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$K_4Nb_{0.96}Ta_{1.04}S_{11}$

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The reaction of K_2S_3, Nb, Ta and S yields single crystals of non-stoichiometric tetrapotassium niobium tantalum undecasulfide, $K_4Nb_{0.96}Ta_{1.04}S_{11}$. The compound is isotypic with $K_4Nb_2S_{11}$ and the orthorhombic modification of $K_4Ta_2S_{11}$. The structure consists of discrete K^+ cations and complex $[M_2S_{11}]^{4-}$ (M = Nb and Ta) anions, in which the Nb and Ta atoms occupy the same Wyckoff positions statistically. Both M atoms are sevenfold coordinated by S_2^{2-} and S^{2-} anions. The coordination polyhedra can be described as distorted pentagonal bipyramids. Two such bipyramids share a common face, thus forming the $[M_2S_{11}]^{4-}$ anion.

Key indicators

Single-crystal X-ray study
T = 180 K
Mean σ(S–S) = 0.002 Å
Disorder in main residue
R factor = 0.021
wR factor = 0.056
Data-to-parameter ratio = 25.5

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

Comment

Reactions in alkali–polychalcogenide melts (Sunshine *et al.*, 1987) have led to a broad variety of new compounds with interesting new structures (Bensch *et al.*, 1999). During the investigations of reactions of group 5 elements in such melts, a number of new ternary chalcogenometallates were successfully synthesized, *e.g.* $A_4M_2Q_{11}$ (A = K, Rb, Cs and Tl; M = Nb and Ta; Q = S and Se) (Bensch & Dürichen, 1996*b*; Dürichen & Bensch, 1998; Herzog *et al.*, 1999; Teske & Bensch, 2001; Teske *et al.*, 2002), $K_4Nb_2S_{14}$ (Bensch & Dürichen, 1997), $A_6M_4Q_{22}$ (A = K, Rb and Cs; M = Nb and Ta; Q = S and Se) (Bensch & Dürichen, 1996*a*; Stoll *et al.*, 2000*a*, 2000*c*, 2002), $A_6M_4S_{25}$ (A = K and Rb; M = Nb and Ta) (Bensch & Dürichen, 1996*c*; Stoll *et al.*, 2000*b*), $Rb_{12}Nb_6Se_{35}$ (Dürichen, Bolte & Bensch, *et al.*, 1998), $NaNbS_6$ (Dürichen, Näther & Bensch *et al.*, 1998) and $KTaS_5$ (Wu *et al.*, 2005). Most of these compounds contain an M_2Q_{11} unit composed of two face-sharing pentagonal bipyramids as the main structural building block.

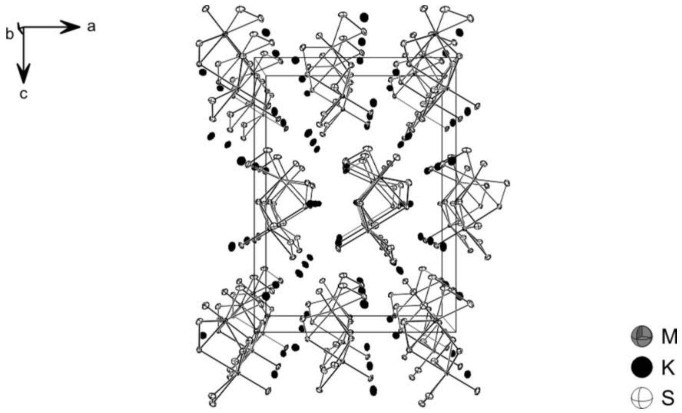

Figure 1
Crystal structure of $K_4Nb_{0.96}Ta_{1.04}S_{11}$, viewed parallel to the crystallographic b axis. Displacement ellipsoids are drawn at the 50% probability level.

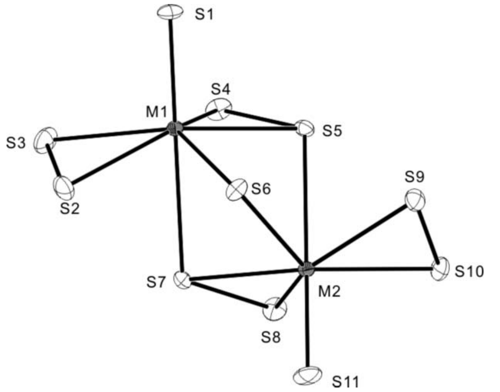

Figure 2
View of the $[M_2S_{11}]^{4-}$ (M = Nb and Ta) anion in $K_4Nb_{0.96}Ta_{1.04}S_{11}$, with the atom labelling and with displacement ellipsoids drawn at the 50% probability level.

$K_4Nb_{0.96}Ta_{1.04}S_{11}$ is isotypic with the previously reported sulfides $K_4Ta_2S_{11}$ (Schreiner *et al.*, 1989) and $K_4Nb_2S_{11}$ (Bensch & Dürichen, 1996*b*). We note that the tantalum compound shows dimorphism and $K_4Nb_{0.96}Ta_{1.04}S_{11}$ described here is isotypic with the orthorhombic modification of $K_4Ta_2S_{11}$. The structure of the title compound consists of complex $[M_2S_{11}]^{4-}$ (M = Nb, Ta) anions that are well separated by K^+ cations (Fig. 1). The anion $[M_2S_{11}]^{4-}$ is best described as two face-sharing distorted pentagonal MS_7 bipyramids (Fig. 2). In both bipyramids, one apical position is occupied by a terminal monosulfide S^{2-} anion and the second by one S atom of a neighbouring S_2^{2-} dumbbell. Within the pentagonal plane, two η^2-S_2^{2-} anions and one μ_2-S^{2-} anion bridging the two M^{5+} centres are found. Therefore, the anion may be described as $[M_2(\mu\text{-}S)(\mu\text{-}\eta^2,\eta^1\text{-}S_2)_2(\eta^2\text{-}S_2)_2(S)_2]^{4-}$. The M—S bonds can be divided into three groups, *viz.* one short bond of 2.2372 (10) Å (M1—S1) or 2.2299 (12) Å (M2—S11), five M—S distances in the range 2.4427 (12)–2.5075 (12) Å (see Table 1), and in the *trans* position to the shortest M—S distances long M—S bonds of 2.8299 (10) Å (M1—S7) and 2.8265 (11) Å (M2—S5) to an S atom of a η^2-S_2^{2-} anion connected to the neighbouring M atom. The S—S distances in the S_2^{2-} anions are between 2.0764 (15) and 2.0838 (18) Å [average 2.080 (3) Å] and are typical for S—S single bonds. The two M atoms are displaced from the pentagonal plane towards the terminal S atom by 0.4682 (3) Å (M1) and 0.4732 (3) Å (M2). The dihedral angle between these planes is 49.98 (2)°. The M—M distance of 3.4614 (4) Å is too long for any metal to metal interaction [radii: 0.69 Å for Nb^{5+} and Ta^{5+} (CN7) (Shannon, 1976)]. All geometric parameters are in accordance with data published for ternary alkali niobium and tantalum sulfides. The four independent K^+ ions are in irregular environments. With a cutoff of 4 Å the mean K—S distances are 3.389 Å for K1 (CN9), 3.306 Å for K2 (CN8), 3.344 Å for K3 (CN7) and 3.365 Å for K4 (CN8). These values are in good agreement with the sum of the ionic radii [1.84 Å for S^{2-} and 1.51 Å for K^+(CN8) (Shannon, 1976)].

Experimental

K_4NbTaS_{11} was synthesized from a mixture of K_2S_3, Nb, Ta and S in the ratio 4:1:1:8. K_2S_3 was prepared from stoichiometric amounts of K and S in liquid ammonia under argon atmosphere. The starting materials were thoroughly mixed and loaded into Pyrex-glass tubes in a dry nitrogen-filled glove-box. After evacuating to 10^{-3} mbar the tubes were flame sealed and placed in a computer-controlled furnace. Heat treatment was as follows: in 24 h to 773 K, holding for 6 d, cooling to 373 K at 2 K h^{-1}, then switching off the furnace. The resulting product was washed with dry *N*,*N*-dimethylformamide and diethyl ether. The residue was dried in a vacuum. The product consisted of dark-red platelet-like crystals. The crystals are stable in dry air for several months.

Crystal data

$K_4Nb_{1.04}Ta_{0.96}S_{11}$
M_r = 779.33
Orthorhombic, $Pca2_1$
a = 13.1554 (10) Å
b = 7.4520 (4) Å
c = 17.9508 (10) Å
V = 1759.79 (19) Å^3
Z = 4
D_x = 2.941 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8000 reflections
θ = 10–24°
μ = 8.85 mm^{-1}
T = 180 (2) K
Platelets, dark red
0.12 × 0.08 × 0.05 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)
T_{min} = 0.429, T_{max} = 0.638
14338 measured reflections
4000 independent reflections
3956 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 28.0°
$h = -17 \rightarrow 17$
$k = -8 \rightarrow 9$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.057
S = 1.05
4000 reflections
157 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 1.0044P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.73 e Å^{-3}
$\Delta\rho_{min}$ = −0.96 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0042 (3)
Absolute structure: Flack (1983), 1966 Friedel pairs
Flack parameter: −0.006 (6)

Table 1
Selected interatomic distances (Å).

M1—S1	2.2372 (10)	K2—S10	3.1186 (15)
M1—S2	2.4427 (12)	K2—S1^{v}	3.1681 (15)
M1—S4	2.4573 (10)	K2—S9^{vi}	3.3150 (16)
M1—S6	2.4975 (10)	K2—S3^{vii}	3.4691 (17)
M1—S5	2.4989 (11)	K2—S8	3.4890 (16)
M1—S3	2.5075 (12)	K2—S4^{vii}	3.6164 (16)
M1—S7	2.8299 (10)	K3—S10	3.2651 (18)
M2—S11	2.2299 (12)	K3—S4^{vii}	3.2731 (16)
M2—S8	2.4601 (11)	K3—S3^{iv}	3.2963 (18)
M2—S9	2.4666 (11)	K3—S6^{viii}	3.2974 (15)
M2—S7	2.4900 (10)	K3—S1^{viii}	3.3402 (15)
M2—S10	2.4938 (12)	K3—S2^{viii}	3.3613 (16)
M2—S6	2.4959 (10)	K3—S7^{iv}	3.5730 (17)
M2—S5	2.8265 (11)	K4—S3	3.2124 (17)
K1—S4^{i}	3.2139 (14)	K4—S10^{ix}	3.2511 (16)
K1—S5^{ii}	3.2669 (14)	K4—S8^{x}	3.2528 (16)
K1—S8^{i}	3.2669 (15)	K4—S11^{xi}	3.2890 (18)
K1—S11	3.3432 (18)	K4—S5^{ix}	3.3654 (16)
K1—S6	3.3612 (15)	K4—S6^{xi}	3.4092 (15)
K1—S1^{ii}	3.3726 (16)	K4—S9^{xi}	3.5499 (16)
K1—S2	3.4770 (18)	K4—S9^{ix}	3.5863 (16)
K1—S9^{ii}	3.5145 (15)	S2—S3	2.0838 (18)
K1—S7	3.6858 (15)	S4—S5	2.0764 (15)
K2—S11^{iii}	3.0516 (16)	S7—S8	2.0803 (15)
K2—S2^{iv}	3.0855 (16)	S9—S10	2.0805 (15)

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

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Nb and Ta atoms were refined as disordered on common sites. Refinement of the site occupation factors for Nb1/Ta1 and Nb2/Ta2 yields 0.473 (3)/0.527 (3) and 0.485 (3)/0.515 (3), leading to the final composition $K_4Nb_{0.958\,(3)}Ta_{1.042\,(3)}S_{11}$. The composition of the compound was additionally proved by EDX measurements, which revealed an element ratio of 3.97:0.98:1:02:11.02 for K:Nb:Ta:*S*.

Data collection: *IPDS Program Package* (Stoe & Cie, 1998); cell refinement: *IPDS Program Package*; data reduction: *IPDS Program Package*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXTL*.

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