are around 2.2 Å (m.v. = 2.254 Å and s.d. = 0.097 Å), with the two smallest bond angles being opposite the oxygen edges that are shared in CdO_5 bipyramids. The potassium cation is weakly bonded to as many as nine neighboring O atoms in a highly irregular coordination environment. The B–O group type is the same as in β-BaB_2O_4 (Frölich, 1984); the dihedral angles between the planar B_3O_6 groups are 0, 167.0 (1), 13.0 (1) and 180° in the unit cell.

$KCdB_3O_6$ is structurally very close to triclinic $LiCdBO_3$ (Sokolova *et al.*, 1979). $LiCdBO_3$ has two crystal forms – triclinic and hexagonal (Sokolova *et al.*, 1980) – which are the only two borates made from CdO_5 units. Generally, Cd atoms in borates will adopt four- or sixfold coordination. The CdO_5 unit in hexagonal $LiCdBO_3$ has a square-pyramidal geometry and is therefore not analogous to the triclinic form. Triclinic $LiCdBO_3$ is composed of CdO_5 trigonal bipyramidal chains that are interlinked by smaller BO_3 units with lithium cations filling the cavities. Replacing BO_3 with the larger B_3O_6 units of the title compound creates larger voids for the cation (K^+ ion). Another similar compound is PKU-6 [$Al_2(OH)B_3O_7$; Yang *et al.*, 2007], which features infinite AlO_5 chains connected by parallel B_3O_7 units.

Experimental

Crystals of the title compound were grown by spontaneous nucleation in a platinum crucible using an electric muffle furnace. Starting materials were prepared from a mixture of K_2CO_3 [analytical reagent (AR) grade], CdO (AR), and H_3BO_3 (99.99%) in a 1:2:6 molar ratio. Crystal growth was carried out at 1093 K after decomposition of the carbonate and elimination of water. The melt was cooled at a rate of 1 K h^{-1} to 973 K and then to room temperature naturally. Small transparent colorless crystals appeared in the crucible and a suitable one was chosen for single-crystal X-ray analysis.

Crystal data

$KCdB_3O_6$
$M_r = 279.93$
Monoclinic, $C2/c$
$a = 7.1779$ (6) Å
$b = 13.2152$ (12) Å
$c = 12.5113$ (11) Å
$\beta = 106.156$ (2)°
$V = 1139.92$ (17) $Å^3$
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 4.52$ mm^{-1}
$T = 298$ K
0.3 × 0.2 × 0.1 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.289$, $T_{max} = 0.638$
4846 measured reflections
2082 independent reflections
2052 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.093$
$S = 1.20$
2082 reflections
100 parameters
$\Delta\rho_{max} = 1.64$ e $Å^{-3}$
$\Delta\rho_{min} = -1.92$ e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

O1—B1	1.312 (4)	O5—B2	1.393 (4)
O2—B1	1.397 (4)	O3—B3	1.397 (3)
O3—B1	1.402 (4)	O5—B3	1.388 (4)
O2—B2	1.395 (4)	O6—B3	1.332 (4)
O4—B2	1.332 (4)		
$O1—Cd1—O6^{i}$	121.83 (9)	$O4^{ii}—Cd1—O6^{iii}$	88.99 (9)
$O1—Cd1—O4^{ii}$	118.86 (8)	$O1—Cd1—O4^{iv}$	85.27 (9)
$O6^{i}—Cd1—O4^{ii}$	119.30 (8)	$O6^{i}—Cd1—O4^{iv}$	102.53 (8)
$O1—Cd1—O6^{iii}$	103.56 (9)	$O4^{ii}—Cd1—O4^{iv}$	81.20 (10)
$O6^{i}—Cd1—O6^{iii}$	78.30 (9)	$O6^{iii}—Cd1—O4^{iv}$	169.19 (9)

Symmetry codes: (i) $x+\frac{1}{2}, y-\frac{1}{2}, z$; (ii) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (iii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$; (iv) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3024). Services for accessing these data are described at the back of the journal.

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