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A new quaternary thiophosphate, $RbNb_2(S_2)_3(PS_4)$

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The structure of the new quaternary thiophosphate rubidium diniobium tris(disulfide) tetrathiophosphate, $RbNb_2(S_2)_3(PS_4)$, is made up of one-dimensional $_\infty^1[Nb_2(S_2)_3(PS_4)^-]$ chains along the [101] direction, and these chains are separated from one another by Rb^+ ions. The chain is basically built up from $[Nb_2S_{12}]$ units and tetrahedral $[PS_4]$ groups. The $[Nb_2S_{12}]$ units are linked together to form a linear $[Nb_2S_9]$ chain by sharing the S–S prism edge. Short and long Nb—Nb distances [2.888 (2) and 3.760 (2) Å, respectively] alternate along the chain, and the anionic species S_2^{2-} and S^{2-} are observed.

Comment

Group V transition metal thiophosphates have been extensively investigated due to the structural variety endowed by the many different P—S catenations and their interesting properties (Rouxel, 1986). In particular, their low-dimensional nature makes them of potential importance as cathode materials for high energy density secondary batteries (Evain *et al.*, 1987). However, no stable intercalated product in the group V metal–P–S system has been well characterized. Thus, we have used alkali metal halides as reactive fluxes to find new phases (Do & Yun, 1996) and to investigate the structural features in this system.

The title compound, $RbNb_2(S_2)_3(PS_4)$ or $RbNb_2PS_{10}$, has a structure similar to that of the previously reported KNb_2PS_{10} (Do & Yun, 1996) and is closely related to those of the other group V metal thiophosphates studied to date, namely V_2PS_{10} (Brec, Ouvrard *et al.*, 1983), $Nb_4P_2S_{21}$ (Brec, Evain *et al.*, 1983) and Nb_2PS_{10} (Brec, Grenouilleau *et al.*, 1983). The structure of $RbNb_2(S_2)_3(PS_4)$ consists of one-dimensional $_\infty^1[Nb_2PS_{10}^-]$ chains along the [101] direction (Fig. 1), and these are well separated by Rb^+ ions (Fig. 2). There are only van der Waals interactions between the chains. The Rb^+ ions in this van der Waals gap stabilize the structure through ionic interactions.

As shown in other phases in the *M*–P–S family (*M* is V or Nb), each chain is made up of bicapped biprismatic $[Nb_2S_{12}]$ units and tetrahedral $[PS_4]$ groups. Atoms Nb1 and Nb2 are surrounded by eight S atoms in a bicapped trigonal prismatic arrangement. Two prisms share a rectangular face to form an $[Nb_2S_{12}]$ unit (Fig. 3). This unit shows an approximate twofold rotation symmetry, which is also found in KNb_2PS_{10}. The rotation axis bisects the short Nb1—Nb2 distance and the $(S–S)_2$ sides of the rectangular face shared by each trigonal prism. One of the S atoms at the prism edge and two other capping S atoms are bound to the P atom, and an additional S atom (S9) is attached to the P atom to complete the PS_4 tetrahedral coordination. The average P—S distance within the PS_4 unit [2.042 (6) Å] is in good agreement with the P—S distances found in other related phases. Atom S9 is the only terminal atom in the compound, and this is responsible for the short P—S9 distance [1.979 (6) Å] and the large atomic displacement parameter of atom S9 (Do & Yun, 1996).

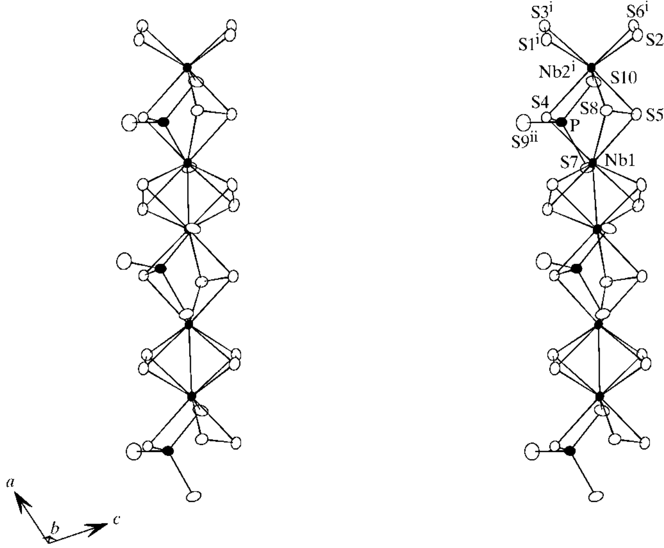

Figure 1
A stereoscopic view of the one-dimensional $_\infty^1[Nb_2PS_{10}^-]$ chain in $RbNb_2(S_2)_3(PS_4)$. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y, z + \frac{1}{2}$.]

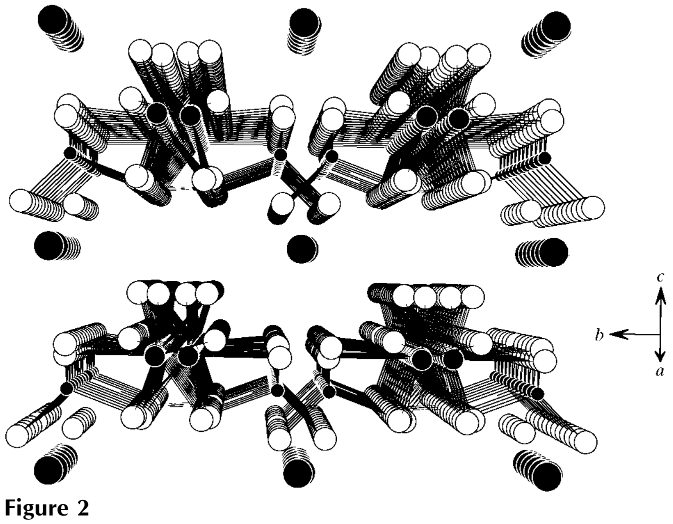

Figure 2
A view of $RbNb_2(S_2)_3(PS_4)$ down the chain axis, showing the one-dimensional nature of the compound. Large, medium and small filled circles represent Rb, Nb and P atoms, respectively, while large open circles represent S atoms.

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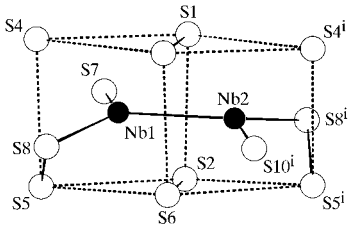

Figure 3
A perspective view of the $[Nb_2S_{12}]$ unit in $RbNb_2(S_2)_3(PS_4)$. Small filled circles represent Nb atoms and large open circles represent S atoms. Nb—S bonds have been omitted for clarity, except for the capping S atoms. [Symmetry code: (i) $x-\frac{1}{2}, -y-1, z-\frac{1}{2}$.]

Along the chains, the Nb atoms associate in pairs, with Nb···Nb interactions alternating in the sequence of one short and one long distance. The short distance [2.888 (2) Å] is typical of Nb^{4+}—Nb^{4+} bonding interactions (Angenault *et al.*, 2000). However, the long distance [3.760 (2) Å] implies that there is no significant Nb···Nb interaction, and such an arrangement is consistent with the highly resistive and diamagnetic nature of the compound.

The classical charge balance of $RbNb_2(S_2)_3(PS_4)$ may be represented as $[Rb^+][Nb^{4+}]_2[P^{5+}][S_2^{2-}]_3[S^{2-}]_4$. Studies to solubilize this compound with highly polar solvents (Tarascon *et al.*, 1985), to obtain an isolated polymeric ${}^{1}_{\infty}[Nb_2PS_{10}^{-}]$ chain, are underway.

Experimental

The title compound was prepared by the reaction of Nb, P and S in an elemental ratio of 2:1:10 in an eutectic mixture of RbCl/LiCl. The starting materials, Nb powder (CERAC, 99.8%), P powder (CERAC, 99.5%) and S powder (Aldrich, 99.999%), were placed in a quartz tube. The mass ratio of reactants and halide fluxes was 1:2. The tube was evacuated to 10^{-2} Torr (1 Torr = 133.322 Pa), sealed and heated to 973 K, at which temperature it was kept for 7 d. Afterwards, the tube was cooled to room temperature at a rate of 4 K h^{-1}. Dark-red needle-shaped crystals of $RbNb_2(S_2)_3(PS_4)$ were isolated from the flux with distilled water. The crystals are stable both in water and in air. Electron microprobe analysis of the crystals established their homogeneity and the presence of Rb, Nb, P and S.

Crystal data

$RbNb_2(S_2)_3(PS_4)$
$M_r = 622.86$
Monoclinic, *Pn*
$a = 12.773$ (3) Å
$b = 7.529$ (2) Å
$c = 7.108$ (2) Å
$\beta = 104.37$ (2)°
$V = 662.2$ (3) Å^3
$Z = 2$

$D_x = 3.124$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10.0$–$15.0°$
$\mu = 7.03$ mm^{-1}
$T = 293$ (2) K
Needle, dark red
0.54 × 0.04 × 0.03 mm

Data collection

MacScience MXC3 diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{min} = 0.691$, $T_{max} = 0.794$
1293 measured reflections
1198 independent reflections
1169 reflections with $I > 2\sigma(I)$

$R_{int} = 0.031$
$\theta_{max} = 25°$
$h = 0 \rightarrow 15$
$k = -8 \rightarrow 0$
$l = -8 \rightarrow 8$
2 standard reflections every 100 reflections intensity decay: 0.0 (15)%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.114$
$S = 1.10$
1198 reflections
128 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0771P)^2 + 1.6949P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.44$ e Å^{-3}
$\Delta\rho_{min} = -1.41$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0073 (14)
Absolute structure: Flack (1983), 52 Friedel pairs
Flack parameter = 0.04 (3)

Table 1
Selected geometric parameters (Å, °).

Nb1—S1	2.535 (4)	Nb2—S4^{i}	2.642 (4)
Nb1—S2	2.475 (4)	Nb2—S5^{i}	2.543 (4)
Nb1—S3	2.478 (4)	Nb2—S6	2.468 (4)
Nb1—S4	2.646 (4)	Nb2—S8^{i}	2.565 (4)
Nb1—S5	2.576 (4)	Nb2—S10^{i}	2.566 (4)
Nb1—S6	2.515 (4)	P—S4	2.085 (6)
Nb1—S7	2.604 (4)	P—S7	2.060 (6)
Nb1—S8	2.561 (4)	P—S9^{ii}	1.979 (6)
Nb1—Nb2	2.888 (2)	P—S10	2.042 (6)
Nb2—S1	2.475 (4)	S1—S3	2.034 (6)
Nb2—S2	2.515 (4)	S2—S6	2.029 (6)
Nb2—S3	2.540 (4)	S5—S8	2.056 (6)
S9^{ii}—P—S10	112.9 (3)	S9^{ii}—P—S4	114.7 (3)
S9^{ii}—P—S7	113.0 (3)	S10—P—S4	103.2 (2)
S10—P—S7	111.9 (3)	S7—P—S4	100.2 (2)

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

Data collection: *MXC3 Software* (MacScience Corporation, 1994); cell refinement: *MXC3 Software*; data reduction: *MXC3 Software*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: locally modified version of *ORTEP*II (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1362). Services for accessing these data are described at the back of the journal.

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