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Key indicators

Single-crystal X-ray study
 $T = 500\text{ K}$
Mean $\sigma(\text{S-O}) = 0.011\text{ \AA}$
 R factor = 0.058
 wR factor = 0.138
Data-to-parameter ratio = 12.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**Rb₂Cd₃(SO₄)₃(OH)₂·2H₂O: structural stability
at 500 K**The title compound, dirubidium tricadmium tris(sulfate) dihydroxide dihydrate, consists of sheets of CdO₆ octahedra and sulfate tetrahedra propagating in the (100) plane, with Rb⁺ ions in the interlayer positions. It is isostructural with K₂Co₃(SO₄)₃(OH)₂·2H₂OReceived 11 January 2006
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Comment

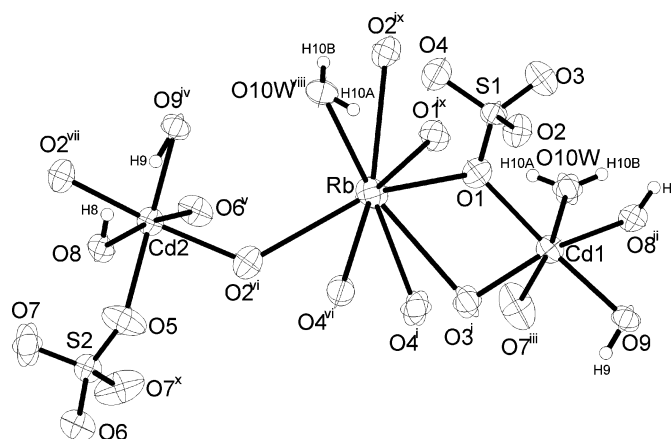
We are interested in evaluating the thermal stability of hydrated mineral salts and the possibility of obtaining intermediate phases during the dehydration process. Thermogravimetric studies on the double salt K₂Mn₃(SO₄)₄·5H₂O (Hidalgo *et al.*, 1996) and on Rb₂Cd₃(SO₄)₄·5H₂O (Swain & Guru Row, 2005) indicated that the water molecules are lost on heating to temperatures above 350 K.The title compound, Rb₂Cd₃(SO₄)₃(OH)₂·2H₂O, (I), which arose as an unexpected product during the attempted synthesis of an Rb₃Cd₂(SO₄) langbeinite-type phase (Nalini & Guru Row, 2002), displays unusual structural stability beyond 500 K and we present here its structure (Fig. 1) at 500 K to prove this point. It is isomorphous with K₂Co₃(SO₄)₃(OH)₂·2H₂O (Effenberger *et al.*, 1984).The structure of (I) consists of CdO₆ polyhedra and SO₄ tetrahedra which are linked by common vertices (Table 1). The CdO₆ polyhedra are linked into dimeric pairs through common edges. This entire network extends in (100) (Fig. 2). The Rb ions occupy inter-layer sites with coordination number 8. The Cd ions are octahedrally coordinated by O atoms variously belonging to water molecules, sulfate groups and

Figure 1

View of a fragment of (I), with displacement ellipsoids for non-H atoms drawn at the 50% probability level. [Symmetry codes: (i) $x, -y, z - \frac{1}{2}$; (ii) $\frac{1}{2} - x, -\frac{1}{2} - y, \frac{1}{2} + z$; (iii) $\frac{1}{2} + x, -\frac{1}{2} - y, \frac{1}{2} + z$; (iv) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (v) $-x, -y, \frac{1}{2} + z$; (vi) $\frac{1}{2} - x, -\frac{1}{2} - y, z - \frac{1}{2}$; (vii) $x - \frac{1}{2}, -\frac{1}{2} - y, z - \frac{1}{2}$; (viii) $\frac{1}{2} - x, y - \frac{1}{2}, z$; (ix) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (x) $-x, y, z$.

hydroxy groups. There are two types of Cd atoms, one in a general position and the other in a special position with site symmetry m . It is noteworthy that atom Cd1 in a general position is coordinated by a water molecule and its overall coordination is less distorted than that of atom Cd2. The water molecule is also coordinated to Rb.

Various O—H···O hydrogen bonds (Table 2) help to stabilize the structure. The enhanced thermal stability of (I) relative to the related pentahydrate phases mentioned above may be due to these interactions.

Experimental

Compound (I) was obtained by the slow evaporation of equimolar aqueous solutions containing Rb_2SO_4 and CdSO_4 , followed by dehydration at 873 K for 24 h. The resulting dehydrated powder was crystallized from water at 353 K in an attempt to obtain the langbeinite form. Colourless cylindrical crystals of (I) of reasonable size were obtained after 15 d. The evaporation rate was slowed down considerably by sealing the 5 ml beaker containing the solution under thermostatic control.

Crystal data

$\text{Rb}_2\text{Cd}_3(\text{SO}_4)_3(\text{OH})_2 \cdot 2\text{H}_2\text{O}$	Mo $K\alpha$ radiation
$M_r = 866.43$	Cell parameters from 746 reflections
Orthorhombic, $Cmc2_1$	$\theta = 0.9\text{--}27.3^\circ$
$a = 19.116(4) \text{ \AA}$	$\mu = 10.88 \text{ mm}^{-1}$
$b = 8.0147(13) \text{ \AA}$	$T = 500(2) \text{ K}$
$c = 10.0475(17) \text{ \AA}$	Block, colourless
$V = 1539.4(5) \text{ \AA}^3$	$0.30 \times 0.25 \times 0.20 \text{ mm}$
$Z = 4$	
$D_x = 3.738 \text{ Mg m}^{-3}$	

Data collection

Bruker SMART CCD area-detector diffractometer	1616 independent reflections
φ and ω scans	1585 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 1996)	$R_{\text{int}} = 0.033$
$T_{\text{min}} = 0.043$, $T_{\text{max}} = 0.114$	$\theta_{\text{max}} = 27.3^\circ$
7592 measured reflections	$h = -23 \rightarrow 23$
	$k = -9 \rightarrow 9$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1068P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.058$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.138$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.18$	$\Delta\rho_{\text{max}} = 1.95 \text{ e \AA}^{-3}$
1616 reflections	$\Delta\rho_{\text{min}} = -1.17 \text{ e \AA}^{-3}$
133 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	with 665 Friedel pairs
	Flack parameter: 0.04 (2)

Table 1

Selected bond lengths (\AA).

Cd1—O3 ⁱ	2.241 (9)	Cd2—O8	2.234 (10)
Cd1—O8 ⁱⁱ	2.270 (8)	Cd2—O9 ^{iv}	2.262 (11)
Cd1—O9	2.280 (7)	Cd2—O6 ^v	2.280 (13)
Cd1—O1	2.303 (9)	Cd2—O2 ^{vi}	2.309 (8)
Cd1—O10W	2.343 (10)	Cd2—O2 ^{vii}	2.309 (8)
Cd1—O7 ⁱⁱⁱ	2.352 (11)	Cd2—O5	2.370 (16)

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

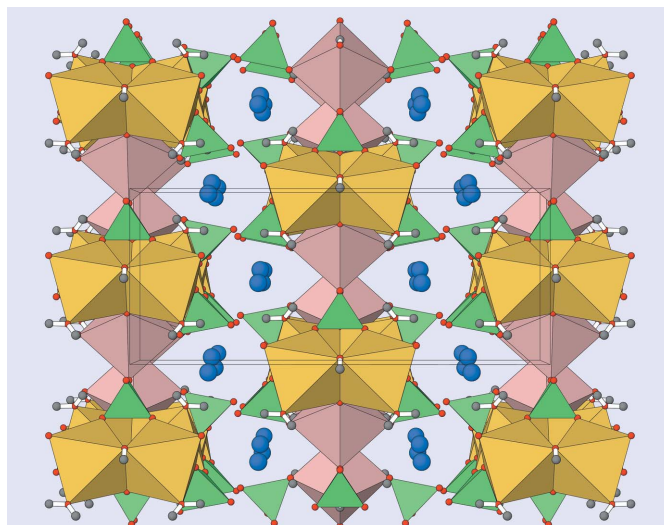


Figure 2

The packing of (I) in a polyhedral representation, viewed down [001]. Colour key: Cd1 octahedra orange, Cd2 octahedra pink, sulfate tetrahedra green, O atoms red, Rb atoms blue and H atoms grey.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O8—H8···O7 ^{viii}	0.86	2.56	3.347 (18)	152
O8—H8···O7 ^{ix}	0.86	2.56	3.347 (18)	152
O10W—H10A···O4 ^x	0.82	2.07	2.776 (13)	145
O10W—H10B···O6 ^{xi}	0.82	2.42	3.133 (12)	147
O10W—H10B···O6 ^{xii}	0.82	2.42	3.133 (12)	147
O10W—H10B···O7 ^{xi}	0.82	2.51	3.008 (17)	120

Symmetry codes: (viii) $-x, -y - 1, z + \frac{1}{2}$; (ix) $x, -y - 1, z + \frac{1}{2}$; (x) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (xi) $x + \frac{1}{2}, y + \frac{1}{2}, z + 1$; (xii) $-x + \frac{1}{2}, y + \frac{1}{2}, z + 1$.

On account of their rather anisotropic displacement ellipsoids, split-site refinements were attempted for atoms O5 and O7 but no improvement in the refinement resulted. It appears that atoms O5 and O7 naturally have higher anisotropy in this structure. H atoms of water molecules and hydroxyl groups were positioned geometrically (O—H = 0.82 and 0.86 \AA , respectively) and refined as riding with the constraint $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ applied.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *CAMERON* (Betteridge *et al.*, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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