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$Rb_6Nb_4S_{24.4}O_{0.6}$

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The new rubidium niobium sulfide, $Rb_6Nb_4S_{24.4}O_{0.6}$, consists of discrete $[Nb_4S_{24.4}O_{0.6}]^{6-}$ anions and Rb^+ cations. Every Nb^{5+} ion is in a sevenfold coordination by sulfide ions in a strongly distorted pentagonal bipyramid, forming a Nb_2S_{11} unit. Two of these units are interconnected by an S_3 fragment, yielding the complete anion. The anions are stacked parallel to the crystallographic *b* axis and are separated by the Rb^+ ions.

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(S–S) = 0.002 Å
Disorder in main residue
R factor = 0.031
wR factor = 0.077
Data-to-parameter ratio = 22.5

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

Comment

In recent years, our interest was focused on investigations in the $A/M/Q$ system (with A = alkali metal; M = Nb, Ta; Q = O, S, Se). In many compounds, the M_2Q_{11} unit is the general structural motif (Bensch *et al.*, 1999). These M_2Q_{11} units occur as monomeric units or are connected, either directly or *via* additional chalcogenide ligands, to form dimers or polymers. In a preliminary report (Krause *et al.*, 2000), the main features of $Rb_6Nb_4S_{25}$ were given. Here we report the details of the synthesis and characterization of this new ternary niobium polysulfide. Each Nb^{5+} ion is in a sevenfold coordination, forming a strongly distorted pentagonal bipyramid (see Fig. 1). Neglecting the O atom, the coordination mode of the resulting $[Nb_4S_{25}]^{6-}$ anion can be described as $[(Nb_2(\mu_2\text{-}\eta^2,\eta^1\text{-}S_2)_3\text{-}(\eta^2\text{-}S_2)(S)_2)_2(\mu_2\text{-}\eta^1,\eta^1\text{-}S_5)]^{6-}$. Each Nb atom has a short bond to the axial S^{2-} of 2.172 (2) Å (Nb1—S1) or 2.2150 (15) Å (Nb2—S10). Five Nb—S separations are found, in the range 2.5–2.6 Å [2.4587 (15), 2.4567 (15), 2.4416 (13), 2.4578 (14) and 2.5859 (15) Å for Nb1—S, and 2.4951 (15), 2.4637 (15), 2.4382 (14) and 2.4647 (14) Å for Nb2—S]. In a position *trans* to the short Nb—S bonds, long interatomic Nb—S distances of 2.9380 (15) Å (Nb1—S8) and 2.8605 (15) Å (Nb2—S5) are observed, to an S atom of an $\eta^2\text{-}S_2^{2-}$ anion attached to the neighboring Nb atom. As expected, the longer Nb—S distance (Nb1—S8) is *trans* to the shorter terminal Nb—S bond (Nb1—S1). Refined as sulfur, S1 showed larger anisotropic displacement parameters than the other S atoms. In the IR

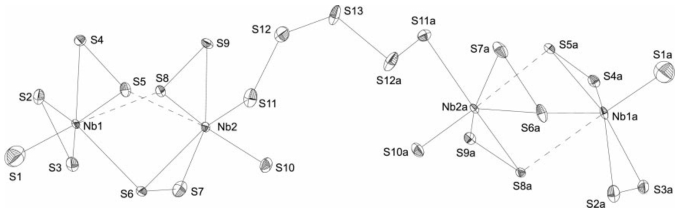

Figure 1
The dimeric $[Nb_4S_{25}]^{6-}$ anion in $Rb_6Nb_4S_{25}$. Ellipsoids are drawn at the 50% probability level. The dashed lines represent the long Nb—S contacts. The O atom, partially substituting for S1, is not shown.

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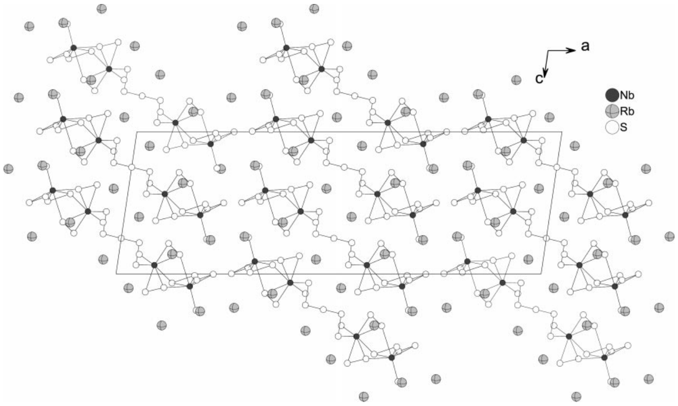

Figure 2
Crystal structure of $Rb_6Nb_4S_{25}$, viewed parallel to the crystallographic *b* axis. The O atoms are not displayed.

spectrum, a weak Nb—O absorption band was observed. Hence, during the structure refinement it was assumed that S1 is partially substituted by oxygen. The refined site-occupation factors for S1/O were 0.7/0.3, yielding the final composition $Rb_6Nb_4S_{24.4}O_{0.6}$. The partial substitution of S1 by O may be responsible for the slight disorder of the Rb3 atom (see below). It is noted that the title compound is not isostructural with the potassium niobium compound $K_6Nb_4S_{25}$ (Bensch & Dürichen, 1996*a*), but is isostructural with $Rb_6Ta_4S_{25}$ (Stoll *et al.*, 2000). The main difference between the anions in both structures is a different conformation around the S_3 unit. It can be assumed that the difference is induced by the larger Rb^+ cation. The S—S distances in the S_2^{2-} anions are between 2.0475 (19) and 2.0912 (19) Å (average 2.073 Å) and are typical for S—S single bonds. The two Nb atoms are displaced from the pentagonal planes composed of S atoms, towards the terminal S atom, by 0.5702 Å (Nb1) and 0.4949 Å (Nb2). The dihedral angle between these planes is 49.9°. The Nb—Nb distance is 3.574 (2) Å, which is too long for any metal-to-metal interaction [radius: 0.69 Å for Nb^{5+} (CN7)] (Shannon, 1976). All values agree well with those reported for $Rb_6Ta_4S_{25}$ (Stoll *et al.*, 2000) and $A_6Nb_4S_{22}$ (A = K, Rb, Cs; Bensch & Dürichen, 1996*b*; Stoll *et al.*, 2002). The three crystallographically independent rubidium cations are in an irregular sulfur environment. Using a cutoff of 4 Å, the mean Rb—S distances are 3.534 for Rb1 (CN9), 3.545 for Rb2 (CN12) and 3.553 Å for Rb3 (CN 10). These values are in good agreement with the sum of the ionic radii [1.84 Å for S^{2-} and 1.66 Å for Rb^{1+} (CN10)] (Shannon, 1976). Rb3 is slightly disordered, influencing particularly the displacement parameters of S1 (see Fig. 1). During refinement the sum of the site-occupation factor of Rb3 and Rb3′ was fixed at 1.00. We note that the Rb3′—S1 distance is rather short, but can be explained on the basis of the partial substitution of S1 by O (see above).

Fitting the $[Nb_4S_{24.4}O_{0.6}]^{6-}$ anion of the title compound to the $[Ta_4S_{25}]^{6-}$ anion of the isotypic $Rb_6Ta_4S_{25}$ compound (Stoll *et al.*, 2000), a mean deviation of only 0.0239 Å is obtained, demonstrating that the geometry of the anion is only slightly influenced by replacing niobium with tantalum and by the small amount of oxygen. The thermal behavior of $Rb_6Nb_4S_{24.4}O_{0.6}$ was investigated using differential scanning calorimetry (DSC). As for $Rb_6Ta_4S_{25}$ (Stoll *et al.*, 2000), the compound decomposes to form the sulfur-poorer compound $Rb_6Nb_4S_{22}$ (Bensch & Dürichen, 1996*b*) at temperatures above 743 K.

Experimental

The compound $Rb_6Nb_4S_{24.4}O_{0.6}$ was prepared by the reaction of Rb_2S_3, Nb and S in the ratio 2:1:12. Rb_2S_3 was prepared from stoichiometric amounts of Rb and S in liquid ammonia under an argon atmosphere. The starting materials were thoroughly mixed in a dry box and sealed into a Pyrex-glass ampoule, which was evacuated to 10^{-3} Pa. The ampoule was heated at 673 K for 4 d, cooled down to 373 K at 3 K h^{-1} and then to room temperature at 12 K h^{-1}. The resulting melt was washed with dry dimethylformamide and the residue was dried *in vacuo*. It consists of orange–red polyhedra, which are slightly contaminated with a yellow powder that has thus far not been identified. The crystals are stable in air for several weeks.

In the IR spectra of $Rb_6Nb_4S_{24.4}O_{0.6}$ the vibrations of the short Nb—S bonds occur at 477.3 and 460.5 cm^{-1}. These values are comparable with those of $K_6Nb_4S_{25}$ (Bensch & Dürichen, 1996*a*), which are found at 478.0 and 459.0 cm^{-1}. In the transformed UV-vis reflectance spectrum, the band gap was determined as 1.98 eV, in agreement with the observed color of $Rb_6Nb_4S_{24.4}O_{0.6}$.

Crystal data

$Nb_4O_{0.6}Rb_6S_{24.4}$
M_r = 1676.32
Monoclinic, $C2/c$
a = 36.868 (7) Å
b = 8.1185 (16) Å
c = 12.515 (3) Å
β = 98.36 (3)°
V = 3706.1 (13) $Å^3$
Z = 4

D_x = 3.004 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7956 reflections
θ = 3–27.2°
μ = 10.42 mm^{-1}
T = 293 (2) K
Polyhedron, red–orange
0.13 × 0.10 × 0.09 mm

Data collection

Stoe Imaging Plate Diffraction System diffractometer
φ scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)
T_{min} = 0.187, T_{max} = 0.327
15576 measured reflections

3889 independent reflections
3296 reflections with $I > 2\sigma(I)$
R_{int} = 0.064
θ_{max} = 26.9°
$h = -46 \rightarrow 46$
$k = -10 \rightarrow 10$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.077
S = 1.05
3889 reflections
173 parameters

$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 14.4654P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 2.23 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.79 e $Å^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00047 (5)

Table 1
Selected geometric parameters (Å).

Nb1—O1	1.71 (2)	Rb2—S10^{iv}	3.6703 (15)
Nb1—S1	2.198 (2)	Rb2—S6	3.8539 (15)
Nb1—S4	2.4419 (12)	Rb2—S6^{iv}	3.9109 (15)
Nb1—S3	2.4568 (13)	Rb3—S1^{vi}	3.346 (2)
Nb1—S5	2.4585 (12)	Rb3—O1	3.45 (2)
Nb1—S2	2.4587 (13)	Rb3—S4	3.457 (2)
Nb1—S6	2.5862 (13)	Rb3—S2^{vi}	3.472 (2)
Nb1—S8	2.9386 (14)	Rb3—S4^{v}	3.474 (2)
Nb2—S10	2.2149 (13)	Rb3—S3^{vii}	3.481 (2)
Nb2—S8	2.4386 (12)	Rb3—S1	3.505 (3)
Nb2—S7	2.4635 (13)	Rb3—S8^{v}	3.505 (2)
Nb2—S9	2.4650 (12)	Rb3—O1^{vi}	3.54 (2)
Nb2—S6	2.4951 (13)	Rb3—S9^{v}	3.658 (2)
Nb2—S11	2.5275 (13)	Rb3—S2^{v}	3.749 (2)
Nb2—S5	2.8600 (13)	Rb3—S5	3.885 (2)
Rb1—S7^{i}	3.4355 (15)	Rb3′—S1^{vi}	2.885 (6)
Rb1—S11^{ii}	3.4614 (15)	Rb3′—O1^{vi}	3.10 (2)
Rb1—S12	3.467 (2)	Rb3′—S2^{vi}	3.379 (8)
Rb1—S10^{i}	3.4978 (14)	Rb3′—S4	3.407 (8)
Rb1—S10^{ii}	3.5148 (15)	Rb3′—S3^{vii}	3.460 (8)
Rb1—S6^{i}	3.5717 (14)	Rb3′—O1	3.50 (2)
Rb1—S9	3.590 (2)	Rb3′—S1	3.546 (9)
Rb1—S10	3.5948 (15)	Rb3′—S4^{v}	3.799 (7)
Rb1—S11^{iii}	3.6682 (14)	Rb3′—S2^{v}	3.887 (8)
Rb2—S1	3.294 (2)	Rb3′—S8^{v}	3.942 (6)
Rb2—S7	3.322 (2)	Rb3′—Nb1^{vi}	3.959 (7)
Rb2—O1	3.34 (2)	S2—S3	2.072 (2)
Rb2—S8^{iv}	3.3583 (13)	S4—S5	2.091 (2)
Rb2—S9^{v}	3.4031 (13)	S6—S7	2.081 (2)
Rb2—S4^{v}	3.4144 (15)	S8—S9	2.066 (2)
Rb2—S12^{v}	3.426 (2)	S11—S12	2.082 (2)
Rb2—S3^{iv}	3.435 (2)	S12—S13	2.048 (2)
Rb2—S5^{v}	3.4758 (13)		

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

Data collection: *IPDS Program Package* (Stoe & Cie, 1998); cell refinement: *IPDS Program Package*; data reduction: *IPDS Program Package*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXTL*.

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