

Table 1. Selected geometric parameters (Å, °)

As—S ¹	2.236 (3)	Li2—S2	2.44 (2)
As—S2	2.255 (3)	Li2—S3 ⁱⁱ	2.44 (2)
As—S1 ⁱⁱⁱ	2.266 (2)	Li2—S1	2.46 (2)
Li1—S3	2.46 (2)	Li2—S2 ⁱⁱⁱ	2.48 (2)
Li1—S3 ⁱⁱⁱ	2.48 (2)	Li3—S2 ^{vi}	2.39 (2)
Li1—S2 ^{iv}	2.56 (2)	Li3—S1	2.51 (2)
Li1—S1	2.70 (2)	Li3—S3	2.56 (2)
Li1—S1 ^v	2.76 (2)	Li3—S1 ^{vii}	2.58 (2)
S1 ⁱⁱ —As—S2	100.25 (9)	S3 ⁱⁱ —Li2—S1	122.2 (7)
S1 ⁱⁱⁱ —As—S3 ⁱ	102.14 (9)	S3 ⁱⁱ —Li2—S2 ⁱⁱⁱ	117.7 (7)
S2—As—S3 ⁱ	103.81 (8)	S3 ⁱⁱ —Li2—S2	100.0 (6)
S3—Li1—S3 ⁱⁱⁱ	110.5 (7)	S2—Li2—S2 ⁱⁱⁱ	110.6 (7)
S3—Li1—S1 ^v	109.1 (7)	S2—Li2—S1	105.1 (6)
S3—Li1—S1	99.3 (6)	S1—Li2—S2 ⁱⁱⁱ	100.5 (5)
S3—Li1—S2 ^{iv}	96.5 (6)	S2 ⁱⁱ —Li3—S1	126.1 (7)
S3 ⁱⁱⁱ —Li1—S2 ^{iv}	152.8 (8)	S2 ^{vi} —Li3—S1 ^{vii}	112.3 (7)
S3 ⁱⁱⁱ —Li1—S1	89.7 (6)	S2 ^{vi} —Li3—S3	102.5 (6)
S3 ⁱⁱⁱ —Li1—S1 ^v	83.6 (5)	S1—Li3—S1 ^{vii}	114.5 (6)
S2 ^{iv} —Li1—S1	82.5 (5)	S1—Li3—S3	102.0 (7)
S2 ^{iv} —Li1—S1 ^v	90.9 (6)	S3—Li3—S1 ^{vii}	90.8 (6)
S1—Li1—S1 ^v	151.4 (8)		

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

Single-crystal analyses were performed using crystals loaded into glass capillaries in a glove box under a dry argon atmosphere. The symmetry and space group were determined by Weissenberg and Buerger photographs. Data collection covered half the reciprocal space (6423 reflections). As the single crystals were of poor quality and correcting for the absorption by the crystal and the capillary was difficult, we chose to consider only $\frac{3}{8}$ of the reciprocal space (removing reflections with $h < 0$ and $k < 0$, the great majority of which showed a systematic lowering of intensity). Empirical absorption corrections were carried out using ψ scans of nine reflections in the range $5.7 < \theta < 35.8^\circ$. The structure was solved in the non-centrosymmetric space group $Pna2_1$ by Patterson function deconvolution and heavy-atom methods, using the 1069 independent reflections for which $I > 3\sigma(I)$. $\Delta\rho_{\max}$ and $\Delta\rho_{\min}$ were found near As atoms (at distances of 0.75 and 0.69 Å, respectively). This unusual approach to the structure determination seemed to us to be the best available after several trials with different single crystals. In spite of the preparation and handling difficulties, crystallochemical considerations and bond-valence calculations confirmed that the structural model is correct.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: local programs. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *CERIUS* (Molecular Simulations, 1993). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1180). Services for accessing these data are described at the back of the journal.

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Trirubidium Tetrathioniobate

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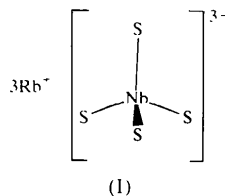
(Received 21 October 1997; accepted 27 January 1998)

Abstract

The reaction of Rb₂S₃, NbO and S yields single crystals of trirubidium tetrathioniobate, Rb₃NbS₄. The crystal structure is based on discrete tetrahedral NbS₄³⁻ anions, which are connected via Rb⁺ cations. The compound crystallizes with the K₃VS₄ structure type and is isotypic with previously reported K and Cs analogues.

Comment

The title compound, (I), was obtained as a by-product during the synthesis of new oxo-chalcogenide compounds containing alkali and Group 5 metals.



Chalcogenometallates of the alkali metals of composition A_3BX_4 (A = alkali metal; B = V, Nb, Ta; X = S, Se) crystallize with the K₃VS₄ structure type (van den Berg & de Vries, 1964). The following compounds of this type have been reported: the potassium salts K₃NbS₄,

K_3NbSe_4 , K_3TaSe_4 and K_3TaSe_4 (Latroche & Ibers, 1990), the homologous caesium compounds Cs_3NbSe_4 and Cs_3TaSe_4 (Yun *et al.*, 1988), and also $(NH_4)_3VS_4$ (Schäfer, Moritz & Weiss, 1965). Only one isostructural oxometallate, K_3FeO_4 (Hoppe & Mader, 1990), has been reported. This structure type has also been found for thio and seleno salts of Group 15 elements, such as K_3PS_4 (Schäfer, Schäfer & Weiss, 1965), K_3AsS_4 (Palazzi *et al.*, 1974), K_3SbS_4 (Bensch & Dürichen, 1997), K_3SbSe_4 (Eisenmann & Zagler, 1989), Rb_3AsSe_4 (Wachhold & Sheldrick, 1996), Rb_3SbS_4 (Bensch & Dürichen, 1996), Rb_3SbSe_4 (Wachhold & Sheldrick, 1996), $(NH_4)_3SbS_4$ (Wachhold & Sheldrick, 1996) and $(NH_4)_3AsS_4$ (Graf & Schäfer, 1976), and for one Group 13 thiophosphate, Tl_3PS_4 (Taffoli *et al.*, 1981). Depending on the radius ratio $r(A^+)/r(X^-)$, these compounds

crystallize either in the orthorhombic or in a related cubic structure type. In the case of larger cations like Rb or Cs, the orthorhombic structure type is preferred. The lower symmetry arises from the increase of the coordination number around the larger alkali metal cations.

Rb_3NbS_4 crystallizes in the centrosymmetric space group $Pnma$. The crystal structure contains discrete tetrahedral complex anions which are connected by rubidium cations. The average Nb—S distance of 2.263 (4) Å and the S—Nb—S angles of 108.32 (5)–112.18 (10)° are in the range observed for other niobium(V) sulfides. There are two crystallographically independent Rb^+ cations in the asymmetric unit. The Rb1 ion is coordinated by seven S atoms of four symmetry-related NbS_4^{3-} anions within an irregular polyhedron. The average Rb1—S distance is 3.446 (3) Å. In contrast, the Rb2 ion is coordinated by seven S atoms of five symmetry-related NbS_4^{3-} anions. This cation exhibits one short Rb—S distance [3.249 (4) Å], four medium Rb—S distances [average 3.519 (4) Å] and one long Rb—S distance [3.908 (3) Å].

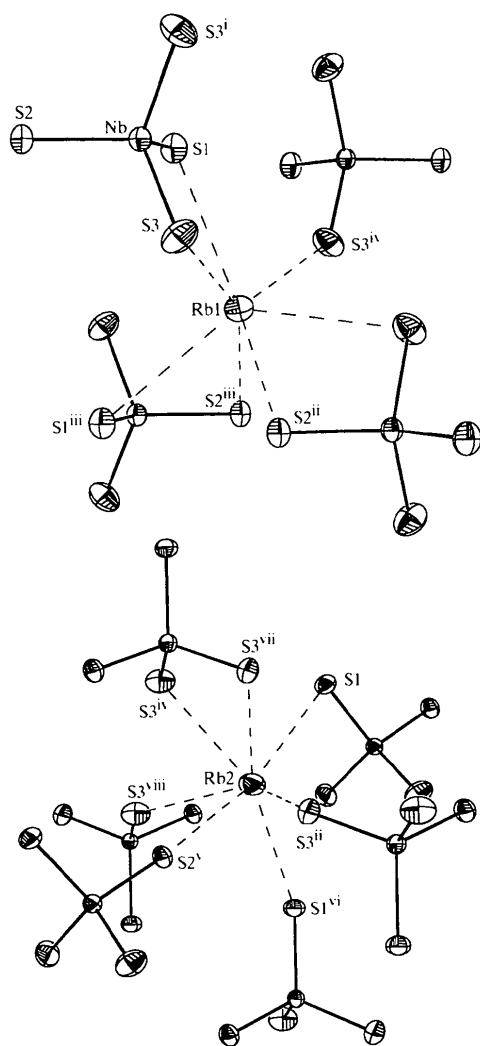


Fig. 1. Coordination spheres of the Rb cations with labelling and displacement ellipsoids drawn at the 50% probability level (symmetry codes are as given in Table 1).

Experimental

Single crystals of Rb_3NbS_4 were obtained under the following conditions; all manipulations were performed under nitrogen using a glove box and conventional Schlenk techniques. The starting compounds, Rb_2S_3 , NbO and S, were thoroughly mixed in a 2:1:2 ratio and sealed in a Pyrex ampoule, which was evacuated to 6×10^{-7} Pa. (Rb_2S_3 was prepared by the reaction of stoichiometric amounts of Rb and S in liquid ammonia under an argon atmosphere.) The ampoule was heated to 350 K over a period of 6 d and then cooled to room temperature at a rate of 3 K h^{-1} . The resulting melt was washed with DMF and ether, and the residue was dried *in vacuo*. The product consists of three different compounds: grey Rb_3NbO_8 powder, red crystals of $Rb_4Nb_2S_{10}O$ (Krause *et al.*, 1998) and yellow transparent crystals of Rb_3NbS_4 . The title compound is sensitive to humidity and must be stored under dry conditions.

Crystal data

Rb_3NbS_4
 $M_r = 477.56$
 Orthorhombic
Pnma
 $a = 9.627(2) \text{ \AA}$
 $b = 11.119(2) \text{ \AA}$
 $c = 9.562(2) \text{ \AA}$
 $V = 1023.5(4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 3.099 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 94 reflections
 $\theta = 15.0\text{--}21.5^\circ$
 $\mu = 16.085 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Block
 $0.15 \times 0.10 \times 0.07 \text{ mm}$
 Yellow

Data collection

Stoe AED-II four-circle diffractometer
 ω – θ scans

917 reflections with
 $I > 2\sigma(I)$
 $R_{int} = 0.037$

Absorption correction: $\theta_{\max} = 27.23^\circ$
 empirical via ψ scans $h = -4 \rightarrow 12$
 (XEMP in SHELXTL/PC; $k = 0 \rightarrow 14$
 Siemens, 1990) $l = 0 \rightarrow 12$
 $T_{\min} = 0.190$, $T_{\max} = 0.331$ 4 standard reflections
 1737 measured reflections frequency: 120 min
 1187 independent reflections intensity decay: < 1%

Refinement

Refinement on F^2 $\Delta\rho_{\max} = 1.531 \text{ e } \text{\AA}^{-3}$
 $R[F^2 > 2\sigma(F^2)] = 0.029$ $\Delta\rho_{\min} = -0.658 \text{ e } \text{\AA}^{-3}$
 $wR(F^2) = 0.075$ Extinction correction:
 $S = 1.016$ SHELXL93 (Sheldrick,
 1187 reflections 1993)
 44 parameters Extinction coefficient:
 $w = 1/[\sigma^2(F_o^2) + (0.0349P)^2$ 0.0238 (9)
 $+ 3.2812P]$ Scattering factors from
 where $P = (F_o^2 + 2F_c^2)/3$ *International Tables for*
 $(\Delta/\sigma)_{\max} < 0.001$ *Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Nb—S2	2.250 (2)	Rb1—S1	3.532 (2)
Nb—S3	2.265 (2)	Rb1—S1 ⁱⁱⁱ	3.613 (2)
Nb—S3 ⁱ	2.265 (2)	Rb2—S2 ^v	3.249 (2)
Nb—S1	2.273 (2)	Rb2—S1 ^{vi}	3.419 (2)
Rb1—S2 ⁱⁱ	3.341 (2)	Rb2—S1	3.519 (2)
Rb1—S2 ⁱⁱⁱ	3.355 (2)	Rb2—S3 ^{vii}	3.569 (2)
Rb1—S3 ^{iv}	3.399 (2)	Rb2—S3 ^{ix}	3.569 (2)
Rb1—S3	3.400 (2)	Rb2—S3 ^x	3.908 (2)
Rb1—S3 ⁱⁱ	3.486 (2)	Rb2—S3 ^{xiii}	3.908 (2)
S2—Nb—S3	108.32 (5)	S2—Nb—S1	108.48 (8)
S2—Nb—S3 ⁱ	108.32 (6)	S3—Nb—S1	109.73 (5)
S3—Nb—S3 ⁱ	112.18 (10)	S3 ⁱ —Nb—S1	109.73 (5)

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

All atoms were refined with anisotropic displacement parameters. The highest residual electron-density peak is located near S3 (1.06 \AA).

Data collection: DIF4 (Stoe & Cie, 1992a). Cell refinement: DIF4. Data reduction: REDU4 (Stoe & Cie, 1992b). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP in SHELXTL/PC (Siemens,

1990). Software used to prepare material for publication: CIFTAB in SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1159). Services for accessing these data are described at the back of the journal.

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