

Dirubidium dicadmium sulfate at
293 K

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The structure of $\text{Rb}_2\text{Cd}_2(\text{SO}_4)_3$ at room temperature has been refined using X-ray diffraction data. The structure is similar to that of other cubic langbeinites. However, the title compound differs from other type I langbeinites in that the bond-valence sums of the metal cations (in particular the Rb atoms) are practically equal to their nominal chemical valences.

Comment

Dirubidium dicadmium sulfate, $\text{Rb}_2\text{Cd}_2(\text{SO}_4)_3$ (RCdS), belongs to the langbeinite family, whose general formula is $A_2B_2(\text{XY}_4)_3$, where A is K, Tl, Cs, Rb or NH_4 , B is Mg, Zn, Fe, Ni, Cd, Co, Ca or Mn, and XY_4 is a divalent tetrahedral group, such as SO_4 , BeF_4 or SeO_4 . Langbeinites have a common high-temperature cubic phase (space group $P2_13$) and take their names from the natural mineral $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$ (langbeinite), the structure of which was solved at room temperature by Zemmann & Zemmann (1957). RCdS undergoes three successive phase transitions, at 129, 103 and 68 K, which have been studied by several experimental techniques, *viz.* dielectric measurements (Hikita *et al.*, 1976, 1980; Maeda, 1980), X-ray diffraction (Yamada & Kawano, 1977), thermal expansion (Kahrizi & Steinitz, 1988), elastic measurements (Hikita *et al.*, 1976; Maeda, 1980), electric polarization (Yamada, 1979), light scattering (Latush *et al.*, 1983) and electron paramagnetic resonance (Franco *et al.*, 1996). On the basis of the theoretical work of Dvorák (1972, 1974), the space groups of the three low-temperature phases were determined to be $P2_1$, $P1$ and $P2_12_12_1$, respectively (Hikita *et al.*, 1976; Yamada & Kawano, 1977; Maeda, 1980). Nevertheless, none of the four phases of RCdS has been determined. The present work reports the structure of RCdS at room temperature.

The cubic structure of RCdS (Fig. 1) is similar to that of the sulfates of the langbeinite family (Speer & Salje, 1986; Abrahams *et al.*, 1978; Yamada *et al.*, 1981; Zemmann & Zemmann, 1957; Guelylah, Madariaga & Breczewski, 1996) and comprises SO_4 tetrahedra and distorted coordination polyhedra around the Rb and Cd cations. The metal cations occupy

special positions along the threefold axes. Each Rb atom is surrounded by nine O atoms (up to the third coordination shell, *i.e.* contacts below 3.3 Å) that form complicated polyhedra of similar volume (Fig. 2). Atoms Cd1 and Cd2 are each coordinated by six O atoms, forming distorted octahedra that are generated by the application of the threefold axes on the symmetry independent O3, O4, O1 and O2 atoms. Atoms Cd1 and Cd2 are not at the mid-points of the octahedra, but are shifted by 0.033 (2) Å toward the O4 triplet for Cd1 and by 0.139 (2) Å toward the O2 triplet for Cd2. These displacements within the octahedra are practically identical to those observed in the cubic structure of TCdS (Guelylah, Madariaga & Breczewski, 1996). In contrast to the SO_4 deformation observed in the cubic structure of TCdS, the SO_4 group in RCdS is regular (Table 1), with S—O distances in the range 1.449 (6)–1.464 (7) Å [mean value 1.455 (6) Å] and O—S—O angles in the range 107.5 (4)–112.0 (4)° [mean value

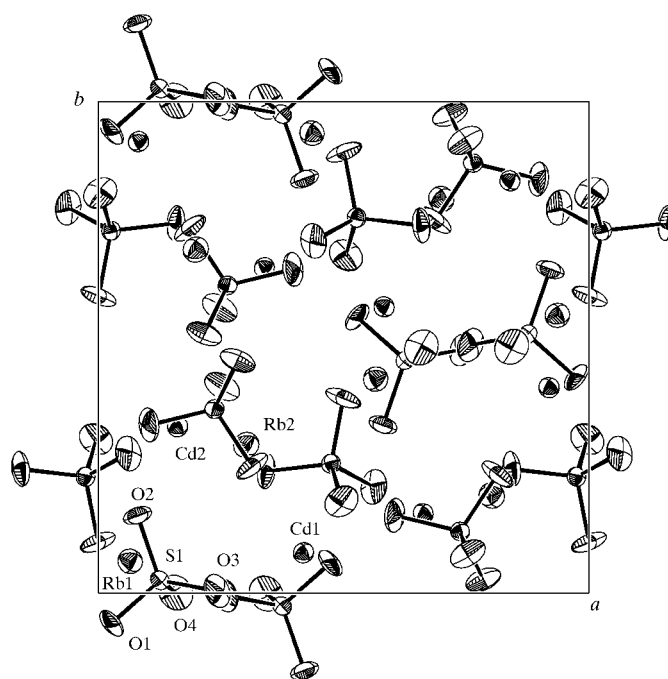


Figure 1
Projection of the cubic structure of $\text{Rb}_2\text{Cd}_2(\text{SO}_4)_3$ along the (001) direction, showing displacement ellipsoids at the 50% probability level. Only the asymmetric unit has been labeled.

109.5 (4)°]. The atomic displacement parameters of the Rb, Cd and S atoms are virtually identical. As seen for other langbeinite compounds, there is strong anisotropy for the O atoms, which show small displacements along and large displacements perpendicular to the S—O direction. The displacement ellipsoids are, therefore, very large and disc-shaped. This anisotropy is a common characteristic of the sulfate groups in cubic langbeinite structures and has also been observed in different potassium langbeinites (Abrahams *et al.*, 1978; Yamada *et al.*, 1981; Speer & Salje, 1986), TCdS and $\text{K}_2\text{Mn}_2(\text{BeF}_4)_3$ (Guelylah, Breczewski & Madariaga, 1996).

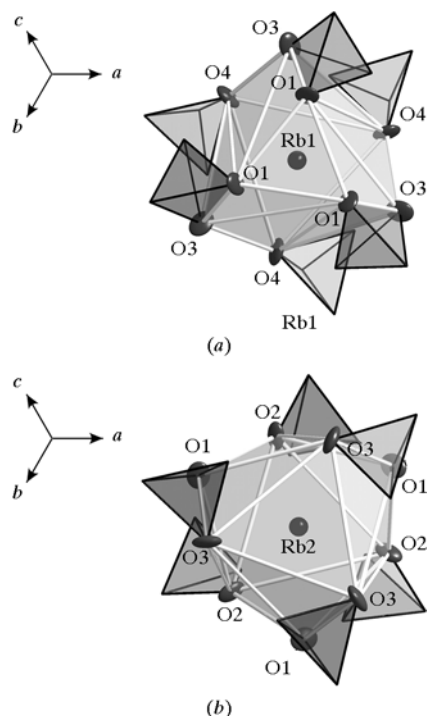


Figure 2
Projection along the $(\bar{1}, \bar{1}, 1)$ direction of the coordination polyhedra of cations Rb1 (a) and Rb2 (b). The O1/O3 pairs belong to the same SO₄ tetrahedron and define edges of the cation cage. Atoms O4 (for Rb1) and O2 (for Rb2) are common vertices of both the cation polyhedron and the corresponding tetrahedral sulfate ion.

In order to compare the cation binding, the bond-valence sums (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991) were calculated (Table 2). Unlike the TCdS structure, in which some atoms were loosely bonded (T11) and others tightly bonded (S), bond-valence sums in RCdS are closer to the respective chemical valences, indicating that the atoms are normally bonded. Even the strong asymmetry in bond strength observed in TCdS for the T11 and T12 cations is reduced in RCdS, although it is still higher than 0.14 v.u. (valence units). Nevertheless, for type II langbeinites, such as K₂Cd₂(SO₄)₃ (KCdS), which differ only in the monovalent cations from RCdS and TCdS, the bond-valence sums for the two K atoms are almost equal (0.83 and 0.88 for K1 and K2, respectively; Guelylah, Madariaga & Breczewski, 1996). This asymmetry in the bond strength of monovalent cations could be responsible for the different sequence of phase transitions observed in both types of langbeinites.

Experimental

Single crystals of Rb₂Cd₂(SO₄)₃ were grown from stoichiometric saturated aqueous solutions by a steady-state method at 363 K. The stock reagents used for the synthesis were chemically pure Rb₂CO₃, CdCO₃ and H₂SO₄. The product of the synthesis was purified by recrystallization from distilled water; the pH of the solution was adjusted to be approximately 1.5. The crystals measured 4 × 4 × 4 mm, and were colorless and of good optical quality. Their morphology was similar to that of Rb₂Cd₂(SO₄)₃ and Tl₂Cd₂(SO₄)₃

crystals obtained by Brezina & Havránková (1974). A sphere of radius 0.18 (1) mm, ground using an Enraf–Nonius grinder, was mounted on a glass fiber for data collection.

Crystal data

Rb₂Cd₂(SO₄)₃
M_r = 683.9
Cubic, *P*2₁3
a = 10.391 (2) Å
V = 1121.8 (4) Å³
Z = 4
D_x = 4.048 Mg m⁻³
Mo Kα radiation

Cell parameters from 1357 reflections
θ = 2.8–26.1°
μ = 13.03 mm⁻¹
T = 293 K
Sphere, colorless
0.18 (1) mm radius

Data collection

Stoe IPDS diffractometer
Image plate with oscillating crystal geometry
Absorption correction: spherical (*IPDS Software*; Stoe & Cie, 1998)
15 800 measured reflections

745 independent reflections
712 reflections with *I* > 3σ(*I*)
R_{int} = 0.072
θ_{max} = 26.1°
h = -12 → 12
k = -12 → 12
l = -12 → 12

Refinement

Refinement on *F*²
R(*F*) = 0.025
wR(*F*²) = 0.054
S = 2.79
745 reflections
60 parameters
w = 1/[σ²(*I*) + 0.000144 *I*²]
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.95 e Å⁻³

Δρ_{min} = -1.02 e Å⁻³
Extinction correction: B–C type 1
Lorentzian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 0.0274 (16)
Absolute structure: Flack (1983),
307 Friedel reflections
Flack parameter = -0.01 (2)

Table 1

Selected geometric parameters (Å, °).

| | | | |
|----------------------|-----------|-----------------------|-----------|
| Rb1–O1 | 3.223 (6) | Cd1–O4 ⁱ | 2.254 (6) |
| Rb1–O3 | 3.258 (7) | Cd2–O1 ⁱⁱⁱ | 2.294 (6) |
| Rb1–O4 ⁱ | 2.986 (7) | Cd2–O2 | 2.263 (6) |
| Rb2–O1 ⁱ | 3.071 (6) | S1–O1 | 1.454 (6) |
| Rb2–O2 ⁱⁱ | 2.978 (6) | S1–O2 | 1.459 (6) |
| Rb2–O3 ⁱ | 3.212 (7) | S1–O3 | 1.464 (7) |
| Cd1–O3 | 2.276 (6) | S1–O4 | 1.449 (6) |
| O1–S1–O2 | 108.6 (3) | O2–S1–O3 | 110.6 (4) |
| O1–S1–O3 | 107.6 (4) | O2–S1–O4 | 110.6 (4) |
| O1–S1–O4 | 112.0 (4) | O3–S1–O4 | 107.5 (4) |

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

Table 2

Bond-valence sums (v.u.) of atoms of Rb₂Cd₂(SO₄)₃ and Tl₂Cd₂(SO₄)₃ (Guelylah, Madariaga & Breczewski, 1996).

| | Rb ₂ Cd ₂ (SO ₄) ₃ | Tl ₂ Cd ₂ (SO ₄) ₃ |
|-----|---|---|
| Rb1 | 0.846 (6) | 0.61 (3) (T11) |
| Rb2 | 0.995 (5) | 0.83 (4) (T12) |
| Cd1 | 2.264 (15) | 2.13 (10) |
| Cd2 | 2.181 (14) | 2.03 (9) |
| S | 6.29 (5) | 6.7 (3) |
| O1 | 2.12 (3) | 1.96 (9) |
| O2 | 2.08 (3) | 2.18 (9) |
| O3 | 2.05 (3) | 2.17 (11) |
| O4 | 2.13 (3) | 2.25 (9) |

Data collection: *IPDS Software* (Stoe & Cie, 1998); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to refine structure: *JANA2000* (Petricek & Dusek, 2000); molecular graphics: *ORTEP* in *Xtal3.7 System* (Davenport *et al.*, 1999); software used to prepare material for publication: *JANA2000*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1599). Services for accessing these data are described at the back of the journal.

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