

bonds *trans* to Cu are longer than in the parent (P₂W₁₈O₆₂)⁶⁻. The bond-valence sums (Brown & Altermatt, 1985) are calculated from the averaged bond lengths to be 5.19 for Nb(1,2,3) and 6.02, 6.13, 6.30 for W(1,2,3), W(4-9) and W(10-15) respectively, and the bond-valence sums for O atoms in the sequence Nb—O—W_{belt}—O—W_{belt}—O—W_{cap} are 2.01, 2.07, 1.99.

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Structure of RbNaS

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Abstract. Rubidium sodium sulfide, RbNaS, $M_r = 140.524$, tetragonal, $P4/nmm$, $a = 4.696$ (1), $c = 7.559$ (1) Å, $V = 166.69$ Å³, $Z = 2$, $D_x = 2.799$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 85.12$ cm⁻¹, $F(000) = 126$, $T = 293$ K, $R = 0.0223$ for 169 unique reflections. The structure is characterized by layers of ${}^2_2[\text{NaS}_{4/4}]$ tetrahedra separated by double layers of Rb to form a PbFCl-type geometry.

Introduction. Our investigations into the existence of ternary alkali-metal oxides led to the characterization of KNaO (Sabrowsky & Schröer, 1982), RbNaO (Sabrowsky, Vogt-Mertens & Thimm, 1985), KLiO (Sabrowsky, Mertens & Thimm, 1985) and RbLiO (Sabrowsky & Vogt, 1987). Subsequently we extended our studies into the field of the interalkali-metal sulfides. Meanwhile we have succeeded in preparing NaLiS (Sabrowsky, Thimm & Vogt-Mertens, 1985a), KLiS (Sabrowsky, Thimm & Vogt-Mertens, 1985b), RbLiS (Sabrowsky, Hippler, Hitzbleck, Sitta, Thimm, Vogt & Wortmann, 1990) and KNaS (Sabrowsky, Thimm, Vogt & Harbrecht,

1987). NaLiS, KLiS and RbLiS are isotypic and crystallize in the PbFCl structure type whereas KNaS forms crystals of PbCl₂-type geometry. Here we present the results of a single-crystal structure determination of RbNaS which has been prepared recently.

Experimental. Well-shaped colourless single crystals of RbNaS were obtained by sintering equimolar mixtures of Na₂S and Rb₂S in closed silver crucibles in an argon atmosphere at 783 K. The crystals are sensitive to air and moisture. D_m was not measured. A plate-like crystal with dimensions 0.1 × 0.2 × 0.5 mm mounted in a Lindemann tube was available for the data collection. The unit-cell parameters were determined by least-squares treatment of the adjusted angular settings of 50 reflections ($2\theta = 16$ –27°) measured on an Enraf–Nonius CAD-4 diffractometer. The intensity measurements were carried out at 293 K with graphite-monochromated Mo $K\alpha$ radiation and the ω -2 θ scan technique. A total of 3400 reflections were collected for $2\theta = 2$ –72°

Table 1. Atomic coordinates and thermal parameters (\AA^2) for RbNaS
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

		x	y	z	$U_{11} = U_{22}$	U_{33}	U_{eq}
Rb	2(c)	0	0.5	0.6493 (1)	0.0224 (3)	0.0224 (4)	0.0224 (3)
Na	2(a)	0	0	0	0.0150 (8)	0.0125 (11)	0.0142 (9)
S	2(c)	0	0.5	0.2056 (3)	0.0171 (5)	0.0188 (8)	0.0177 (6)

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]. \quad U_{12} = U_{13} = U_{23} = 0.$$

($h: -8 \rightarrow 8$, $k: -8 \rightarrow 8$, $l: -13 \rightarrow 13$) and 169 of these were unique ($R_{int} = 0.0180$). All 169 reflections had $F_o > 2\sigma(F_o)$ and were considered as observed and used in refinement. Three strong reflections (040, 314, 305) monitored periodically during data collection exhibited no significant intensity variation. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected with *DIFABS* (Walker & Stuart, 1983). Max. and min. transmission factors 1.25, 0.89. The structure was solved by Patterson and Fourier methods using *SHELX76* (Sheldrick, 1976). Least-squares refinement on F of 12 parameters with anisotropic thermal parameters led to the atomic parameters given in Table 1. * Final $R = 0.0223$, $wR = 0.0223$, $\{w = [k/\sigma^2(F) + gF^2]; k = 1.0003, g = 0.0\}$, $(\Delta\rho)_{max} = 1.187$, $(\Delta\rho)_{min} = -1.5 \text{ e \AA}^{-3}$. $(\Delta/\sigma)_{max} = 0.05$. Atomic scattering factors and f' , f'' values were taken from *International Tables for X-ray Crystallography* (1974). Fig. 1 shows a schematic representation of the structure. Selected interatomic distances are shown in Table 2.

Discussion. RbNaS is isotypic to NaLiS, KLiS and RbLiS and crystallizes in the PbFCl structure type ($P4/nmm$). Since KNaO and RbNaO both crystallize in the PbFCl structure type, it is remarkable that RbNaS is not isostructural to KNaS which crystallizes in the PbCl₂ structure type ($Pnma$). In RbNaS sodium is surrounded tetrahedrally by four S atoms (Na—S = 2.815 Å) to form layers of $2_{\infty}^2[\text{NaS}_{4/4}]$ anions perpendicular to the c axis which are separated by double layers of rubidium cations. Every rubidium is therefore pentacoordinated by the S atoms. Four S atoms form a square around the Rb atom (Rb—S = 3.497 Å) and the fifth S atom is situated centrally above the square (Rb—S = 3.354 Å). Sulfur is surrounded by four Na and five Rb atoms. In comparison with the sum of the molecular volumes of sodium sulfide and rubidium sulfide ($V_M = 56.85 \text{ cm}^3 \text{ mol}^{-1}$) a volume contraction of 11.7% is observed for the formation of RbNaS ($V_M = 50.2 \text{ cm}^3 \text{ mol}^{-1}$).

* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52959 (2 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected interatomic distances (Å) for RbNaS

Na—S	2.816 (1)	4 ×	S—Rb	3.354 (1)	1 ×
Na—Na	3.321 (2)	4 ×	S—Rb	4.205 (2)	1 ×
Na—Rb	3.541 (2)	4 ×	Rb—Rb	4.015 (2)	4 ×
S—Rb	3.497 (2)	4 ×	S—S	5.553 (2)	4 ×

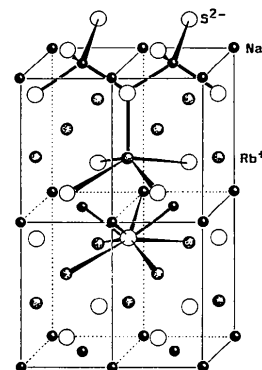


Fig. 1. Four elementary cells of tetragonal RbNaS with accentuation of the potassium, oxygen and bromine coordination.

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