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Single-Crystal Structure Determination of $Na_4P_2S_6 \cdot 6H_2O$

T. Fincher, G. LeBret, and D. A. Cleary

Department of Chemistry, Gonzaga University, Spokane, Washington 99258

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The single-crystal structure of $Na_4P_2S_6 \cdot 6H_2O$ is reported. Thermogravimetric analysis (23.6% weight loss) showed that $Na_4P_2S_6 \cdot 6H_2O$ converted to $Na_4P_2S_6$ as it was heated from room temperature to 80°C. The room temperature infrared spectrum of $Na_4P_2S_6 \cdot 6H_2O$ was analyzed in terms of the symmetry of the $P_2S_6^{-4}$ group. $Na_4P_2S_6 \cdot 6H_2O$ crystallized in the monoclinic space group *P*2(1)/*c* with $a = 25.4761(4)$ Å, $b = 7.10350(10)$ Å, and $c = 20.3282(3)$ Å, $\beta = 113.482°$, and $Z = 8$. The cell volume was calculated to be 3374.12(9) Å^3, and the density was calculated to be 1.565 Mg/m^3. The single crystal structure was also solved at −60°C. The low temperature crystal data were $a = 25.3961(3)$ Å, $b = 7.06480(10)$ Å, and $c = 20.22160(10)$ Å, $\beta = 113.431(1)°$, $Z = 8$. The −60°C-cell volume was calculated to be 3328.95(6) Å^3, and the density was calculated to be 1.586 Mg/m^3. © 1998 Academic Press

INTRODUCTION

The sodium salt of hypothiophosphoric acid was isolated by Falius in 1968 (1). Since then, the hypothiophosphate ion, $P_2S_6^{-4}$ has enjoyed considerable attention (2–4). This anion complexes with a large number of transition-metal and post-transition-metal ions to form a class of compounds that have been investigated for their interesting magnetic, optical, electrochemical, and structural properties (5–7). The single-crystal structure of $Na_4P_2S_6 \cdot 6H_2O$ has not yet been reported, although Falius reported the space group to be monoclinic with cell dimensions $a = 20.3$ Å, $b = 7.1$ Å, $c = 23.3$ Å, $\alpha = \beta = \gamma = 90°$ (1). In a number of papers, the point symmetry of the $P_2S_6^{-4}$ ion has been shown to be D_{3d} (8, 9). The single crystal structure of $Na_4P_2S_6 \cdot 6H_2O$ revealed that four crystallographically distinct $P_2S_6^{-4}$ ions exist within the lattice, all with point symmetry close to D_{3d} but actually C_1 due to the SPPS dihedral angle ranging from 175° to 179°.

EXPERIMENTAL DETAILS

Synthesis. The synthesis of $Na_4P_2S_6 \cdot 6H_2O$ closely followed the procedure described by Falius (1). $Na_2S \cdot 9H_2O$ (75 g, 0.3123 mol) was dissolved in water (100 mL) with stirring. PCl_3 (6.60 mL, 0.0756 mol) was added dropwise from a buret. The PCl_3 was added slowly (30 min) because of its violent reaction with water. Initially, no reaction was observed when the PCl_3 drop hit the water, but as each drop was added, a more noticeable reaction was observed. After the PCl_3 was added, the reaction vessel was placed in an ice bath, and the solution was stirred for 20 min. Next, the vessel was removed from the ice bath, and the solution was stirred at room temperature for 1 h. Finally, the reaction vessel was placed in a refrigerator for 18 h. A white crystalline powder was recovered after this time. This crude product ($\approx$ 10 g) was recrystallized from a hot ($\approx$ 80°C) water : ethanol solution (75 : 25). Large colorless rhombus-shaped crystals ($\approx$ 1 mm edge) were obtained. These crystals were used in all subsequent analysis. The dehydrated phase, $Na_4P_2S_6$, was prepared by heating the hexahydrate to 100°C. The dehydrated phase was a white powder.

Characterization. The product crystals were subjected to thermogravimetric analysis, infrared absorption spectroscopy, and single-crystal X-ray diffraction. Thermogravimetric analysis was performed on a Perkin-Elmer TGA-7. A single crystal (3.956 mg) was heated in a nitrogen atmosphere from 25°C to 80°C at 0.5°C/min. The mass of the sample as a function of temperature is shown in Fig. 1. Infrared absorption spectroscopy was performed on a Perkin–Elmer Spectrum 2000 Fourier transform infrared spectrophotometer. A single crystal of $Na_4P_2S_6 \cdot 6H_2O$ was ground in mineral oil, and a transmission spectrum was recorded at 1 cm^{-1} resolution from 400 cm^{-1} to 7800 cm^{-1}. Both fully hydrated and dehydrated samples were examined. Infrared spectra were analyzed using PeakFit to extract the individual absorption peaks. The results of such fitting are shown in Figs. 2 and 3. Single-crystal X-ray diffraction analysis was performed on a Siemens CCD diffractometer. The experimental details are summarized in Table 1. The structure was determined at both −60°C and room temperature in an effort to discover multiple phases of $Na_4P_2S_6 \cdot 6H_2O$. The *R* values did not decrease after an absorption correction (SADABS). The maximum and minimum transmission values were 0.8865 and 0.7261,

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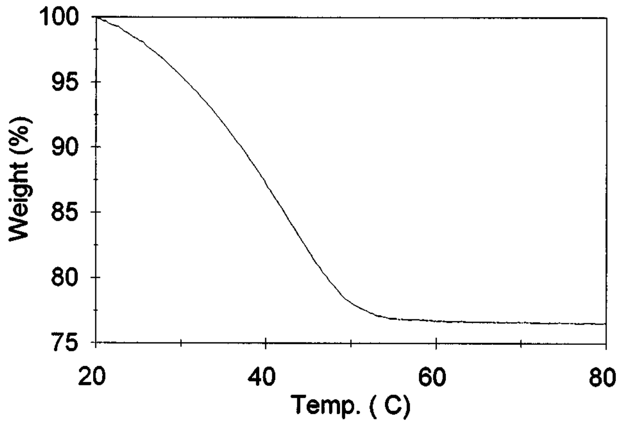

FIG. 1. Thermogravimetric analysis data from $Na_4P_2S_6 \cdot 6H_2O$. The heating rate was 0.5°C/min, and the sample mass was 3.956 mg. The experiment was performed in 1 atm of nitrogen gas.

respectively. The crystasl-to-detector distance was 4.949 cm. Omega scans were used (width = 0.3°) in collecting the diffraction data.

RESULTS AND DISCUSSION

The chemical reaction responsible for the formation of $Na_4P_2S_6 \cdot 6H_2O$ from $Na_2S \cdot 9H_2O$ and PCl_3 remains unclear. A strong $H_2S(g)$ odor was detectable during the reaction. In addition, one must assume that some $PCl_3(l)$ reacts with the water to form $H_3PO_3(aq)$.

The thermogram shown in Fig. 1 is consistent with a 23.79% weight loss expected for complete dehydration of $Na_4P_2S_6 \cdot 6H_2O$:

$$Na_4P_2S_6 \cdot 6H_2O(s) \rightarrow Na_4P_2S_6(s) + 6H_2O(g).$$

Two points are worth noting. First, the dehydration temperature is low ($\approx$ 55°C), suggesting that the water molecules are weakly bound in the lattice. Second, the weight loss curve, even with a heating rate as slow as 0.5°C/min, showed no constant weight regions after dehydration began suggesting that no stable compounds (at 1 atm $N_2(g)$) with the formula $Na_4P_2S_6 \cdot nH_2O$ exist with $n < 6$. The total weight loss was 23.6 $\pm$ 0.1%.

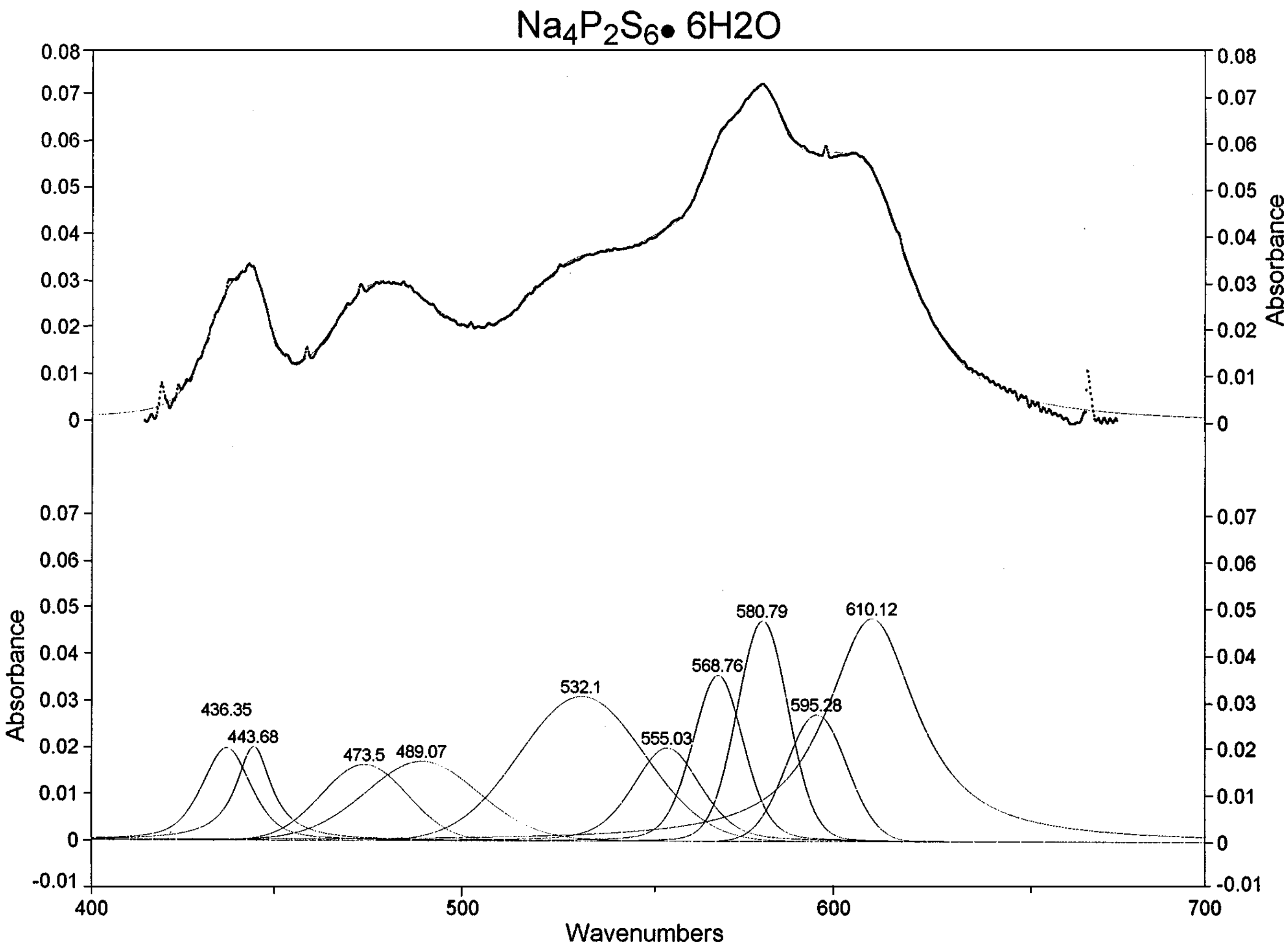

FIG. 2. Infrared absorption spectrum of $Na_4P_2S_6 \cdot 6H_2O$. The spectrum was recorded at room temperature and the peaks were determined as described in the text.

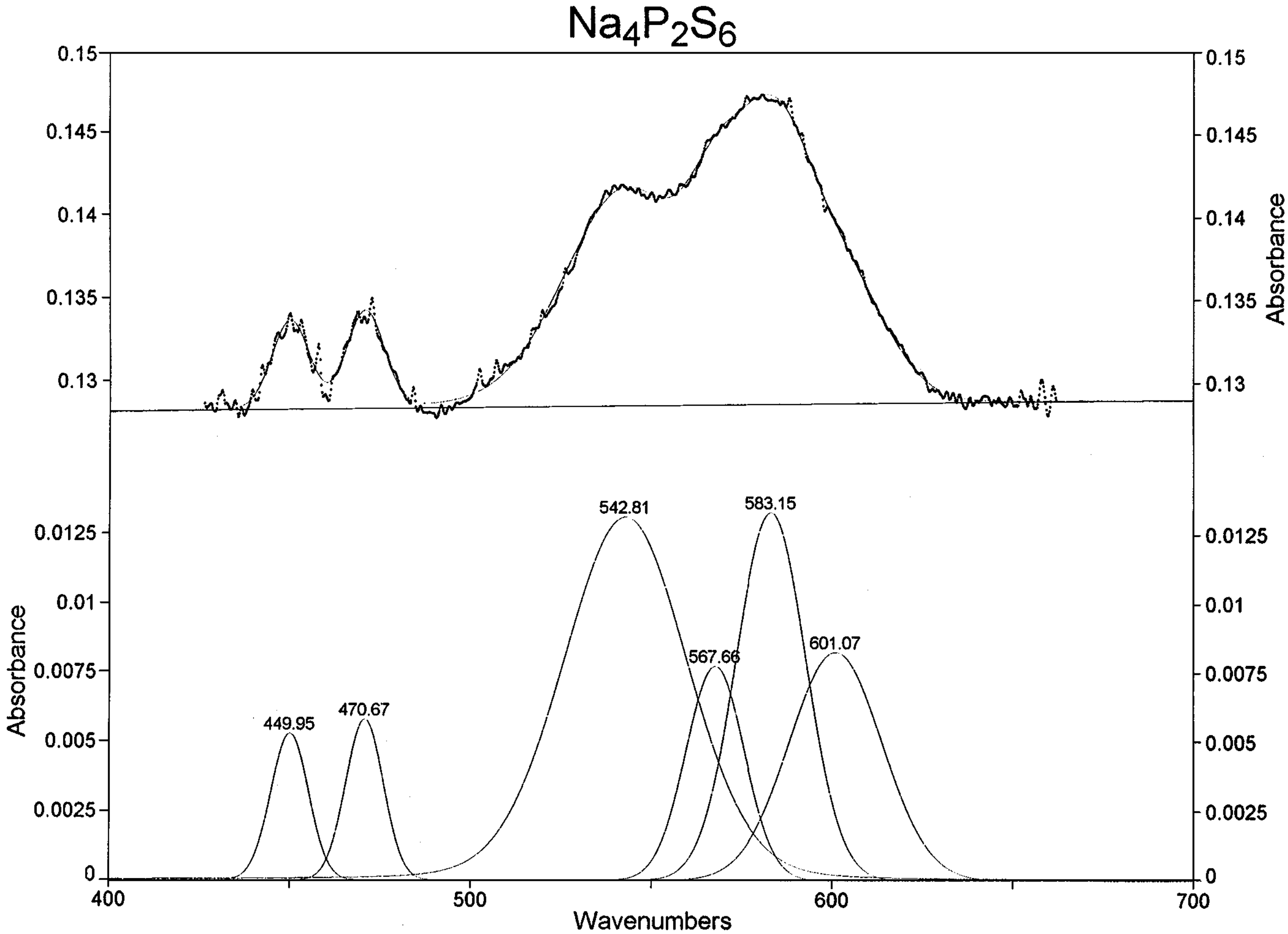

FIG. 3. Infrared absorption spectrum of $Na_4P_2S_6$. The spectrum was recorded at room temperature and the peaks were determined as described in the text.

The infrared absorption spectrum and corresponding fit for $Na_4P_2S_6 \cdot 6H_2O$ are shown in Fig. 2. The infrared absorption spectrum of the anhydrous form ($Na_4P_2S_6$), prepared from thermal dehydration of $Na_4P_2S_6 \cdot 6H_2O$, is shown in Fig. 3. Absorption peak assignments are summarized in Table 2. The spectrum for $Na_4P_2S_6 \cdot 6H_2O$ is consistent with $P_2S_6^{-4}$ adopting C_1 point symmetry. Using *ab initio* calculations at the 6-31G* level, one would predict six bands (see Table 2) in the displayed infrared region for a molecule or ion with a point symmetry of C_1 with four unresolvable bands around 580 cm^{-1}. The infrared spectrum of $P_2S_6^{-4}$ analyzed in terms of D_{3d} symmetry has been reported (10–12). The allowed infrared transitions for D_{3d} symmetry are reported to be at 585/606 cm^{-1} (E_u) and 444 cm^{-1} (A_{2u}). The structural data for $Na_4P_2S_6 \cdot 6H_2O$ show four distinct $P_2S_6^{-4}$ groups in the lattice, which would further complicate the infrared absorption spectrum. While the infrared absorption spectrum of anhydrous $Na_4P_2S_6$ is shown in Fig. 3, no structural data are available to determine the point symmetry of the $P_2S_6^{-4}$ ion.

Two views of the room-temperature crystal structure of $Na_4P_2S_6 \cdot 6H_2O$ are shown in Fig. 4 and 5. The hydrogen atoms are not shown. In Fig. 4, the octahedra are NaO_6, the square planes are NaO_4, the large spheres are sulfur atoms, and the small spheres are phosphorus atoms. In Fig. 5, the white circles are sodium atoms, the black circles are oxygen atoms, the large gray circles are sulfur atoms, and the small dark gray circles are phosphorus atoms.

Fractional coordinates, selected bond lengths and angles, and temperature factors are listed in Tables 3–5. $Na_4P_2S_6 \cdot 6H_2O$ crystallized in the monoclinic space group $P2(1)/c$ with $a = 25.4761(4)$ Å, $b = 7.10350(10)$ Å, and $c = 20.3282(3)$ Å, $\beta = 113.48°$, and $Z = 8$. The cell volume was calculated to be 3374.12(9) $Å^3$, and the density was calculated to be 1.565 Mg/m^3. The single-crystal structure was also solved at $-60°C$. The low-temperature crystal

TABLE 1
Crystal Data and Structure Refinement for $Na_4P_2S_6 \cdot 6H_2O$

Empirical formula	$H_{12}\,Na_4\,O_6\,P_2\,S_6$
Formula weight	454.36
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions	$a = 25.4761(4)$ Å $\alpha = 90°$
	$b = 7.10350(10)$ Å $\beta = 113.48°$
	$c = 20.3282(3)$ Å $\gamma = 90°$
Volume, Z	3374.12(9) Å^3,
Density (calculated)	1.565 Mg/m^3
Absorption coefficient	0.971 mm^{-1}
$F(000)$	1610
Crystal size	$0.25 \times 0.25 \times 0.10$ mm
Theta range for data collection	1.74° to 25.00°
Limiting indices	$-30 \le h \le 32,\ -8 \le k \le 9,$
	$-26 \le l \le 26$
Reflections collected	16,484
Independent reflections	5918 [R(int) = 0.0403]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5918/0/325
Goodness-of-fit on F^2	1.308
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0830$, w$R2 = 0.2001$
R indices (all data)	$R1 = 0.0969$ w$R2 = 0.2050$
Largest diff. peak and hole	0.735 and -0.664 e$\cdot$ Å^{-3}

data were $a = 25.3961(3)$ Å, $b = 7.06480(10)$ Å, $c = 20.22160(10)$ Å, $\beta = 113.431(1)°$, and $Z = 8$. The -60°C cell volume was calculated to be 3328.95(6) Å^3, and the density was calculated to be 1.586 Mg/m^3. These results are similar to those reported by Falius (1).

The structure of $Na_4P_2S_6 \cdot 6H_2O$ consists of chains of edge-shared octahedra where the octahedra alternate

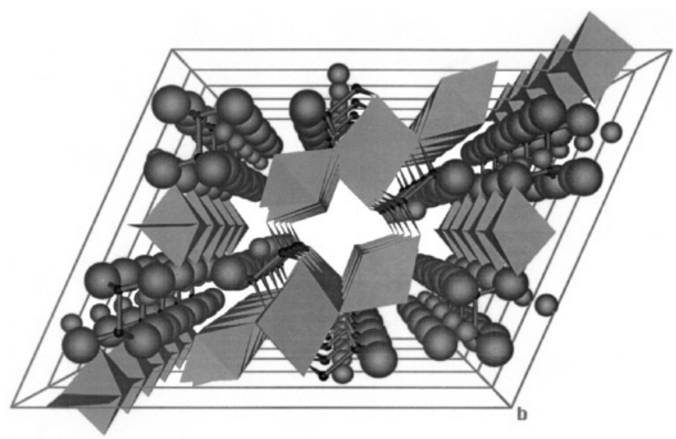

FIG. 4. Crystal structure of $Na_4P_2S_6 \cdot 6H_2O$ viewed along the *b* axis. The octahedra are NaO_6, the square planes are NaO_4, the large spheres are sulfur atoms, and the small spheres are phosphorus atoms.

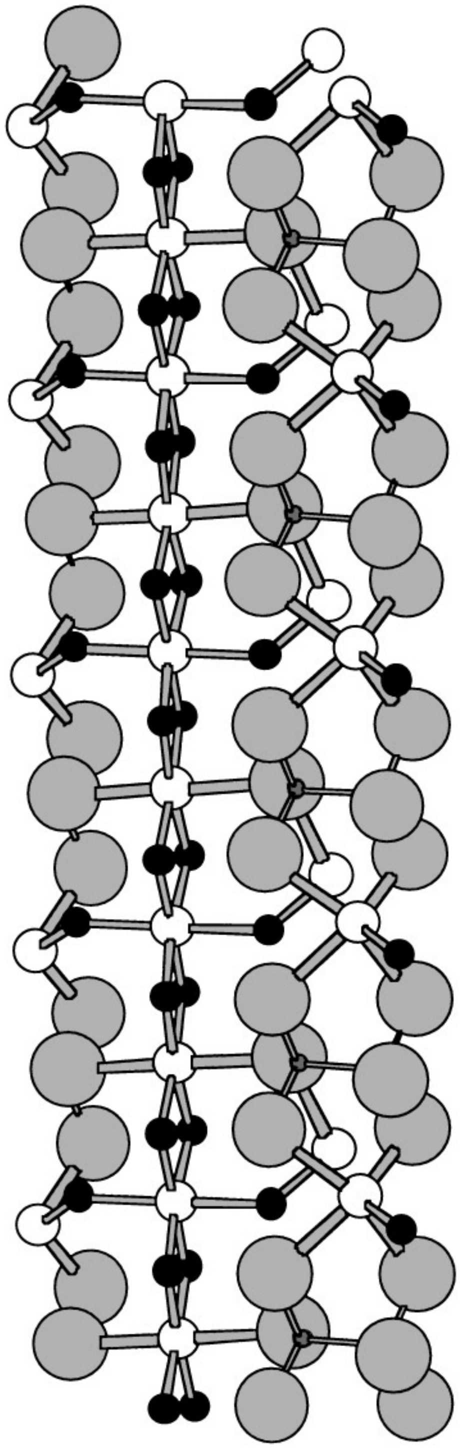

FIG. 5. Crystal structure of $Na_4P_2S_6 \cdot 6H_2O$ viewed perpendicular to the *b* axis. The white circles are sodium atoms, the black circles are oxygen atoms, the large gray circles are sulfur atoms, and the small dark gray circles are phosphorus atoms.

between NaO_6 and NaO_4S_2. These chains run parallel to the *b* axis. The view in Fig. 4 is along the *b* axis and parallel to these chains. The NaO_4S_2 octahedra are shown in

TABLE 2
Observed Infrared Absorbtion Peaks (cm^{-1}) for $Na_4P_2S_6 \cdot 6H_2O$, $Na_4P_2S_6$, and Calculated Values for $P_2S_6^{-4}$

$Na_4P_2S_6 \cdot 6H_2O$	$Na_4P_2S_6$	$P_2S_6^{-4}$, calc.
434		
442	449	437.8
471	470	
484		
533	542	524.2
556		
568	566	
579	582	584.5, 584.1
590		
609	601	586.7, 586.4

TABLE 3
Atomic Coordinates ($\times 10^{-4}$) and Equivalent Isotropic Displacement Parameters (Å$\times 10^{-3}$) for $Na_4P_2S_6 \cdot 6H_2O$

	x	*y*	*z*	*U* (eq)
P (3)	1419 (1)	2926 (3)	2979 (1)	18 (1)
P (4)	1020 (1)	2741 (3)	1773 (1)	20 (1)
P (1)	3578 (1)	− 2357 (4)	1560 (1)	21 (1)
P (2)	3979 (1)	2459 (4)	754 (1)	21 (1)
S (9)	1898 (1)	5305 (4)	3229 (1)	28 (1)
S (6)	3310 (1)	− 2765 (4)	− 193 (1)	31 (1)
S (8)	1891 (1)	545 (3)	3318 (1)	26 (1)
S (3)	4226 (1)	− 2139 (4)	2554 (1)	28 (1)
S (7)	772 (1)	3077 (4)	3326 (1)	26 (1)
S (12)	594 (1)	5220 (4)	1449 (1)	28 (1)
S (11)	483 (1)	492 (4)	1543 (1)	30 (1)
S (5)	4518 (1)	− 4696 (4)	1045 (1)	32 (1)
S (4)	4407 (1)	37 (4)	875 (1)	31 (1)
S (10)	1689 (1)	2377 (4)	1497 (1)	31 (1)
S (2)	3060 (1)	− 74 (4)	1334 (1)	30 (1)
S (1)	3146 (1)	− 4826 (4)	1431 (1)	29 (1)
Na (1)	6334 (2)	− 2229 (6)	1385 (2)	36 (1)
Na (2)	3671 (2)	− 2203 (6)	3603 (2)	37 (1)
Na (3)	1332 (2)	− 2166 (6)	4946 (2)	35 (1)
Na (4)	1331 (2)	2854 (6)	4929 (2)	35 (1)
Na (5)	1469 (2)	8112 (6)	2037 (2)	40 (1)
Na (6)	3537 (2)	2853 (7)	573 (2)	46 (1)
Na (7)	185 (2)	− 364 (6)	2843 (2)	41 (1)
Na (8)	5188 (2)	− 588 (6)	2351 (2)	42 (1)
O (1)	6940 (3)	275 (11)	2045 (4)	39 (2)
O (2)	3022 (3)	292 (11)	2942 (4)	36 (2)
O (3)	690 (3)	311 (11)	4892 (4)	34 (2)
O (4)	5911 (3)	− 2554 (11)	2307 (4)	39 (2)
O (5)	5688 (3)	274 (11)	786 (4)	38 (2)
O (6)	1942 (3)	5360 (11)	4866 (4)	39 (2)
O (7)	695 (3)	− 4622 (11)	4983 (4)	40 (2)
O (8)	5698 (3)	− 4649 (11)	731 (4)	38 (2)
O (9)	909 (3)	− 2279 (11)	3602 (4)	41 (2)
O (10)	1977 (3)	320 (11)	4947 (4)	40 (2)
O (11)	3115 (3)	1875 (13)	− 610 (4)	46 (2)
O (12)	1875 (3)	6995 (13)	1271 (4)	49 (2)

Note. *U* (eq) is defined as one third of the trace of the orthogonalized *Uij* tensor.

Fig. 4 as square planes of NaO_4 with sulfurs above and below the plane. This can be seen better in Fig. 5 where a view perpendicular to the chains is presented. In Fig. 5 the alternating NaO_6 and NaO_4S_2 octahedra are clearly seen below a chain of P_2S_6 units. The P_2S_6 units are connected by a sodium bridge atom.

The $P_2S_6^{-4}$ units are bidentate to the Na^+ similar to what is observed in the layered transition metal phosphorus chalcogenides. However, unlike the transition metal compounds, only two of the $P_2S_6^{-4}$ ions are bound to the Na^+. Instead of a third $P_2S_6^{-4}$ completing an octahedral arrangement of sulfurs around the metal ion, an oxygen atom occupies this site. This arrangement of $P_2S_6^{-4}$ ions and oxygen can be seen in Fig. 5.

The NaO_6 octahedra consist of four Na–O(equatorial) bonds and two Na–O(axial) bonds. The equatorial Na–O bond lengths for a typical NaO_6 octahedron (Na(3)-centered) are 2.375(8), 2.404(8), 2.412(9), and 2.395(9) Å. The axial Na–O bond lengths for this octahedron are 2.508(8) Å and 2.493(8) Å. The equatorial Na–O bond lengths for a typical NaO_4S_2 (Na(4)-centered) are 2.448(9), 2.401(8), 2.429(9), and 2.417(8) Å. The axial Na–S bond lengths for this octahedron are 2.996(4) and 2.950(4) Å. The two axial Na–S bonds are longer than the two axial Na–O bonds due to sulfur's larger size compared to oxygen.

The structure of $P_2S_6^{-4}$ was already mentioned with respect to its effect on the infrared absorption spectrum. $Na_4P_2S_6 \cdot 6H_2O$ contains four different $P_2S_6^{-4}$ ions consisting of P–P bonds of 2.251(3) and 2.254(3) Å and six different P–S bond lengths ranging from 2.011(3) to 2.037(3) Å. For comparison, the $P_2S_6^{-4}$ ion in $Li_4P_2S_6$ is reported to have D_{3d} symmetry with a P–P bond length of 2.256(13) Å and P–S bonds of 2.032(5) Å. A comparison of $Na_4P_2S_6 \cdot 6H_2O$, $Li_4P_2S_6$, and SnP_2S_6 is shown in Table 6.

CONCLUSION

We reported the single-crystal structure of $Na_4P_2S_6 \cdot 6H_2O$ along with thermogravimetric analysis data and the infrared absorption spectrum. This compound contained four distinct $P_2S_6^{-4}$ ions in the crystal structure, none of which adopted the ideal D_{3d} ethane-like structure expected for X_2Y_6. This structural information is important for the interpretation of the infrared spectrum. The thermogravimetric analysis suggested that the hexahydrate is the only stable hydrate of $Na_4P_2S_6$.

TABLE 4
Bond Lengths (Å) and Angles (°) for $Na_4P_2S_6 \cdot 6H_2O$

P (3)–S (9)	2.027 (3)	Na (4)–O (6)	2.401 (8)	S (4)–P (2)–P (1)	105.02 (14)
P (3)–S (8)	2.029 (3)	Na (4)–O (3)	2.417 (8)	P (3)–S (9)–Na (5)	111.35 (14)
P (3)–S (7)	2.037 (3)	Na (4)–O (10)	2.429 (9)	P (2)–S (6)–Na (2) #2	111.75 (14)
P (3)–P (4)	2.254 (3)	Na (4)–O (7) #10	2.448 (9)	P (3)–S (8)–Na (5) #1	103.33 (13)
P (4)–S (10)	2.011 (3)	Na (4)–S (10) #9	2.950 (4)	P (1)–S (3)–Na (8) #3	101.4 (2)
P (4)–S (12)	2.035 (3)	Na (4)–Na (3) #10	3.538 (6)	P (1)–S (3)–Na (8)	106.74 (14)
P (4)–S (11)	2.033 (3)	Na (5)–O (12)	2.324 (8)	Na (8) #3–S (3)–Na (8)	83.38 (8)
P (4)–Na (5) #1	3.453 (5)	Na (5)–S (11) #10	2.859 (5)	P (1)–S (3)–Na (2)	106.18 (13)
P (1)–S (2)	2.025 (4)	Na (5)–S (8) #10	2.949 (5)	Na (8) #3–S (3)–Na (2)	108.90 (14)
P (1)–S (1)	2.031 (4)	Na (5)–S (10) #10	3.344 (5)	Na (8)–S (3)–Na (2)	141.5 (2)
P (1)–S (3)	2.041 (3)	Na (5)–P (4) #10	3.453 (5)	P (3)–S (7)–Na (7)	102.91 (14)
P (1)–P (2)	2.251 (3)	Na (5)–Na (3) #5	4.178 (6)	P (3)–S (7)–Na (7) #4	105.80 (14)
P (2)–S (6)	2.012 (3)	Na (6)–O (11)	2.315 (8)	Na (7)–S (7)–Na (7) #4	83.59 (8)
P (2)–S (5)	2.027 (3)	Na (6)–S (1) #10	2.853 (5)	P (3)–S (7)–Na (4)	105.92 (13)
P (2)–S (4)	2.044 (4)	Na (6)–S (5) #10	2.879 (5)	Na (7)–S (7)–Na (4)	106.75 (14)
S (9)–Na (5)	2.989 (5)	Na (6)–Na (1) #6	4.147 (6)	Na (7) #4–S (7)–Na (4)	143.27 (14)
S (6)–Na (2) #2	2.938 (5)	Na (7)–O (9)	2.316 (8)	P (4)–S (12)–Na (7) #4	95.63 (14)
S (8)–Na (5) #1	2.949 (5)	Na (7)–S (7) #11	2.865 (5)	P (4)–S (12)–Na (5)	104.74 (14)
S (3)–Na (8) #3	2.836 (5)	Na (7)–S (12) #11	2.907 (5)	Na (7) #4–S (12)–Na (5)	117.36 (14)
S (3)–Na (8)	2.861 (5)	Na (7)–Na (7) #11	3.795 (3)	P (4)–S (11)–Na (5) #1	88.13 (14)
S (3)–Na (2)	2.993 (5)	Na (7)–Na (7) #4	3.795 (3)	P (4)–S (11)–Na (7)	109.31 (14)
S (7)–Na (7)	2.830 (5)	Na (8)–O (4)	2.343 (9)	Na (5) #1–S (11)–Na (7)	93.69 (14)
S (7)–Na (7) #4	2.865 (5)	Na (8)–S (3) #7	2.836 (5)	P (2)–S (5)–Na (6) #1	88.9 (2)
S (7)–Na (4)	2.996 (4)	Na (8)–S (5) #7	3.105 (5)	P (2)–S (5)–Na (8) #3	108.58 (14)
S (12)–Na (7) #4	2.907 (5)	Na (8)–Na (8) #3	3.789 (3)	Na (6) #1–S (5)–Na (8) #3	92.39 (14)
S (12)–Na (5)	2.916 (5)	Na (8)–Na (8) #7	3.789 (3)	P (2)–S (4)–Na (6)	104.5 (2)
S (11)–Na (5) #1	2.859 (5)	O (1)–Na (2) #7	2.395 (9)	P (2)–S (4)–Na (8)	96.02 (14)
S (11)–Na (7)	3.087 (5)	O (2)–Na (1) #7	2.425 (8)	Na (6)–S (4)–Na (8)	118.8 (2)
S (5)–Na (6) #1	2.879 (5)	O (5)–Na (2) #7	2.410 (8)	P (4)–S (10)–Na (4) #5	112.15 (14)
S (5)–Na (8) #3	3.105 (5)	O (6)–Na (3) #10	2.395 (9)	P (4)–S (10)–Na (5) #1	75.78 (12)
S (4)–Na (6)	2.865 (5)	O (7)–Na (4) #1	2.448 (9)	Na (4) #5–S (10)–Na (5) #1	106.49 (13)
S (4)–Na (8)	2.898 (5)	O (8)–Na (2) #3	2.444 (9)	P (1)–S (2)–Na (6)	107.43 (14)
S (10)–Na (4) #5	2.950 (4)	O (11)–Na (1) #6	2.506 (8)	P (1)–S (1)–Na (6) #1	106.0 (2)
S (10)–Na (5) #1	3.344 (5)	O (12)–Na (3) #5	2.493 (8)	O (8)–Na (1)–O (1)	177.6 (3)
S (2)–Na (6)	3.113 (6)	S (9)–P (3)–S (8)	113.22 (14)	O (8)–Na (1)–O (5)	94.3 (3)
S (1)–Na (6) #1	2.853 (5)	S (9)–P (3)–S (7)	111.01 (14)	O (1)–Na (1)–O (5)	83.8 (3)
Na (1)–O (8)	2.373 (8)	S (8)–P (3)–S (7)	112.16 (14)	O (8)–Na (1)–O (2) #3	87.0 (3)
Na (1)–O (1)	2.388 (8)	S (9)–P (3)–P (4)	106.66 (13)	O (1)–Na (1)–O (2) #3	94.8 (3)
Na (1)–O (5)	2.399 (9)	S (8)–P (3)–P (4)	105.72 (13)	O (5)–Na (1)–O (2) #3	176.5 (3)
Na (1)–O (2) #3	2.425 (8)	S (7)–P (3)–P (4)	107.61 (13)	O (8)–Na (1)–O (11) #6	98.5 (3)
Na (1)–O (11) #6	2.506 (8)	S (10)–P (4)–S (12)	115.1 (2)	O (1)–Na (1)–O (11) #6	83.0 (3)
Na (1)–O (4)	2.516 (8)	S (10)–P (4)–S (11)	113.7 (2)	O (5)–Na (1)–O (11) #6	92.8 (3)
Na (1)–Na (2) #3	3.533 (6)	S (12)–P (4)–S (11)	112.48 (14)	O (2) #3–Na (1)–O (11) #6	90.3 (3)
Na (1)–Na (2) #7	3.571 (6)	S (10)–P (4)–P (3)	104.17 (13)	O (8)–Na (1)–O (4)	87.3 (3)
Na (1)–Na (6) #6	4.147 (6)	S (12)–P (4)–P (3)	104.64 (13)	O (1)–Na (1)–O (4)	91.3 (3)
Na (2)–O (1) #3	2.395 (9)	S (11)–P (4)–P (3)	105.45 (13)	O (5)–Na (1)–O (4)	92.1 (3)
Na (2)–O (5) #3	2.410 (8)	S (10)–P (4)–Na (5) #1	69.85 (12)	O (2) #3–Na (1)–O (4)	84.7 (3)
Na (2)–O (2)	2.432 (8)	S (12)–P (4)–Na (5) #1	167.24 (14)	O (11) #6–Na (1)–O (4)	172.1 (3)
Na (2)–O (8) #7	2.444 (9)	S (11)–P (4)–Na (5) #1	55.83 (12)	O (8)–Na (1)–Na (2) #3	43.6 (2)
Na (2)–S (6) #8	2.938 (5)	P (3)–P (4)–Na (5) #1	84.72 (11)	O (1)–Na (1)–Na (2) #3	138.1 (2)
Na (2)–Na (1) #7	3.533 (6)	S (2)–P (1)–S (1)	113.02 (14)	O (5)–Na (1)–Na (2) #3	137.8 (2)
Na (2)–Na (1) #3	3.571 (6)	S (2)–P (1)–S (3)	111.1 (12)	O (2) #3–Na (1)–Na (2) #3	43.4 (2)
Na (3)–O (3)	2.375 (8)	S (1)–P (1)–S (3)	112.1 (2)	O (11) #6–Na (1)–Na (2) #3	96.3 (2)
Na (3)–O (6) #1	2.395 (9)	S (2)–P (1)–P (2)	107.71 (14)	O (4)–Na (1)–Na (2) #3	84.2 (2)
Na (3)–O (7)	2.404 (8)	S (1)–P (1)–P (2)	104.94 (13)	O (8)–Na (1)–Na (2) #7	136.4 (2)
Na (3)–O (10)	2.412 (9)	S (3)–P (1)–P (2)	107.47 (13)	O (1)–Na (1)–Na (2) #7	41.8 (2)
Na (3)–O (12) #9	2.493 (8)	S (6)–P (2)–S (5)	114.3 (2)	O (5)–Na (1)–Na (2) #7	42.2 (2)
Na (3)–O (9)	2.508 (8)	S (6)–P (2)–S (4)	114.6 (2)	O (2) #3–Na (1)–Na (2) #7	136.5 (2)
Na (3)–Na (4) #1	3.538 (6)	S (5)–P (2)–S (4)	112.2 (2)	O (11) #6–Na (1)–Na (2) #7	84.7 (2)
Na (3)–Na (4)	3.566 (6)	S (6)–P (2)–P (1)	104.08 (13)	O (4)–Na (1)–Na (2) #7	94.8 (2)
Na (3)–Na (5) #9	4.178 (6)	S (5)–P (2)–P (1)	105.27 (14)	Na (2) #3–Na (1)–Na (2) #7	179.0 (2)

TABLE 4—*Continued*

O (8) –Na (1)–Na (6) #6	71.5 (2)	O (9)–Na (3)–Na (4)	91.3 (2)	S (8) #10–Na (5)–Na (3) #5	147.8 (2)
O (1) –Na (1)–Na (6) #6	109.7 (2)	Na (4) #1–Na (3)–Na (4)	178.9 (2)	S (9)–Na (5)–Na (3) #5	124.96 (14)
O (5) –Na (1)–Na (6) #6	83.8 (2)	O (3)–Na (3)–Na (5) #9	86.7 (2)	S (10) #10–Na (5)–Na (3) #5	76.66 (11)
O (2) #3–Na (1)–Na (6) #6	99.7 (2)	O (6) #1–Na (3)–Na (5) #9	99.1 (2)	P (4) #10–Na (5)–Na (3) #5	96.13 (12)
O (11) #6–Na (1)–Na (6) #6	29.3 (2)	O (7)–Na (3)–Na (5) #9	68.6 (2)	O (11)–Na (6)–S (1) #10	132.7 (3)
O (4) –Na (1)–Na (6) #6	157.9 (2)	O (10)–Na (3)–Na (5) #9	109.6 (2)	O (11)–Na (6)–S (4)	90.7 (3)
Na (2) #3–Na (1)–Na (6) #6	84.34 (13)	O (12) #9–Na (3)–Na (5) #9	28.7 (2)	S (1) #10–Na (6)–S (4)	134.5 (2)
Na (2) #7–Na (1)–Na (6) #6	96.60 (13)	O (9)–Na (3)–Na (5) #9	158.3 (2)	O (11)–Na (6)–S (5) #10	120.6 (3)
O (1) #3–Na (2)–O (5) #3	83.4 (3)	Na (4) #1–Na (3)–Na (5) #9	81.28 (12)	S (1) #10–Na (6)–S (5) #10	85.07 (14)
O (1) #3–Na (2)–O (2)	95.2 (3)	Na (4)–Na (3)–Na (5) #9	99.79 (13)	S (4)–Na (6)–S (5) #10	81.73 (13)
O (5) #3–Na (2)–O (2)	177.7 (3)	O (6)–Na (4)–O (3)	175.5 (3)	O (11)–Na (6)–S (2)	101.8 (3)
O (1) #3–Na (2)–O (8) #7	179.5 (3)	O (6)–Na (4)–O (10)	95.7 (3)	S (1) #10–Na (6)–S (2)	77.39 (12)
O (5) #3–Na (2)–O (8) #7	96.1 (3)	O (3)–Na (4)–O (10)	83.8 (3)	S (4)–Na (6)–S (2)	81.29 (14)
O (2)–Na (2)–O (8) #7	85.3 (3)	O (6)–Na (4)–O (7) #10	85.1 (3)	S (5) #10–Na (6)–S (2)	134.2 (2)
O (1) #3–Na (2)–S (6) #8	95.8 (2)	O (3)–Na (4)–O (7) #10	95.6 (3)	O (11)–Na (6)–Na (1) #6	32.0 (2)
O (5) #3–Na (2)–S (6) #8	86.4 (2)	O (10)–Na (4)–O (7) #10	176.8 (3)	S (1) #10–Na (6)–Na (1) #6	146.1 (2)
O (2)–Na (2)–S (6) #8	95.5 (2)	O (6)–Na (4)–S (10) #9	99.9 (2)	S (4)–Na (6)–Na (1) #6	77.34 (12)
O (8) #7–Na (2)–S (6) #8	84.2 (2)	O (3)–Na (4)–S (10) #9	84.6 (2)	S (5) #10–Na (6)–Na (1) #6	89.67 (13)
O (1) #3–Na (2)–S (3)	90.4 (2)	O (10)–Na (4)–S (10) #9	91.6 (2)	S (2)–Na (6)–Na (1) #6	127.0 (2)
O (5) #3–Na (2)–S (3)	87.9 (2)	O (7) #10–Na (4)–S (10) #9	85.3 (2)	O (9)–Na (7)–S (7)	96.1 (3)
O (2)–Na (2)–S (3)	90.3 (2)	O (6)–Na (4)–S (7)	86.5 (2)	O (9)–Na (7)–S (7) #11	121.0 (3)
O (8) #7–Na (2)–S (3)	89.5 (2)	O (3)–Na (4)–S (7)	89.0 (2)	S (7)–Na (7)–S (7) #11	141.2 (2)
S (6) #8–Na (2)–S (3)	171.0 (2)	O (10)–Na (4)–S (7)	94.6 (2)	O (9)–Na (7)–S (12) #11	105.9 (2)
O (1) #3–Na (2)–Na (1) #7	138.5 (2)	O (7) #10–Na (4)–S (7)	88.5 (2)	S (7)–Na (7)–S (12) #11	94.35 (14)
O (5) #3–Na (2)–Na (1) #7	138.1 (2)	S (10) #9–Na (4)–S (7)	170.6 (2)	S (7) #11–Na (7)–S (12) #11	86.69 (13)
O (2)–Na (2)–Na (1) #7	43.2 (2)	O (6) –Na (4)–Na (3) #10	42.4 (2)	O (9)–Na (7)–S (11)	106.5 (2)
O (8) #7–Na (2)–Na (1) #7	42.0 (2)	O (3) –Na (4)–Na (3) #10	138.2 (2)	S (7)–Na (7)–S (11)	81.40 (13)
S (6) #8–Na (2)–Na (1) #7	89.96 (14)	O (10) –Na (4)–Na (3) #10	138.0 (2)	S (7) #11–Na (7)–S (11)	77.54 (12)
S (3)–Na (2)–Na (1) #7	89.63 (14)	O (7) #10–Na (4)–Na (3) #10	42.7 (2)	S (12) #11–Na (7)–S (11)	147.6 (2)
O (1) #3–Na (2)–Na (1) #3	41.6 (2)	S (10) #9–Na (4)–Na (3) #10	92.67 (13)	O (9)–Na (7)–Na (7) #11	73.2 (2)
O (5) #3–Na (2)–Na (1) #3	41.9 (2)	S (7)–Na (4)–Na (3) #10	87.48 (13)	S (7)–Na (7)–Na (7) #11	162.9 (2)
O (2)–Na (2)–Na (1) #3	136.8 (2)	O (6)–Na (4)–Na (3)	138.0 (2)	S (7) #11–Na (7)–Na (7) #11	47.81 (13)
O (8) #7–Na (2)–Na (1) #3	137.9 (2)	O (3)–Na (4)–Na (3)	41.5 (2)	S (12) #11–Na (7)–Na (7) #11	101.4 (2)
S (6) #8–Na (2)–Na (1) #3	89.06 (14)	O (10)–Na (4)–Na (3)	42.4 (2)	S (11)–Na (7)–Na (7) #11	88.8 (2)
S (3)–Na (2)–Na (1) #3	91.36 (14)	O (7) #10–Na (4)–Na (3)	136.9 (2)	O (9)–Na (7)–Na (7) #4	144.1 (3)
Na (1) #7–Na (2)–Na (1) #3	179.0 (2)	S (10) #9–Na (4)–Na (3)	86.28 (13)	S (7)–Na (7)–Na (7) #4	48.60 (8)
O (3)–Na (3)–O (6) #1	174.0 (3)	S (7)–Na (4)–Na (3)	93.52 (13)	S (7) #11–Na (7)–Na (7) #4	93.0 (2)
O (3)–Na (3)–O (7)	94.5 (3)	Na (3) #10–Na (4)–Na (3)	178.9 (2)	S (12) #11–Na (7)–Na (7) #4	86.0 (2)
O (6) #1–Na (3)–O (7)	86.2 (3)	O (12)–Na (5)–S (11) #10	122.0 (3)	S (11)–Na (7)–Na (7) #4	67.09 (14)
O (3)–Na (3)–O (10)	85.1 (3)	O (12)–Na (5)–S (12)	87.6 (3)	Na (7) #11–Na (7)–Na (7) #4	138.7 (2)
O (6) #1–Na (3)–O (10)	94.4 (3)	S (11) #10–Na (5)–S (12)	81.41 (13)	O (4)–Na (8)–S (3) #7	96.7 (2)
O (7)–Na (3)–O (10)	178.2 (3)	O (12)–Na (5)–S (8) #10	133.6 (3)	O (4)–Na (8)–S (3)	120.5 (3)
O (3)–Na (3)–O (12) #9	95.1 (3)	S (11) #10–Na (5)–S (8) #10	85.59 (13)	S (3) #7–Na (8)–S (3)	141.3 (2)
O (6) #1–Na (3)–O (12) #9	90.8 (3)	S (12)–Na (5)–S (8) #10	136.4 (2)	O (4)–Na (8)–S (4)	106.1 (2)
O (7)–Na (3)–O (12) #9	95.3 (3)	O (12)–Na (5)–S (9)	101.5 (3)	S (3) #7–Na (8)–S (4)	93.7 (2)
O (10)–Na (3)–O (12) #9	83.1 (3)	S (11) #10–Na (5)–S (9)	131.7 (2)	S (3)–Na (8)–S (4)	86.22 (13)
O (3)–Na (3)–O (9)	89.1 (3)	S (12)–Na (5)–S (9)	80.51 (13)	O (4)–Na (8)–S (5) #7	107.3 (2)
O (6) #1–Na (3)–O (9)	84.9 (3)	S (8) #10–Na (5)–S (9)	77.75 (12)	S (3) #7–Na (8)–S (5) #7	81.46 (13)
O (7)–Na (3)–O (9)	90.5 (3)	O (12)–Na (5)–S (10) #10	85.0 (3)	S (3)–Na (8)–S (5) #7	77.91 (12)
O (10)–Na (3)–O (9)	91.2 (3)	S (11) #10–Na (5)–S (10) #10	65.63 (11)	S (4)–Na (8)–S (5) #7	146.6 (2)
O (12) #9–Na (3)–O (9)	172.5 (3)	S (12)–Na (5)–S (10) #10	134.8 (2)	O (4)–Na (8)–Na (8) #3	72.5 (2)
O (3)–Na (3)–Na (4) #1	137.9 (2)	S (8) #10–Na (5)–S (10) #10	73.10 (12)	S (3) #7–Na (8)–Na (8) #3	163.4 (2)
O (6) #1–Na (3)–Na (4) #1	42.5 (2)	S (9)–Na (5)–S (10) #10	144.6 (2)	S (3)–Na (8)–Na (8) #3	48.03 (13)
O (7)–Na (3)–Na (4) #1	43.7 (2)	O (12)–Na (5)–P (4) #10	115.4 (3)	S (4)–Na (8)–Na (8) #3	101.3 (2)
O (10)–Na (3)–Na (4) #1	136.9 (2)	S (11) #10–Na (5)–P (4) #10	36.04 (8)	S (5) #7–Na (8)–Na (8) #3	89.7 (2)
O (12) #9–Na (3)–Na (4) #1	93.3 (3)	S (12)–Na (5)–P (4) #10	117.06 (14)	O (4)–Na (8)–Na (8) #7	144.8 (3)
O (9)–Na (3)–Na (4) #1	87.7 (2)	S (8) #10–Na (5)–P (4) #10	63.94 (10)	S (3) #7–Na (8)–Na (8) #7	48.59 (8)
O (3)–Na (3)–Na (4)	42.4 (2)	S (9)–Na (5)–P (4) #10	138.8 (2)	S (3)–Na (8)–Na (8) #7	93.1 (2)
O (6) #1–Na (3)–Na (4)	137.0 (2)	S (10) #10–Na (5)–P (4) #10	34.37 (7)	S (4)–Na (8)–Na (8) #7	84.8 (2)
O (7)–Na (3)–Na (4)	136.7 (3)	O (12)–Na (5)–Na (3) #5	31.0 (2)	S (5) #7–Na (8)–Na (8) #7	67.2 (2)
O (10)–Na (3)–Na (4)	42.7 (2)	S (11) #10–Na (5)–Na (3) #5	91.86 (13)	Na (8) #3–Na (8)–Na (8) #7	139.3 (2)
O (12) #9–Na (3)–Na (4)	87.7 (3)	S (12)–Na (5)–Na (3) #5	74.32 (11)	Na (2) #7–O (1)–Na (1)	96.6 (3)

TABLE 4—*Continued*

Na (1) #7–O (2)–Na (2)	93.4 (3)	Na (4)–O (6)–Na (3) #10	95.0 (3)	Na (3)–O (10)–Na (4)	94.9 (3)
Na (3)–O (3)–Na (4)	96.2 (3)	Na (3)–O (7)–Na (4) #1	93.6 (3)	Na (6)–O (11)–Na (1) #6	118.6 (3)
Na (8)–O (4)–Na (1)	123.4 (3)	Na (1)–O (8)–Na (2) #3	94.3 (3)	Na (5)–O (12)–Na (3) #5	120.2 (3)
Na (1)–O (5)–Na (2) #7	95.9 (3)	Na (7)–O (9)–Na (3)	126.1 (3)		

Note. Symmetry transformations used to generate equivalent atoms: (#1) $x, y-1, z$; (#2) $x, -y-1/2, z-1/2$; (#3) $-x+1, y-1/2, -z+1/2$; (#4) $-x, y+1/2, -z+1/2$; (#5) $x, -y+1/2, z-1/2$, (#6) $-x+1, -y, -z$; (#7) $-x+1, y+1/2, -z+1/2$; (#8) $x, -y-1/2, z+1/2$; (#9) $x, -y+1/2, z+1/2$; (#10) $x, y+1, z$; (#11) $-x, y-1/2, -z+1/2$.

TABLE 5
Anisotropic Displacement Parameters ($Å^2 \times 10^{-3}$) for $Na_4P_2S_6 \cdot 6H_2O$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P (3)	19 (1)	20 (1)	16 (1)	0 (1)	7 (1)	0 (1)
P (4)	21 (1)	23 (1)	15 (1)	− 1 (1)	6 (1)	0 (1)
P (1)	19 (1)	29 (1)	16 (1)	− 3 (1)	7 (1)	0 (1)
P (2)	21 (1)	25 (1)	19 (1)	0 (1)	10 (1)	1 (1)
S (9)	28 (1)	27 (1)	26 (1)	− 4 (1)	10 (1)	− 6 (1)
S (6)	31 (1)	43 (2)	18 (1)	− 2 (1)	7 (1)	− 2 (1)
S (8)	30 (1)	26 (1)	23 (1)	4 (1)	11 (1)	8 (1)
S (3)	24 (1)	40 (2)	18 (1)	− 3 (1)	7 (1)	− 1 (1)
S (7)	23 (1)	35 (1)	22 (1)	− 2 (1)	11 (1)	1 (1)
S (12)	29 (1)	28 (1)	25 (1)	4 (1)	8 (1)	6 (1)
S (11)	29 (1)	29 (1)	26 (1)	− 3 (1)	6 (1)	− 8 (1)
S (5)	30 (1)	34 (1)	37 (1)	7 (1)	18 (1)	11 (1)
S (4)	31 (1)	30 (1)	33 (1)	− 2 (1)	16 (1)	− 7 (1)
S (10)	30 (1)	41 (2)	24 (1)	0 (1)	14 (1)	5 (1)
S (2)	29 (1)	34 (1)	27 (1)	− 4 (1)	10 (1)	8 (1)
S (1)	29 (1)	32 (1)	26 (1)	− 1 (1)	12 (1)	− 5 (1)
Na (1)	36 (2)	36 (2)	36 (2)	− 2 (2)	13 (2)	− 4 (2)
Na (2)	39 (2)	35 (2)	35 (2)	5 (2)	15 (2)	4 (2)
Na (3)	37 (2)	32 (2)	37 (2)	− 2 (2)	16 (2)	− 2 (2)
Na (4)	45 (2)	25 (2)	35 (2)	1 (2)	16 (2)	1 (2)
Na (5)	43 (2)	40 (3)	39 (2)	− 6 (2)	17 (2)	6 (2)
Na (6)	43 (3)	57 (3)	39 (2)	− 14 (2)	16 (2)	− 4 (2)
Na (7)	38 (2)	40 (3)	39 (2)	− 1 (2)	11 (2)	− 1 (2)
Na (8)	37 (2)	42 (3)	49 (3)	0 (2)	19 (2)	− 6 (2)
O (1)	37 (4)	47 (5)	32 (4)	− 7 (3)	11 (3)	− 2 (4)
O (2)	40 (4)	38 (4)	33 (4)	− 5 (3)	17 (3)	5 (3)
O (3)	31 (4)	41 (4)	32 (4)	− 8 (3)	13 (3)	0 (3)
O (4)	42 (4)	38 (4)	38 (4)	8 (4)	17 (3)	5 (4)
O (5)	32 (4)	51 (5)	30 (4)	2 (3)	12 (3)	− 1 (4)
O (6)	28 (4)	49 (5)	35 (4)	− 1 (4)	9 (3)	− 6 (3)
O (7)	36 (4)	48 (5)	35 (4)	2 (4)	14 (3)	− 7 (4)
O (8)	35 (4)	45 (5)	33 (4)	− 1 (3)	13 (3)	− 2 (3)
O (9)	47 (5)	38 (4)	36 (4)	6 (3)	14 (3)	15 (4)
O (10)	43 (4)	46 (5)	33 (4)	5 (4)	16 (3)	− 3 (4)
O (11)	40 (4)	68 (6)	30 (4)	− 8 (4)	14 (3)	− 4 (4)
O (12)	38 (4)	75 (6)	37 (4)	− 3 (4)	19 (4)	4 (4)

Note. The anisotropic displacement factor exponent takes the form $-2\pi^2\,[h^2\,a^{*2}\,U_{11} + \cdots + 2h\,k\,a^*\,b^*\,U_{12}]$.

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TABLE 6
Comparison of $P_2S_6^{-4}$ Bond Lengths in $Na_4P_2S_6 \cdot 6H_2O$, $Li_4P_2S_6$, and SnP_2S_6

Compound	P–P (Å)	P–S (Å)[a]	Ref.
$Na_4P_2S_6 \cdot 6H_2O$	2.251 (3)	2.027 (3)	[b]
	2.254 (3)	2.029 (3)	[b]
		2.037 (3)	[b]
		2.011 (3)	[b]
		2.035 (3)	[b]
		2.033 (5)	[b]
$Li_4P_2S_6$	2.256 (13)	2.032 (5)	(10)
SnP_2S_6	2.210 (3)	2.025 (2)	(8)
		2.034 (2)	

[a] One set from a total of four.
[b] This work.

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