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A new thiophosphate, $Rb_{0.38}Ag_{0.5}Nb_2PS_{10}$

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The structure of the new pentanary thiophosphate rubidium silver diniobium tris(disulfide) tetrathiophosphate, $Rb_{0.38}Ag_{0.5}Nb_2PS_{10}$, is made up of one-dimensional ${}^1_\infty[Nb_2PS_{10}^-]$ chains along the [001] direction. These chains are separated from one another by Ag^+ and disordered Rb^+ ions. The $Nb_2PS_{10}^-$ chain is built up from bicapped trigonal prismatic Nb_2S_{12} units which lie about inversion centres and tetrahedral PS_4 groups. The Nb_2S_{12} units are linked together to form linear Nb_2S_9 chains by sharing S—S prism edges. Short [2.898 (1) and 2.908 (1) Å] and long [3.724 (1) Å] Nb···Nb distances alternate along the chains, and S_2^{2-} and S^{2-} anionic species co-exist in the structure. The Ag^+ cation lies on an inversion centre and has distorted octahedral coordination described as a [2+4]-bonding interaction.

Comment

Due to their low-dimensional structures and interesting anisotropic properties (Rouxel, 1986), group 5 transition metal thiophosphates form an interesting class of compounds. In particular, they have potential applications as cathode materials for high energy density secondary batteries (Evain *et al.*, 1987). The preparation of alkali metal thiophosphates is crucial to understanding the nature of the intercalation and analysing their electronic structure.

Since the report of the first niobium thiophosphates containing alkali metals (Do & Yun, 1996), we have used metal halides as reactive fluxes to find new thiophosphates. This technique exploits metal halides as both flux and reactant. The resultant products usually include various monovalent cations.

The structure of $Rb_{0.38}Ag_{0.5}Nb_2PS_{10}$ is similar to that of the previously reported compounds KNb_2PS_{10} (Do & Yun, 1996), $RbNb_2PS_{10}$ (Kim & Yun, 2002), and $AgNb_2PS_{10}$ and $NaNb_2PS_{10}$ (Goh *et al.*, 2002). It is also closely related to other group 5 metal thiophosphates, *viz.* 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). It consists of one-dimensional ${}^1_\infty[Nb_2PS_{10}^-]$ chains along the [001] direction (Fig. 1), separated by Rb^+ and Ag^+ ions. Each chain is made up of typical bicapped biprismatic Nb_2S_{12} units and tetrahedral PS_4 groups.

Both Nb1 and Nb2 atoms are surrounded by eight S atoms in a bicapped trigonal prismatic fashion. Two adjacent prisms share a rectangular face to form the Nb_2S_{12} unit (Fig. 2). This Nb_2S_{12} unit differs from those found in ANb_2PS_{10} (A = K or Rb) in the arrangement of the $(S—S)^{2-}$ ligands. While the ligands occupy the same sites, an inversion symmetry is found in the title compound, whereas a twofold rotation symmetry is found in ANb_2PS_{10}.

The Nb_2S_{12} units are bound to each other to form infinite ${}^1_\infty[Nb_2S_9]$ chains by sharing S—S prism edges. 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 (S10) is attached to the P atom to complete the PS_4 tetrahedral coordination. The average P—S distance in the PS_4 unit [2.046 (3) Å] is in good agreement with P—S distances found in other related phases. Atom S10 is the only terminal atom in the compound and this accounts for the short P—S10 distance [2.007 (2) Å] and the large anisotropic displacement parameter of atom S10 (Do & Yun, 1996).

Along the chain, the Nb atoms associate in pairs, with Nb···Nb interactions in an alternating sequence of short and

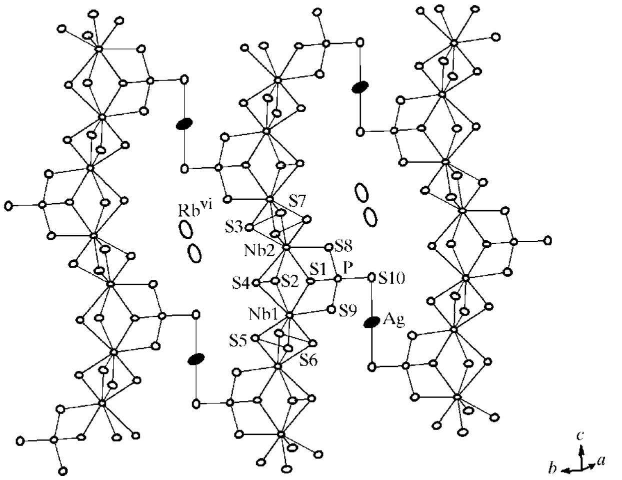

Figure 1
A view of $Rb_{0.38}Ag_{0.5}Nb_2PS_{10}$. Displacement ellipsoids are drawn at the 70% probability level. [Symmetry code: (vi) x, $1 + y$, z.]

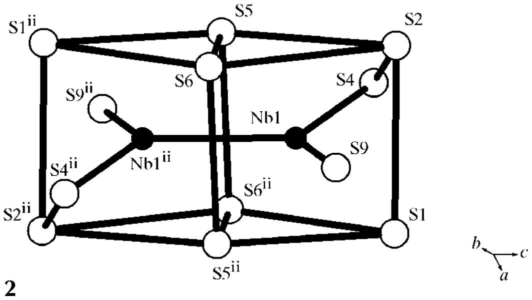

Figure 2
A perspective view of the Nb_2S_{12} unit with inversion symmetry. Small filled circles denote Nb atoms and large open circles denote S atoms. Nb—S bonds have been omitted for clarity, except for those involving capping S atoms. [Symmetry code: (ii) $1 - x$, $2 - y$, $-z$.]

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long distances. The Nb2$\cdots$Nb2 distance [2.898 (1) Å] is in good agreement with typical Nb^{4+}—Nb^{4+} bonding distances (2.86–2.89 Å; Angenault *et al.*, 2000). However, the separation between Nb1 atoms is longer [2.908 (1) Å] and implies that Nb1 could be more oxidized than Nb2. A similar Nb$\cdots$Nb separation [2.961 (1) Å] has been observed for the cation-deficient phase $AuNb_4P_2S_{20}$ (Kim *et al.*, 2003). The long Nb1$\cdots$Nb2 distance [3.724 (1) Å] shows that there is no significant intermetallic bonding interaction, and such an arrangement is consistent with the highly resistive nature of the compound. The classical charge balance of the compound should be represented by $[Rb^+]_{0.38}[Ag^+]_{0.5}[Nb^{4.06+}]_2[P^{5+}]$-$[S_2^{2-}]_3[S^{2-}]_4$. Assuming that the two Nb atoms are not equivalent, oxidation states of 4.12 and 4 can be assigned to Nb1 and Nb2, respectively.

The coordination around the Ag atom can be described as a [2+4]-bonding interaction. Four S atoms are bound to the Ag atoms in the plane [Ag—S6 = 3.048 (2) Å and Ag—S9 = 3.234 (2) Å], whereas two *trans* S atoms are coordinated to the Ag atom [Ag—S10 = 2.471 (2) Å]. These values are comparable with the sums of the ionic radii of each element (2.51 Å for coordination number 2 and 2.99 Å for coordination number 6; Shannon, 1976). A tetragonal contraction would theorectically be favoured for the d^{10} configuration (Burdett & Eisenstein, 1992), and this prediction is compatible with the present results.

Experimental

$Rb_{0.38}Ag_{0.5}Nb_2PS_{10}$ was prepared by the reaction of elemental Nb, P and S using the reactive halide flux technique. Stoichiometric amounts of Nb (CERAC, 99.8%), P (CERAC, 99.5%) and S powders (Aldrich, 99.999%) were mixed in quartz tubes with the addition of a eutectic mixture of RbI/AgI. The mass ratio of reactants and flux was 1:3. The tubes were evacuated (10^{-2} Torr; 1 Torr = 133.322 Pa), sealed and heated gradually to 1073 K, where they were kept for 72 h. The tubes were then cooled to room temperature at a rate of 5 K h^{-1}. The excess halide fluxes were removed with distilled water and dark-red needle-shaped crystals of the title compound were obtained. The crystals are stable in air and water. Qualitative analysis of the crystals with an EDAX-equipped AMRAY 1200 C scanning electron microscope indicated the presence of Rb, Ag, Nb, P and S.

Crystal data

$Rb_{0.38}Ag_{0.5}Nb_2PS_{10}$
M_r = 623.56
Triclinic, $P\bar{1}$
a = 7.011 (2) Å
b = 7.196 (2) Å
c = 12.907 (3) Å
α = 89.51 (3)°
β = 76.24 (2)°
γ = 89.39 (2)°
V = 632.4 (3) $Å^3$

Z = 2
D_x = 3.275 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 10.0–15.0°
μ = 5.73 mm^{-1}
T = 293 (2) K
Needle, dark red
0.40 × 0.03 × 0.03 mm

Data collection

MacScience MXC3 diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
T_{min} = 0.822, T_{max} = 0.844
2797 measured reflections
2666 independent reflections
2233 reflections with $I > 2\sigma(I)$

R_{int} = 0.018
θ_{max} = 27.5°
$h = -9 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -16 \rightarrow 0$
2 standard reflections every 100 reflections intensity decay: 0.5%

Table 1
Selected geometric parameters (Å, °).

Ag—S10	2.4707 (18)	Nb2—S7^{iii}	2.4988 (18)
Ag—S6^{i}	3.0484 (17)	Nb2—S7	2.5197 (18)
Ag—S9	3.2343 (19)	Nb2—S4	2.5646 (17)
Nb1—S6^{ii}	2.4926 (18)	Nb2—S2	2.5824 (17)
Nb1—S6	2.5000 (17)	Nb2—S8	2.5861 (18)
Nb1—S5	2.5027 (17)	Nb2—S1	2.6147 (18)
Nb1—S5^{ii}	2.5055 (18)	Nb1—Nb1^{ii}	2.9075 (13)
Nb1—S4	2.5663 (17)	Nb2—Nb2^{iii}	2.8981 (13)
Nb1—S2	2.5689 (18)	P—S10	2.007 (2)
Nb1—S9	2.5779 (18)	P—S8	2.045 (2)
Nb1—S1	2.6112 (17)	P—S9	2.046 (2)
Nb2—S3^{iii}	2.4875 (17)	P—S1	2.084 (2)
Nb2—S3	2.4942 (18)		
S10—Ag—S6^{i}	93.56 (6)	S6^{i}—Ag—S9	116.90 (5)

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, -y+2, -z$; (iii) $-x+1, -y+2, -z+1$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.067
S = 1.04
2666 reflections
134 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0199P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.82 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.03 e $Å^{-3}$

The occupancy factors for Rb and Ag refined to 0.372 (3) and 0.483 (2), respectively. A full occupancy was thus assigned for the Ag site and the Rb site refined to 0.375 (3). As no evidence was found for ordering of the Rb site, a statistically disordered structure was assumed.

Data collection, cell refinement and data reduction: *MXC3 Software* (MacScience, 1994); structure solution: *SHELXS86* (Sheldrick, 1990); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1066). Services for accessing these data are described at the back of the journal.

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