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Cs_3TaS_4

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Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(Ta–S) = 0.001 Å
R factor = 0.025
wR factor = 0.071
Data-to-parameter ratio = 33.7

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

Tricesium tantalum tetrasulfide, Cs_3TaS_4, crystallizes in space group *Pnma* of the orthorhombic system. It is isostructural with K_3VS_4. In the asymmetric unit, the site symmetries of one of the Cs atoms, the Ta atom, and two of the S atoms are *m*. The structure consists of the packing of discrete Cs^+ cations and nearly regular tetrahedral TaS_4^{3-} anions.

Comment

Cs_3TaS_4 is a member of the large family A_3MQ_4 (A is an alkali metal, M = V, Nb or Ta, and Q = S or Se), which includes 13 compounds whose structures are known from single-crystal X-ray or neutron diffraction powder studies: Na_3VS_4 (Klepp & Gabl, 1997), Na_3NbS_4 (Niewa *et al.*, 1998), Na_3TaS_4 (Herzog, Näther, Dürichen & Bensch, 1998; Niewa *et al.*, 1998), K_3VS_4 (van den Berg & de Vries, 1964; Dürichen & Bensch, 1996), K_3NbS_4 (Latroche & Ibers, 1990), K_3NbSe_4 (Latroche & Ibers, 1990), K_3TaS_4 (Herzog, Näther & Bensch, 1998), Rb_3VS_4 (Emirdag-Eanes & Ibers, 2001), Rb_3NbS_4 (Krause *et al.*, 1998; Niewa *et al.*, 1998), Rb_3TaS_4 (Niewa *et al.*, 1998), Cs_3VS_4 (Emirdag-Eanes & Ibers, 2001), Cs_3NbSe_4 (Krause *et al.*, 1999) and Cs_3TaSe_4 (Yun *et al.*, 1988). Whereas Na_3VS_4 crystallizes in the tetragonal system and Na_3NbS_4 and Na_3TaS_4 crystallize in *F*-centered orthorhombic cells, the K, Rb, and Cs compounds crystallize in space group *Pnma* (standard setting) of the orthorhombic system and are of the K_3VS_4 structure type (van den Berg & de Vries, 1964). We report here the structure of Cs_3TaS_4, which is a new member of this family of isostructural compounds.

Fig. 1 shows the asymmetric unit and Fig. 2 shows the crystal structure, which comprises discrete Cs^+ cations and tetrahedral TaS_4^{3-} anions. The two crystallographically independent Cs cations are each coordinated by seven S atoms in an irregular polyhedron. The Cs1—S distances range from 3.4632 (9) to 3.7274 (11) Å and the Cs2—S distances range from 3.4374 (14) to 4.0975 (11) Å, comparable to those of 3.4061 (9)–3.6082 (9) and 3.4392 (9)–4.118 (1) Å in Cs_3VS_4

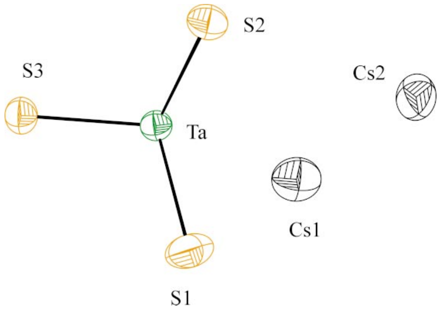

Figure 1
A view of the asymmetric unit of Cs_3TaS_4, with displacement ellipsoids at the 90% probability level.

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(Emirdag-Eanes & Ibers, 2001). The Ta—S bond distances are 2.2691 (9), 2.272 (1) and 2.278 (1) Å, consistent with those of 2.264 (3), 2.266 (2) and 2.269 (2) Å in K_3TaS_4 (Herzog, Näther & Bensch, 1998). The S—Ta—S angles range from 108.38 (3) to 112.16 (5)°, comparable to those of 108.48 (9)–111.43 (12)° in K_3TaS_4 (Herzog, Näther & Bensch, 1998).

Experimental

Cs_3TaS_4 was obtained as colorless flat plates from a solid-state reaction of Cs_2S_3 (1.0 mmol), Ta (Alfa Aesar, 99.9%, 1.0 mmol), Li_2S (0.5 mmol) and S (Aldrich, 99.9%, 1.0 mmol). The Cs_2S_3 reactive flux and Li_2S were prepared by the stoichiometric reaction of Cs (Aldrich, 99.5%) or Li (Aldrich, 99.5%) with S in liquid NH_3. The reactants were loaded in a fused-silica tube that was then evacuated to 10^{-4} Torr (1 Torr = 133.322 Pa). The tube was heated to 773 K, kept at 773 K for 72 h, cooled at 4 K h^{-1} to 373 K, and then the furnace was turned off. The reaction mixture was washed with dimethylformamide. The yield was about 10% based on Ta.

Crystal data

Cs_3TaS_4
$M_r = 707.92$
Orthorhombic, *Pnma*
$a = 9.9205$ (8) Å
$b = 11.5070$ (10) Å
$c = 9.9406$ (9) Å
$V = 1134.77$ (17) Å^3
$Z = 4$
$D_x = 4.144$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 5650 reflections
$\theta = 2.7$–28.8°
$\mu = 19.83$ mm^{-1}
$T = 153$ (2) K
Plate, colorless
0.43 × 0.124 × 0.046 mm

Data collection

Bruker SMART 1000 CCD diffractometer
0.3° ω scans
Absorption correction: numerical face indexed (*SHELXTL*, Sheldrick, 2003)
$T_{min} = 0.037$, $T_{max} = 0.396$
12 415 measured reflections

1482 independent reflections
1462 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 28.8°$
$h = -13 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.071$
$S = 1.20$
1482 reflections
44 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 3.16$ e Å^{-3}
$\Delta\rho_{min} = -3.04$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00075 (13)

Table 1
Selected geometric parameters (Å, °).

Cs1—S3^{i}	3.4632 (9)	Cs2—S2^{vii}	3.5763 (14)
Cs1—S3^{ii}	3.5085 (9)	Cs2—S2	3.6825 (14)
Cs1—S1^{iii}	3.5343 (10)	Cs2—S1^{iii}	3.6915 (10)
Cs1—S1^{iv}	3.5588 (10)	Cs2—S1^{v}	4.0974 (11)
Cs1—S1^{v}	3.6221 (11)	Ta—S1	2.2691 (9)
Cs1—S2	3.6271 (6)	Ta—S3	2.272 (1)
Cs1—S2^{ii}	3.7274 (11)	Ta—S2	2.278 (1)
Cs2—S3^{vi}	3.4374 (14)		
S1^{iv}—Ta—S1	112.16 (5)	S1—Ta—S2	109.56 (3)
S1—Ta—S3	108.38 (3)	S3—Ta—S2	108.74 (4)

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

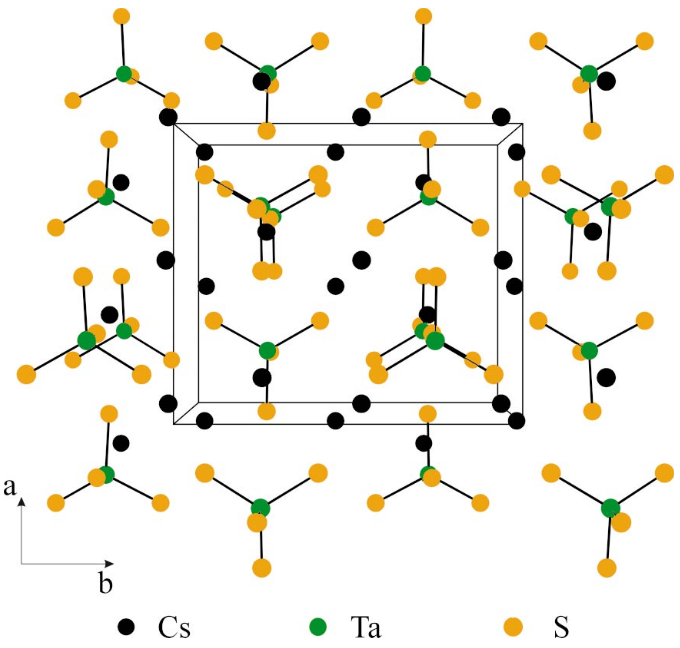

Figure 2
The structure of Cs_3TaS_4, viewed down [001].

The highest residual electron density is 0.04 Å from the Ta site, and the deepest hole is 0.81 Å from this same site.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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