

Synthesis and Crystal Structure of a New One-dimensional Quaternary Thiophosphate, CsNb₂PS₁₀

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Group 5 transition metal thiophosphates form an interesting class of materials due to their low-dimensional structural varieties and interesting anisotropic properties.¹ Especially, these low-dimensional compounds have been extensively investigated for potential applications as cathode materials of high energy density secondary batteries.² Preparation of the alkali metal thiophosphates is crucial to understand the nature of the intercalation and to analyze their behavior during charge and discharge processes. This gives us motivation to insert alkali metals into the thiophosphates. However, no stable alkali metal intercalated product in this system has been obtained and structurally characterized. We believe that the crystallinity of the host structure is not maintained during the electrochemical insertion procedure. During the past decade we have applied halide flux method to bypass this problem. This technique exploits metal halides as a flux and as a reactant. The resultant products usually include various monovalent cations and this technique enabled us to find the first niobium thiophosphates containing alkali metals, KNb₂PS₁₀.³ During an effort to expand the range of compounds within the quaternary alkali metal-group 5 metal-P-S system by substituting alkali metals, we were able to prepare single crystals of CsNb₂PS₁₀. Here we report the synthesis and characterization of a new quaternary thiophosphate, CsNb₂PS₁₀.

The structure of CsNb₂PS₁₀ is closely related to those of the previously reported group 5 metal thiophosphates, KNb₂PS₁₀,³ RbNb₂PS₁₀,⁴ AgNb₂PS₁₀,⁵ AuNb₄P₂S₂₀,⁶ and NaNb₂PS₁₀.⁵ It consists of the one-dimensional ∞¹[Nb₂PS₁₀]⁻ chains along the [001] direction (Fig. 1), and these anionic chains are stabilized by electropositive Cs⁺ ions. A stereoscopic view of the unit cell of CsNb₂PS₁₀ is shown in Figure 2. Like most of the group 5 metal thiophosphates, the chains found in CsNb₂PS₁₀ are composed of the typical bipyramidal [Nb₂S₁₂] and [PS₄] units. Two crystallographically distinct, but chemically identical chains are found in this structure. The Nb atoms are surrounded by 8 S atoms in a bicapped trigonal prismatic fashion. Two prisms are sharing a rectangular face to form the [Nb₂S₁₂] unit (Fig. 3). This unit is similar to those found in ANb₂PS₁₀ (A=K, Rb)^{3,4} in the arrangement of the (S-S)²⁻ ligands. Although the ligands occupy the same sites, a 2-fold rotation symmetry is found in ANb₂PS₁₀,^{3,4} whereas an inversion symmetry is found in

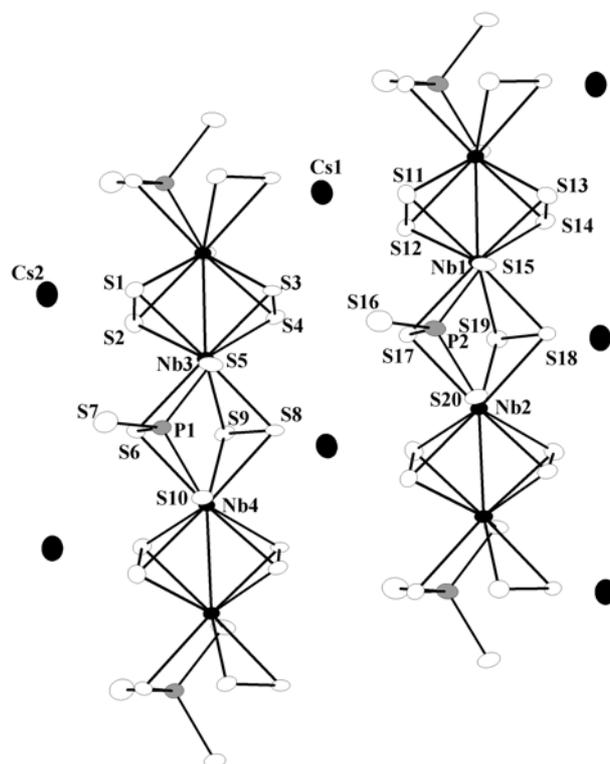


Figure 1. A view of CsNb₂PS₁₀ showing an individual ∞¹[Nb₂PS₁₀]⁻ chains and coordination around Nb and P atoms. Displacement ellipsoids are drawn at the 60% probability level. The labeling scheme is shown. Large and small filled circles are Cs and Nb atoms respectively; open circles and grey circles represent S and P atoms respectively. The Cs-S bonds are omitted for clarity.

A_xAg_{0.5}Nb₂PS₁₀ (A=K, Rb).^{7,8} These units are bound through the S-S prism edges and through one of the capping sulfur atoms to make infinite ∞¹[Nb₂S₉] chains. 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 is attached to the P atom to complete the infinite ∞¹[Nb₂PS₁₀]⁻ chains. The P-S distances are in good agreement with the P-S bonding distances found in other thiophosphates.⁹⁻¹³ Atoms S7 and S16 are terminal atoms and this is responsible for the short distances (P1-S7 1.973(6) Å; P2-S16 1.971(6) Å) and their large displacement parameters.

In the arrangement of Nb atoms, Nb⋯Nb interactions

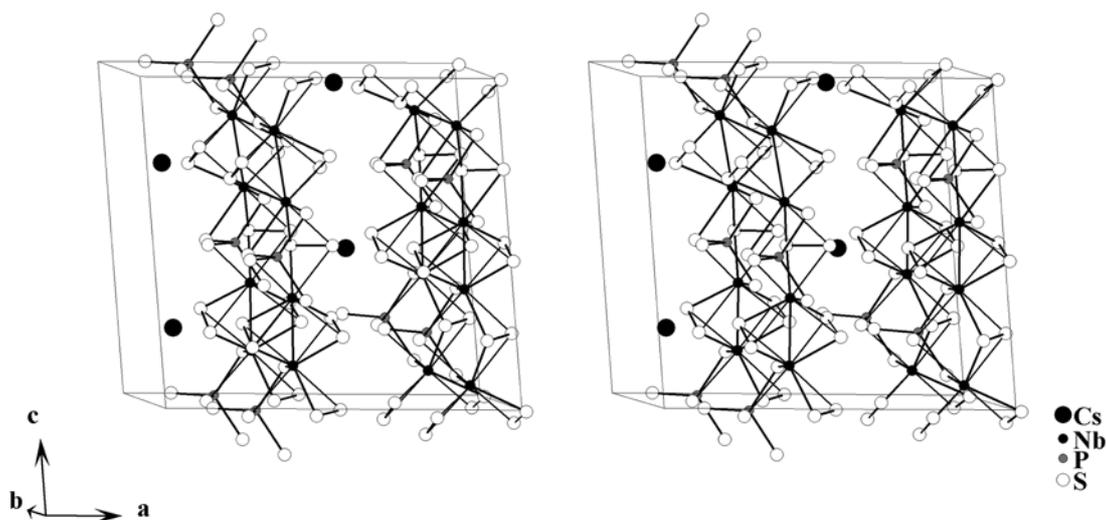


Figure 2. A stereoscopic view of the unit cell of $\text{CsNb}_2\text{PS}_{10}$.

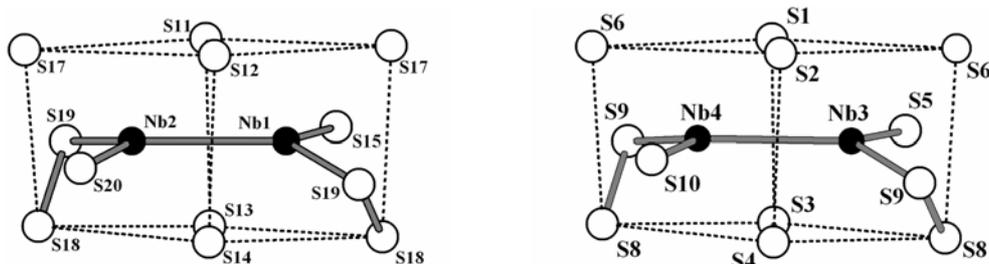


Figure 3. A perspective view of the $[\text{Nb}_2\text{S}_{12}]$ units with approximate 2-fold symmetry. Small filled circles are Nb atoms and large open circles are S atoms. Nb-S bonds are omitted except for the capping S atoms for clarity.

alternate in the sequence of one short (Nb1-Nb2, 2.884(2) Å or Nb3-Nb4, 2.891(2) Å) and one long (Nb1-Nb2, 3.764(2) Å or Nb3-Nb4, 3.758(2) Å). The short distances are typical of $\text{Nb}^{4+}\text{-Nb}^{4+}$ bond¹⁴ and the long Nb...Nb distances show that there is no significant intermetallic bonding interaction and such an arrangement is consistent with the high resistivity of the compound.

There are no interchain interactions except the van der Waals forces. Instead, the Cs^+ cations reside in the van der Waals gap. They are surrounded by eight S atoms if we arbitrarily choose a cutoff of 3.9 Å for the $\text{Cs}\cdots\text{S}$. Thus, the classical charge balance of the compound can be represented by $[\text{Cs}^+][\text{Nb}^{4+}]_2[\text{PS}_4^{3-}][\text{S}_2^{2-}]_3$. Studies to solubilize $\text{NaNb}_2\text{PS}_{10}$ with polar organic solvents such as N-methylformamide (NMF) to obtain nanotubes based on polymeric $[\text{Nb}_2\text{PS}_{10}]^-$ chains have been reported¹⁴ and we believe that $\text{CsNb}_2\text{PS}_{10}$ would be ideal for this purpose because of the highly electropositive nature of the Cs^+ cation.

Experimental Section

Synthesis. The compounds $\text{CsNb}_2\text{PS}_{10}$ was prepared by the reaction of elemental Nb, P, and S with the use of the reactive halide flux technique. Stoichiometric combinations of the pure elements, Nb powder (CERAC 99.8%), P powder (CERAC 99.5%), and S powder (Aldrich 99.999%)

were mixed in a fused silica tube with the addition of eutectic mixture of CsCl/LiCl. The mass ratio of reactants and fluxes was 1:2. The tube was evacuated (10^{-2} Torr), sealed, and heated gradually to 973 K, where they were kept for 7 days. The tube was cooled to room temperature at the rate of 4 K/hr. The excess halide fluxes were removed with distilled water and dark red needle-shaped crystals were obtained. The crystals are stable in air and water. Analysis of this compound with the microprobe of an EDAX-equipped AMRAY 1200C scanning electron microscope indicated the presence of Cs, Nb, P, and S. No other element was detected.

X-ray Crystallography. The crystal structures of $\text{CsNb}_2\text{PS}_{10}$ was determined by single-crystal X-ray diffraction methods. Preliminary examination and data collection were performed on an MXC3 diffractometer (Mac science) equipped with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.7107$ Å). Cell constants and an orientation matrix for data collection were obtained from the least-squares analysis, using the setting angles of 22 reflections in the range $20.0^\circ < 2\theta(\text{MoK}\alpha) < 28^\circ$ that had been automatically centered. The intensities of two standard reflections measured every 100 reflections showed no significant deviations during the data collection. Intensity data for the title compound were collected at 200(2) K with the ω - 2θ scan technique. Additional crystallographic details are described in Table 1. The observed Laue symmetry and the systematic extinction

Table 1. Crystal Data and Structure Refinement

Empirical formula	CsNb ₂ PS ₁₀
Formula weight	670.30
Temperature	200(2) K
Wavelength	0.71073 Å (MoK α)
Crystal system	Monoclinic
Space group	<i>Pc</i>
Unit cell dimensions	a = 14.040(3) Å b = 7.544(2) Å b = 95.72 (2)°. c = 12.972(3) Å
Volume	1367.0(5) Å ³
Z	4
Density (calculated)	3.257 Mg/m ³
Absorption coefficient	5.902 mm ⁻¹
Crystal size	0.70 × 0.04 × 0.04 mm ³
Theta range for data collection	2.70 to 24.99°
Index ranges	-16 ≤ h ≤ 16, -8 ≤ k ≤ 0, 0 ≤ l ≤ 15
Reflections collected	3339
Independent reflections	2519 [R(int) = 0.0427]
Completeness to theta = 24.99°	100.0 %
Absorption correction	Analytical (Tomp and de Meulenaar ¹⁷)
Data / restraints / parameters	2519 / 2 / 253
Goodness-of-fit on F ²	1.125
Final R indices [I > 2σ(I)]	R1 = 0.0364, wR2 = 0.0808
R indices (all data)	R1 = 0.0503, wR2 = 0.0956
Absolute structure parameter	-0.02(3)
Largest diff. peak and hole	1.044 and -1.236 e.Å ⁻³

Table 2. Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10³)

	x	y	z	U(eq) [*]
Cs1	5987(1)	4998(2)	9626(1)	34(1)
Cs2	981(1)	4811(2)	7183(1)	35(1)
Nb1	8712(1)	9436(2)	8597(1)	17(1)
Nb2	8687(1)	9310(2)	5694(1)	16(1)
Nb3	3746(1)	9346(2)	6265(1)	14(1)
Nb4	3719(1)	9389(2)	3366(1)	15(1)
P1	2991(3)	5964(5)	4750(3)	17(1)
P2	7972(3)	5972(5)	7139(3)	20(1)
S1	2503(3)	8611(6)	7489(3)	19(1)
S2	2439(3)	11121(6)	6885(4)	22(1)
S3	4992(3)	8692(6)	7687(3)	21(1)
S4	4997(3)	11281(7)	7226(4)	25(1)
S5	3901(3)	5974(6)	6082(4)	23(1)
S6	2477(3)	8562(5)	4696(3)	16(1)
S7	2009(3)	4092(6)	4734(4)	32(1)
S8	4975(3)	9474(6)	4949(3)	20(1)
S9	4035(3)	11586(5)	4853(3)	18(1)
S10	3701(3)	5959(6)	3435(4)	20(1)
S11	7463(3)	8736(6)	9799(4)	21(1)
S12	7398(3)	11232(6)	9194(3)	20(1)
S13	9999(3)	8899(6)	9999(4)	24(1)
S14	9917(3)	11462(6)	9542(4)	24(1)
S15	8878(3)	6061(6)	8479(4)	22(1)
S16	7003(4)	4085(6)	7157(4)	33(1)
S17	7440(3)	8556(5)	7031(3)	18(1)
S18	9939(3)	9490(6)	7285(3)	18(1)
S19	9001(3)	11578(5)	7146(3)	22(1)
S20	8698(3)	5897(6)	5849(3)	22(1)

^{*}U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.**Table 3.** Selected Bond Lengths [Å] and Angles [deg]

Nb1-S13	2.466(5)	Nb3-S3	2.462(5)
Nb1-S12	2.474(4)	Nb3-S2	2.470(4)
Nb1-S14	2.507(5)	Nb3-S4	2.516(5)
Nb1-S11	2.516(5)	Nb3-S1	2.534(4)
Nb1-S18	2.541(4)	Nb3-S8	2.547(4)
Nb1-S19	2.545(4)	Nb3-S9	2.554(4)
Nb1-S15	2.562(5)	Nb3-S5	2.566(5)
Nb1-S17	2.652(4)	Nb3-S6	2.635(4)
Nb2-S14 ⁱ	2.464(5)	Nb4-S1 ⁱ	2.469(4)
Nb2-S11 ⁱ	2.466(4)	Nb4-S4 ⁱ	2.488(5)
Nb2-S13 ⁱ	2.522(5)	Nb4-S3 ⁱ	2.526(4)
Nb2-S19	2.550(4)	Nb4-S2 ⁱ	2.526(5)
Nb2-S12 ⁱ	2.555(5)	Nb4-S9	2.548(4)
Nb2-S18	2.577(4)	Nb4-S8	2.571(4)
Nb2-S20	2.582(5)	Nb4-S10	2.590(5)
Nb2-S17	2.646(4)	Nb4-S6	2.647(4)
Nb1-Nb2 ⁱⁱ	2.884(2)	Nb3-Nb4 ⁱⁱ	2.891(2)
S11-S12	2.038(6)	S1-S2	2.048(6)
S13-S14	2.022(7)	S3-S4	2.043(7)
S18-S19	2.050(6)	S8-S9	2.064(6)
P2-S16	1.971(6)	P1-S7	1.973(6)
P2-S20	2.046(6)	P1-S5	2.043(6)
P2-S15	2.050(6)	P1-S10	2.060(6)
P2-S17	2.087(6)	P1-S6	2.087(6)
S16-P2-S20	113.0(3)	S7-P1-S5	112.9(3)
S16-P2-S15	112.6(3)	S7-P1-S10	112.6(3)
S20-P2-S15	112.1(3)	S5-P1-S10	112.7(3)
S16-P2-S17	115.7(3)	S7-P1-S6	115.6(3)
S20-P2-S17	100.1(2)	S5-P1-S6	102.2(2)
S15-P2-S17	102.3(2)	S10-P1-S6	99.7(2)

Symmetry transformations used to generate equivalent atoms: (i) x, -y+2, z-1/2, (ii) x, -y+2, z+1/2

(*h0l*: $k + l = 2n + 1$) were indicative of the monoclinic space group *P2/c* or *Pc*. A solution with a low figure of merit could only be obtained in the non-centrosymmetric space group, *Pc*. The initial positions for all atoms were obtained by using direct methods of the SHELXS-86 program.¹⁵ The structure was refined by full-matrix least-squares techniques with the use of the SHELXL-97 program.¹⁶

With the composition established the data for the compound were corrected for absorption with the use of the analytical method of Tompa and de Meulenaar.¹⁷ All atomic displacement parameters were refined anisotropically. The final cycle of refinement performed on F_o^2 with 2519 unique reflections afforded residuals $wR2 = 0.1023$ and conventional $R1$ index based on the reflections having $F_o^2 > 2\sigma(F_o^2)$ is 0.0392. However the Flack parameter $x = 0.36(4)$ implied that the absolute structural determination is wrong.¹⁸ Refinement of the inverse structure leads to $x = -0.02(3)$ and the improved reliability factor ($wR2 = 0.0956$, $R1 = 0.0364$). A difference Fourier synthesis calculated with phase based on the final parameters shows no peak heights greater than 1.044 e/Å³ or lower than -1.236 e/Å³. No additional sym-

metry, as tested by PLATON¹⁹ was detected in this structure.

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