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Cs₂Mn₃Te₄

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Abstract

Dicaesium trimanganese tetratelluride, Cs₂Mn₃Te₄, has been synthesized at 1173 K and its structure determined from single-crystal X-ray data. Cs₂Mn₃Te₄ is isostructural with Cs₂Mn₃S₄. The structure comprises layers of edge-sharing manganese-centered tetrahedra stacked perpendicular to [001].

Comment

The reactive flux method (Sunshine, Kang & Ibers, 1987) has proven to be widely applicable to the preparation of ternary and quaternary metal polychalcogenides containing an alkali metal or copper or both. We initially found that the use of Cs₂Te₃ as a reactive flux afforded an interesting result. Substitution of Cs for K in the flux led from K₄Zr₃Te₁₇ (Keane & Ibers, 1991) to Cs₄Zr₃Te₁₆ (Cody & Ibers, 1994). The one-dimensional

Zr/Te chains in these compounds have different stoichiometries and Te—Te bonding. Further explorations of Cs₂Te₃ as a reactive flux have afforded some interesting quaternary and ternary tellurides (Cody, Mansuetto, Pell, Chien & Ibers, 1995) that have no sulfide or selenide analogues. In the course of this work we synthesized the title ternary compound, Cs₂Mn₃Te₄, which turns out to be isostructural with its sulfide analogue (Bronger, Hendriks & Müller, 1988).

Experimental

Cs₂Te₃, Mn (Johnson Matthey, 99.9%) and Te (Aldrich, 99.8%) were combined in the molar ratio 2:2:3 (total weight 250 mg). Cs₂Te₃ was synthesized at 194 K from the stoichiometric reaction of Cs (Aldrich, 99.5%) and Te in liquid ammonia under an N₂ atmosphere. The reaction mixture was ground together, sealed under vacuum in a fused silica tube, heated to 1173 K for 8 d and then cooled to room temperature at 3 K h⁻¹. The resulting air-sensitive red plates were manually extracted from the melt. EDS analysis of these crystals with a Hitachi S-570 SEM showed the presence of caesium, manganese and tellurium in the approximate ratio 2:3:4.

Crystal data

Cs₂Mn₃Te₄
M_r = 941.04
 Orthorhombic
Ibam
a = 6.454 (2) Å
b = 12.752 (4) Å
c = 15.387 (5) Å
V = 1266.3 (7) Å³
Z = 4
D_x = 4.936 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 24 reflections
 θ = 17.0–18.5°
 μ = 17.58 mm⁻¹
T = 108 (2) K
 Plate
 0.536 × 0.071 × 0.062 mm
 Red

Data collection

Picker diffractometer
 θ–2θ scans
 Absorption correction:
 analytical (de Meulenaer
 & Tompa, 1965)
T_{min} = 0.225, *T_{max}* = 0.414
 3645 measured reflections
 964 independent reflections
 796 reflections with
I > 2σ(*I*)

R_{int} = 0.0733
 θ_{max} = 30.01°
h = –9 → 5
k = –17 → 13
l = –21 → 21
 6 standard reflections
 every 100 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R(*F*) = 0.034
wR(*F*²) = 0.082
S = 1.266
 964 reflections
 25 parameters
w = 1/[σ²(*F_o*²) + (0.04*F_o*²)²]
 (Δ/σ)_{max} < 0.001

Δρ_{max} = 3.39 e Å⁻³
 Δρ_{min} = –1.54 e Å⁻³
 Extinction correction:
 SHELXL93
 Extinction coefficient:
 0.00151 (9)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

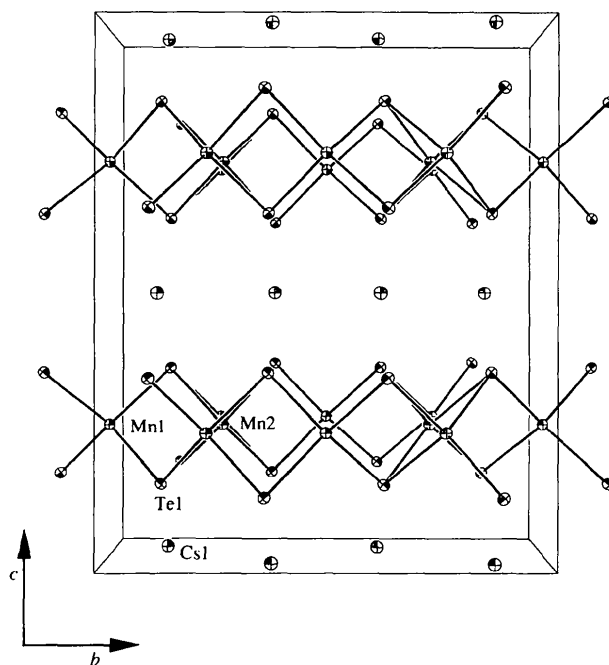


Fig. 1. The unit cell of Cs₂Mn₃Te₄ showing displacement ellipsoids at the 50% probability level.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Cs1	0.23511 (7)	0.12217 (3)	0	0.01346 (16)
Mn1	1/2	0	1/4	0.0100 (3)
Mn2	0	0.24009 (8)	1/4	0.0096 (2)
Te1	0.23314 (5)	0.37052 (2)	0.14642 (2)	0.00973 (15)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Cs1—Te1	3.8865 (10)	Mn1—Te1 ⁱⁱ	2.7442 (6)
Cs1—Te1 ⁱ	3.9263 (10)	Mn2—Te1 ^{iv}	2.7379 (7)
Cs1—Te1 ⁱⁱ	3.9262 (10)	Mn2—Te1 ^v	2.7515 (8)
Cs1—Te1 ⁱⁱⁱ	3.9471 (10)		
Te1 ⁱⁱ —Mn1—Te1 ^{vi}	106.02 (2)	Te1 ^{iv} —Mn2—Te1 ^v	107.73 (2)
Te1 ⁱⁱ —Mn1—Te1 ^{vii}	113.49 (2)	Te1 ^{vii} —Mn2—Te1 ^v	108.56 (2)
Te1 ^{vi} —Mn1—Te1 ^{vii}	108.99 (2)	Te1 ^v —Mn2—Te1	105.62 (4)
Te1 ^{iv} —Mn2—Te1 ^{vii}	117.98 (4)		

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

Cell parameters were taken from a least-squares fit to 24 reflections automatically centered in the range $34 < 2\theta$ ($\text{Mo K}\alpha_1$) $< 37^\circ$. Intensity data were processed (Waters & Ibers, 1977) and corrected for absorption (de Meulenaer & Tompa, 1965) on an IBM RS/6000 series computer. The initial Cs, Mn and Te atom positional parameters were obtained from the structure of the isostructural compound Cs₂Mn₃S₄ (Bronger, Hendriks & Müller, 1988). The structure was refined with the program *SHELXL93* (Sheldrick, 1993). The refinement included anisotropic displacement parameters and an extinction parameter. The final difference electron density map shows no feature with a height greater than 1.6% that of a Cs atom.

Data collection: local program. Cell refinement: local program. Data reduction: local program. Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OH1099). Services for accessing these data are described at the back of the journal.

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Potassium Strontium Tetraborate Decahydrate and Ammonium Calcium Tetraborate Octahydrate

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Abstract

The crystal structures of potassium strontium tetraborate decahydrate, K₂Sr[H₄B₄O₉]₂·10H₂O, and ammonium calcium tetraborate octahydrate, (NH₄)₂Ca[H₄B₄O₉]₂·8H₂O, have been determined. The two structures have similar cell parameters but different space groups. The first compound is homeotypic and the second is isotypic with potassium calcium tetraborate octahydrate and rubidium strontium tetraborate octahydrate. The structures contain alternate layers of tetraborate ions and two of the water molecules, along with the cations and the remaining water molecules. The cation size and the hydrolysis constant of each cation define the space group and the number of water molecules of hydration.

Comment

The crystal structures of tetraborate compounds have been extensively explored in recent years. The structures the following monovalent-ion tetraborates have been solved: NH₄ (Janda, Heller & Pickardt, 1981), Na (Menchetti & Sabelli, 1978; Powell, Gaines, Zerella & Smith, 1991), K (Marezio, Plettinger & Zachariassen, 1963) and Tl (Touboul, Bois & Amoussou, 1983). Only the structures of tetraborates containing Mg (Wan & Ghose, 1977) and Mn (Berzinja, Ozols & Ievinsh, 1975) as divalent ions and [K,Ca] (Solans, Font-Altaba, Solans & Domènech, 1982) and [Rb,Sr] (Ivchenko & Kurkutova, 1975) as mixed monovalent and divalent ions have been solved. The last two compounds are orthorhombic with cell parameters close to $a = 16.7$, $b = 12.7$ and $c = 11.6$ Å, space group $P2_12_12_1$. Potassium strontium tetraborate decahydrate, (1), and ammonium calcium tetraborate octahydrate, (2), have similar cell parameters to the [K,Ca] and [Rb,Sr] compounds but the space group of (1) is $Pna2_1$ while (2) has the same space group as the [K,Ca] tetraborate ($P2_12_12_1$).

The crystal structures of four of the mixed monovalent and divalent compounds and the NH₄ and K compounds contain alternate layers of tetraborate anions and two of the water molecules, and are completed by the cations and the remaining water molecules. Different