A New One-Dimensional Quaternary Metal Thiophosphate: Synthesis and Structure of KNb_2PS_{10}

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The group 5 metal thiophosphates have been reported to have mostly low-dimensional structures.[1] Especially the M_2PS_{10} (M = V, Nb) phases have a two-dimensional layered (Nb_2PS_{10}) or one-dimensional chain (V_2PS_{10}) structure with partially filled and empty orbitals which can accommodate electrons.[2,3] Consequently, they are of potential importance as cathode materials for secondary alkali metal batteries. However, no stable alkali metal intercalated product in this system has been isolated and structurally characterized. This is probably due to the fact that the crystallinity of the host structure is not maintained during the electrochemical insertion procedure. To detour this problem, we use the eutectic alkali metal halide mixtures as reactive fluxes. This synthetic approach appears to be of general utility in preparing new multinary thiophosphates with various alkali metals. Here we report the synthesis and characterization of a new one-dimensional quaternary thiophosphate, KNb_2PS_{10}.

The compound KNb_2PS_{10} was prepared by the reaction of a 2:1:10 ratio of the elements Nb, P, and S in a eutectic mixture of KCl/LiCl. The starting materials were placed in a quartz tube. The tube was evacuated to $\sim 10^{-3}$ Torr, sealed, and heated to 700 °C, where the contents were kept for 7 days. Afterward, the tube was cooled at a rate of 4 °C/h to reach room temperature. The dark red needle-shaped crystals isolated from the flux with distilled water were stable in air. Electron microprobe analysis of the crystals established their homogeneity and the presence of K, Nb, P, and S. The structural details of this compound were determined by a single-crystal X-ray diffraction study.

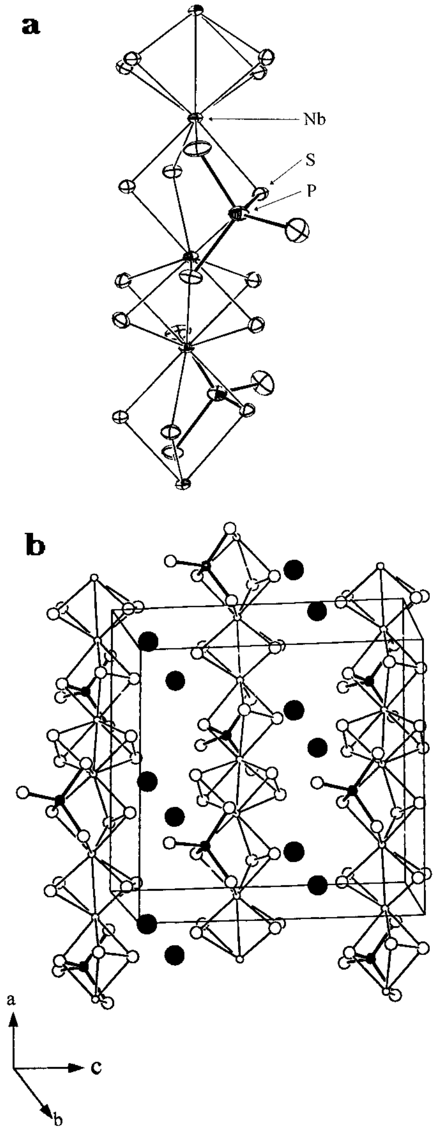

Figure 1. (a) View of the ${}^{1}_{\infty}[Nb_2PS_{10}{}^{-}]$ chain with anisotropic thermal vibration ellipsoids. (b) View of the unit cell of KNb_2PS_{10}. Small open circles are Nb atoms, small filled circles are P atoms, large open circles are S atoms, and large filled circles are K atoms.

Views of the ${}^{1}_{\infty}[Nb_2PS_{10}{}^{-}]$ chain and the unit cell of KNb_2PS_{10} are given in Figure 1.[4] The crystal structure of KNb_2PS_{10} is closely related to that of Nb_2PS_{10}.[2] The typical distorted bicapped biprismatic $[Nb_2S_{12}]$ units are found. However the unit in KNb_2PS_{10} differs from the $[Nb_2S_{12}]$ unit in Nb_2PS_{10} in the arrangement of two $S_2{}^{2-}$ ligands. While the $S_2{}^{2-}$ ligand occupies both a capping and a prismatic coordination site in both structures, a 2-fold rotation symmetry is found in KNb_2PS_{10}, whereas an inversion symmetry is observed in Nb_2PS_{10} (Figure 2). The former symmetry has been reported in other related compounds such as V_2PS_{10} and $Nb_4P_2S_{21}$.[3,5] These

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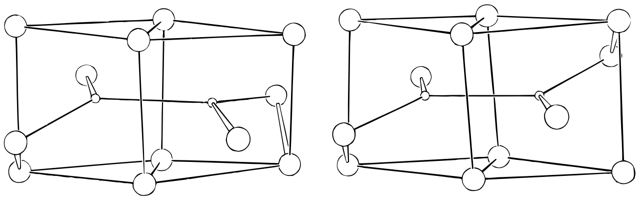
(4) (a) Crystallographic data: $M_r = 576.49$, orthorhombic, space group $Pca2_1$, $a = 12.976(7)$ Å, $b = 7.519(3)$ Å, $c = 13.356(5)$ Å, $V = 1303(1)$ Å^3, $Z = 4$, $D_c = 2.938$ g/cm^3. Preliminary examination and data collection were performed on a Mac Science MXC3 diffractometer equipped with graphite-monochromatized Mo Kα radiation (λ(Kα_1) = 0.7093 Å). Cell constants and an orientation matrix were determined from least-squares analysis, using setting angles of 25 reflections in the range of $20.0° < 2\theta < 28.0°$ that had been automatically centered. A dark red needle-like crystal of dimensions $0.70 \times 0.10 \times 0.10$ mm^3 was used to collect 1453 unique $[F_o{}^2 > 0]$ and 1348 observed $[F_o > 4\sigma(F_o)]$ reflections, using an ω scan. An analytical absorption correction was applied with use of the analytical method ($\mu = 37.57$ cm^{-1}), and the transmission factors were calculated with the values of 0.668−0.710.[4b] Diffraction data $+h,+k,+l$ were collected from the inner-sphere ($3.0° \leq 2\theta$(Mo Kα) $\leq 55.0°$) at room temperature (293(2) K). The structure was solved by direct methods and refined by full-matrix least-squares methods with R1(on F_o for $4\sigma(F_o)$) = 0.0381 and wR2(F^2) = 0.0833.[4c,d] The program STRUCTURE TIDY was used to standardize the positional parameters.[4e] Scattering factors are taken from the usual source.[4f] The Flack parameter x was refined to 0.03(16). (b) de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014. (c) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (d) Sheldrick, G. M. SHELXL 93, Program for the Refinement of Crystal Structure. University of Göttingen, 1993. (e) Gelato, L.; Parthé, E. *J. Appl. Crystallogr.* **1987**, *20*, 139. (f) Cromer, D.; Waber, J. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, Table 2.3.1.



(a) **(b)**

Figure 2. Perspective views of the [Nb_2S_{12}] biprismatic units (a) with 2-fold symmetry and (b) with inversion symmetry. Small circles are Nb atoms, and large circles are S atoms.

[Nb_2S_{12}] units are linked together to form the one-dimensional $^{1}_{\infty}[Nb_2S_9]$ chains by the S−S prism edge. One of the S atoms at the prism edge and two other capping S atoms are bound to a P atom and an additional S atom is attached to the P atom to complete the PS_4 tetrahedral coordination. The arrangement of Nb ions in KNb_2PS_{10} is similar to the ones found in related compounds. The Nb ions associate in pairs with Nb−Nb interactions alternating in the sequence of one short (2.884(2) Å) and one long (3.763(2) Å) distance. The short distance is typical of $Nb^{4+}-Nb^{4+}$ bonding interactions.

The most significant structural deviation of KNb_2PS_{10} from Nb_2PS_{10} is that the [$P_2S_8{}^{4-}$] unit between the chains does not exist anymore. The $(S-S)^{2-}$ bridges that link the chains in Nb_2PS_{10} are not observed, and there are no interchain chemical bonding interactions except the van der Waals forces. Instead, the K^+ cations reside in this van der Waals gap (Figure 3). Consequently, the structure of KNb_2PS_{10} should be regarded as a one-dimensional chain structure rather than a two-dimensional layered structure. The S(3) atom is the only terminal S atom in KNb_2PS_{10}, and this is probably responsible for the short P−S(3) bond distance (1.967(5) Å) compared to other P−S bond distances found in KNb_2PS_{10} (P−S = 2.045(6)−2.078(5) Å) or Nb_2PS_{10} (P−S = 2.007(2)−2.107(2) Å). The one-dimensional chain composed of Nb, P, and S extends along [100] and can be described as $^{1}_{\infty}[Nb_2PS_{10}{}^{-}]$. Thus, the classical charge balance of the compound can be represented by $[K^+][Nb^{4+}]_2[P^{5+}][S_2{}^{2-}]_3[S^{2-}]_4$.

Whangbo et al. conducted tight-binding band electronic structure calculations on the M_2PS_{10} (M = V, Nb) phases based upon their crystal structures.[6] They predicted that the low-lying electron acceptor levels responsible for Li intercalation in these phases should be d-block orbitals of the highly oxidized metals rather than the P−S or S−S antibonding orbitals. It may be inappropriate to apply these results to KNb_2PS_{10} because KNb_2PS_{10} is synthesized at high temperature and the size of K^+ is much larger than that of Li^+. In our studies, the incorporation of alkali metals (Li and K) into the Nb_2PS_{10} host structure by electrochemical processes failed to provide any conclusive results. However, for the high-temperature products, the disulfide bridge in Nb_2PS_{10} would not be retained since the maximum formal charge on the terminal S atoms would be favored to stabilize the highly electropositive alkali metal cations through the electrostatic interactions. Similar structural trends have been observed in the Rb and Cs analogs of KNb_2PS_{10} although these structures are not exactly the same because of the effect of the larger alkali metal cations.[7] Further theoretical and electrochemical studies will be necessary.

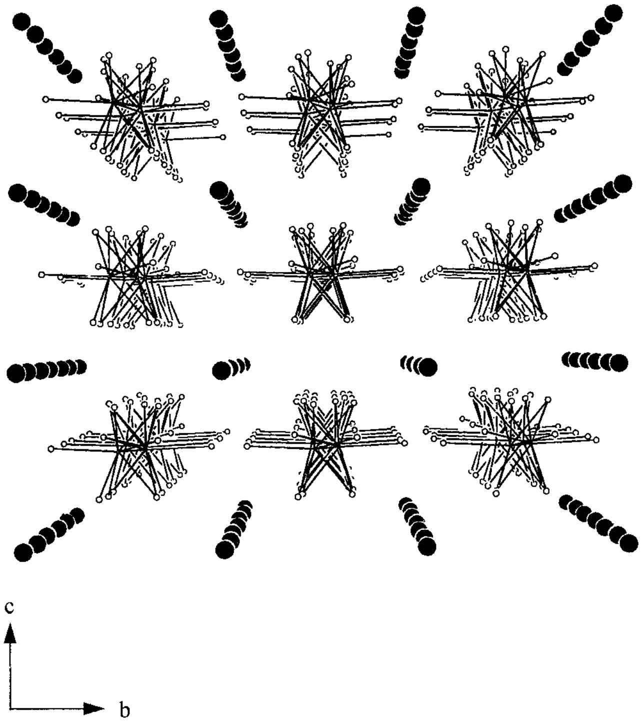


Figure 3. View of KNb_2PS_{10} down the *a* axis showing the one-dimensional nature of the compound. Large filled circles are K atoms; P atoms and one of the S atoms are omitted for clarity.

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Supporting Information Available: Tables of crystallographic details, atomic coordinates, anisotropic thermal parameters, and complete bond distances and angles for KNb_2PS_{10} (5 pages). Ordering information is given on any current masthead page.

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(7) (a) $RbNb_2PS_{10}$: space group *Pn*, $a = 12.773(3)$ Å, $b = 7.528(2)$ Å, $c = 7.108(2)$ Å, $\beta = 104.37(2)°$. (b) $CsNb_2PS_{10}$: space group *Pc*, $a = 14.030(5)$ Å, $b = 7.552(3)$ Å, $c = 12.971(4)$ Å, $\beta = 95.74(3)°$.