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K_2TeS_3

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Abstract

The reaction of K_2S_3, tellurium and sulfur yields light-yellow single crystals of dipotassium tellurium trisulfide, K_2TeS_3. The structure consists of isolated TeS_3^{2-} anions, and K^+ cations coordinated by six S atoms from five different TeS_3^{2-} anions within distorted octahedra.

Comment

This work is part of a project on the synthesis of new ternary and quaternary chalcogenides prepared in reactive alkali-metal polychalcogenide fluxes. The title compound was obtained as light-yellow air-sensitive crystals by the reaction of elemental iron and tellurium in a potassium polysulfide flux at 573 K. In an earlier communication, it was assumed that the compound crystallizes in the orthorhombic crystal system, with a = 9.06 (2), b = 13.13 (2) and c = 6.40 (2) Å (Eisenmann *et al.*, 1969). From the observed extinction rules, the two space groups $Pmn2_1$ and $Pmmn$ were proposed. Unfortunately, no further structural details were reported. Our investigations using single-crystal X-ray experiments demonstrate clearly that the title compound crystallizes in the monoclinic system, with angle β = 90.40 (2)°. The monoclinic symmetry is supported by the low internal R value. Averaging symmetry-related reflections assuming the Laue symmetry mmm leads to an internal R value of 32%. The observed extinction rules for the orthorhombic space group $Pmn2_1$ observed in the work of Eisenmann *et al.* (1969) are the same as in the space group $P2_1/n$.

In the crystal structure, the TeS_3^{2-} anions are arranged in layers parallel to the (101) plane, with the K^+ cations located between them. The Te atoms exhibit three intermolecular contacts to S atoms of 3.680 (2), 4.042 (2) and 4.063 (2) Å, which are too long to be treated as bonds. In the resulting strongly distorted TeS_6 octahedra, the Te atom is shifted from the center of the octahedra, effectively forming only three bonds to the S atom. Another way to describe the structure starts with a close-packed arrangement of S atoms. The K^+ cations occupy two-thirds and the Te atoms one-third of the octahedral sites. The K^+ cation is coordinated by six S atoms within a distorted octahedron, with typical K—S distances in the range 3.136 (2)–3.294 (2) Å for K1, and in the range 3.145 (2)–3.536 (2) Å for K2. The shortest K···Te contact amounts to 4.038 (1) Å. The TeS_3^{2-} anions form trigonal pyramids, with Te—S distances ranging from 2.341 (1) to 2.356 (1) Å (average 2.350 Å). The Te atoms are about 1.023 Å above the plane defined by the three S atoms. The S—Te—S angles [102.14 (3)–103.09 (3)°] deviate from ideal values due to the steric demands of the electron lone pair at the Te atom. The S···S distances within the TeS_3^{2-} anion range from 3.6534 to 3.6767 Å. The geometrical parameters of TeS_3^{2-} are comparable to those in other TeS_3^{2-}-containing compounds like $K_3(SH)TeS_3$ (Dittmar & Schäfer, 1978), $BaTeS_3$ (Jumas *et al.*, 1976) and $(NH_4)_2TeS_3$ (Gerl *et al.*, 1974). We note that the TeS_3^{2-} anion is also found in transition metal compounds like $Cs_6Cu_2(TeS_3)_2(S_6)_2$ (McCarthy *et al.*, 1993), $AMTeS_3$ (A = K, Rb, Cs; M = Cu, Ag; Zhang & Kanatzidis, 1994*a*), $A_2Mn(TeS_3)_2$ (A = Cs, Rb) (Zhang & Kanatzidis, 1994*b*) and $(CuI)_3Cu_2TeS_3$ (Pfitzner & Zimmerer, 1997). A tetraphenylphosphonium salt containing the TeS_3^{2-} anion has also been reported (Rubenheim *et al.*, 1994).

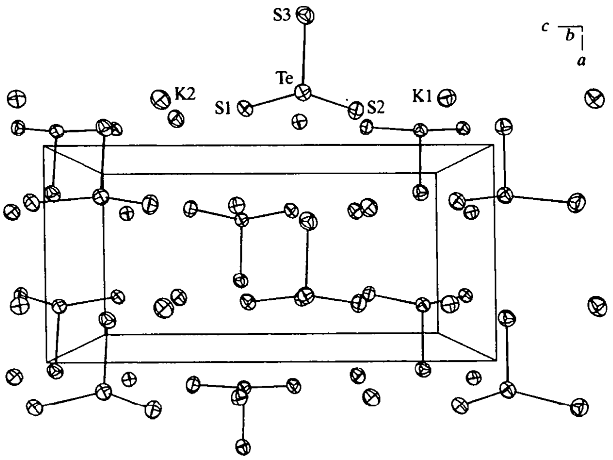

Fig. 1. The crystal structure of K_2TeS_3 viewed along the b axis. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

K_2TeS_3 was prepared by the reaction of K_2S_3, Fe, Te and S in the ratio 2:1:3.3:4. K_2S_3 was prepared from stoichiometric amounts of K and S in liquid ammonia under an argon atmosphere. The starting materials were mixed thoroughly in a dry-box and sealed into a Pyrex-glass ampoule, which was evacuated at 1.0×10^{-3} mbar (1 mbar = 100 Pa). The ampoule was heated at 573 K for 6 d and then cooled down to 293 K at a rate of $3\,\mathrm{K\,h^{-1}}$. The resulting melt was washed with dimethylformamide and the residue was dried in a vacuum.

Crystal data

K_2TeS_3
$M_r = 301.98$
Monoclinic
$P2_1/n$
$a = 6.360\,(1)$ Å
$b = 9.059\,(2)$ Å
$c = 13.224\,(2)$ Å
$\beta = 90.40\,(2)^\circ$
$V = 762.0\,(2)$ Å^3
$Z = 4$
$D_x = 2.632$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 108 reflections
$\theta = 12$–19°
$\mu = 5.699$ mm^{-1}
$T = 293\,(2)$ K
Block
$0.30 \times 0.08 \times 0.08$ mm
Light yellow

Data collection

Stoe AED-II four-circle diffractometer
ω–θ scans
Absorption correction: ψ scan (*XEMP* in *SHELXTL/PC*; Siemens, 1990)
$T_{\min} = 0.421$, $T_{\max} = 0.634$
2676 measured reflections
2219 independent reflections

1955 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.024$
$\theta_{\max} = 30^\circ$
$h = -8 \rightarrow 0$
$k = -12 \rightarrow 1$
$l = -18 \rightarrow 18$
4 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.061$
$S = 1.174$
2218 reflections
56 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0174P)^2 + 1.6156P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.064$ e Å^{-3}
$\Delta\rho_{\min} = -0.623$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0025 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\mathrm{eq}} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Te	0.70511 (3)	0.82165 (2)	0.41785 (2)	0.02610 (7)
S1	0.74723 (13)	0.66526 (10)	0.55871 (6)	0.0293 (2)
S2	0.75806 (14)	0.65838 (11)	0.28173 (6)	0.0318 (2)
S3	0.34131 (14)	0.85992 (10)	0.41104 (7)	0.0303 (2)
K1	0.75257 (11)	0.36719 (9)	0.41616 (6)	0.0305 (2)
K2	0.74136 (13)	0.39334 (9)	0.75045 (6)	0.0350 (2)

Table 2. *Selected geometric parameters (Å, °)*

Te—S3	2.3408 (10)	S1—K1	3.2936 (13)
Te—S1	2.3541 (9)	S1—K2	3.5357 (13)
Te—S2	2.3558 (9)	S2—K1	3.1814 (13)
Te—K1$^{\mathrm{i}}$	4.0385 (9)	S2—K1$^{\mathrm{iv}}$	3.2294 (12)
Te—K2$^{\mathrm{i}}$	4.0892 (10)	S2—K2$^{\mathrm{i}}$	3.2359 (13)
Te—K1	4.1282 (10)	S2—K2$^{\mathrm{ii}}$	3.2491 (14)
S1—K1$^{\mathrm{ii}}$	3.2099 (12)	S3—K1$^{\mathrm{i}}$	3.1355 (12)
S1—K1$^{\mathrm{i}}$	3.2120 (13)	S3—K2$^{\mathrm{v}}$	3.1451 (12)
S1—K2$^{\mathrm{iii}}$	3.2621 (13)	S3—K2$^{\mathrm{i}}$	3.1759 (13)
S3—Te—S1	103.09 (3)	S1—Te—S2	102.16 (3)
S3—Te—S2	102.14 (3)		

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

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *DIAMOND* (Bergerhoff, 1996). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1244). Services for accessing these data are described at the back of the journal.

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