Synthesis and Crystal Structure of SnP_2S_6

Z. Wang and R. D. Willett

Department of Chemistry, Washington State University, Pullman, Washington 99164-4630

R. A. Laitinen and D. A. Cleary*

Department of Chemistry, Gonzaga University, Spokane, Washington 99258

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We report the synthesis and single-crystal analysis of the first layered AP_2S_6 compound. The structure of the title compound, SnP_2S_6, is rhombohedral, space group $R\bar{3}$ with a = 5.999(2) Å and c = 19.424(4) Å and Z = 3. The diffraction data are refined to a final R value of 0.0158. This compound is an ordered defect structure of the $Fe_2P_2S_6$ type where one-half of the metal sites are vacant. Hence, the tin atoms in SnP_2S_6 have a formal oxidation state of +4. This compound has previously been shown by us to display nonlinear optical behavior.

Introduction

The transition-metal hypodithiophosphates, $M_2P_2X_6$, where M is a transition metal and X is sulfur or selenium, were first reported by Hahn and Klingen in 1965.[1] The single-crystal structure of $Fe_2P_2S_6$ was reported by Klingen et al. in 1973.[2] Also in 1973, Klingen et al. reported three different $Sn_2P_2S_6$ phases, one rhombohedral and two monoclinic, which they labeled as monoclinic(I) and monoclinic(II).[3] The rhombohedral phase is isomorphous with $Fe_2P_2Se_6$, while the monoclinic(I) phase was reported to be isomorphous with $Fe_2P_2S_6$. We have recently reported the high-temperature crystal structure of the monoclinic(II) phase.[4] The monoclinic(II) phase crystallizes in massive crystals consistent with its three-dimensional network structure. The material has a large optical density, but very thin crystals are orange in transmission, and the powdered material is orange. The monoclinic(I) phase, however, was reported to crystallize in thin hexagonal platelets which are red in transmission. Under similar conditions, we obtain similar red hexagonal platelets which belong to the rhombohedral crystal class. These crystals are isomorphous with $Fe_2P_2Se_6$, except that one-half of the metal sites are vacant. Hence, while in $Fe_2P_2Se_6$ the metal ions are +2, in SnP_2S_6 the metal ions are +4.

The existence of a $M^{IV}P_2S_6$ lattice should be seen as the limit of the mixed-metal $M_xM'_yP_2S_6$ lattices. A variety of metal combinations have been used including dipositive,[5] dipositive and monopositive,[6] tripositive and monopositive,[7,8] and vacancy tripositive pair.[9] In the present case, M = Sn^{+4}, M′ = vacancy, and the stoichiometry is 1:1.

Our interest in SnP_2S_6 and $Sn_2P_2S_6$ stems from our recent discovery that SnP_2S_6 is a nonlinear-optical material.[10] In that work, we demonstrated that both $Sn_2P_2S_6$ and SnP_2S_6 display significant second harmonic generation efficiency.

Experimental Section

Materials. All of the materials used were from commercial suppliers and used as received. Tin was in the form of −20 mesh granular and was supplied by Mallinckrodt. Red phosphorus powder, amorphous, −100 mesh, was purchased from Alfa. Sulfur powder, −60 mesh, was supplied by Johnson Mathey Inc.

Synthesis. Large crystals of SnP_2S_6 were grown from the elements. Stoichiometric amounts of tin, phosphorus, and sulfur (10 g total) were lightly ground together and then transferred to a quartz reaction tube (15 cm × 1.3 cm o.d., standard wall). The sample was evacuated, sealed, and placed in a tube furnace. A gradient was established in the furnace with a maximum temperature of 450 °C. After several days, large single crystals (5 mm × 5 mm × 0.01 mm) of SnP_2S_6 were produced. The crystals were red, lustrous, and transparent. From the batch, small crystals suitable for single-crystal X-ray diffraction experiments were selected.

Thermal Analysis. When SnP_2S_6 is heated in an oxygen/helium atmosphere to 700 °C, a weight loss of 30% is observed. By comparison, when a sample of $Sn_2P_2S_6$ is subjected to the same heating conditions, a weight loss of only 13% is observed consistent with the greater percent mass of tin in this sample.

X-ray Diffraction. A thin crystalline platelet, approximately 0.4 × 0.3 × 0.05 mm, was oriented on a Syntex $P2_1$, upgraded to Siemens P4 specifications. Monochromatized Mo Kα radiation was used for all diffraction experiments. The crystal was found to belong to the rhombohedral crystal class, with a = 5.999(2) Å and c = 19.424(4) Å for the triply primitive hexagonally indexed cell. Lattice constants were based on the angular coordinates for 25 accurately centered high angle reflections (28° < 2θ < 30°). Empirical absorption corrections, based on ψ scan data, were made with the assumption of a laminar-shaped crystal. Intensity data were collected with ω scans, with variable scan speeds from 3.0 to 60.0°/min., out to a maximum value of 2θ = 55°. A total of 335 independent

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(1) Hahn, H.; Klingen, W. *Naturwissenschaften* **1965**, *52*, 494.

(2) Klinger, W.; Eulenberger, G.; Hahn, H. *Z. Anorg. Allg. Chem.* **1973**, *401*, 97.

(3) Klingen, V. W.; Ott, R.; Hahn, H. *Z. Anorg. Allg. Chem.* **1973**, *396*, 271.

(4) Scott, B.; Pressprich, M.; Willett, R. D.; Cleary, D. A. *J. Solid State Chem.* **1992**, *96*, 294.

(5) Lee, S.; Colombet, P.; Ouvrard, G.; Brec, R. *Inorg. Chem.* **1988**, *27*, 1291.

(6) Poizat, O.; Sourisseau, C.; Mathey, Y. *J. Solid State Chem.* **1988**, *72*, 272.

(7) Payen, C.; Molinie, P.; Colombet, P.; Fillion, G. *J. Magn. Mag. Mater.* **1990**, *84*, 95.

(8) Brec, R. *Solid State Ionics* **1986**, *22*, 3.

(9) Soled, A.; Wold, A. *Mater. Res. Bull.* **1976**, *11*, 657.

(10) Cleary, D. A.; Willett, R. D.; Ghebremichael, F.; Kuzyk, M. *Solid State Commun.* **1993**, *88*, 39.

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Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)[a]

	x	y	z	U(eq)
Sn	6667	3333	0	11(1)
S(1)	3428(3)	3455(3)	846(1)	14(1)
P(1)	3333	6667	577(1)	9(1)
S(2)	−3438(3)	−3393(3)	−849(1)	11(1)
P(2)	3333	6667	−561(1)	10(1)
Sn(1)	0	0	14(27)	37(8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

reflections were collected ($R_{int} = 2.74\%$), of which 333 were classified as observed ($F > 3\sigma(F)$).

No systematic absences were observed, and intensity data indicated the Laue group $R\bar{3}$. Intensity statistics indicated an acentric distribution of intensities, and the existence of a nonlinear optical effect indicated a polar space group. Thus, the initial structure solution was found in the space group $R\bar{3}$ via analysis of the Patterson function. This solution was forced into the $Sn_2P_2S_6$ stoichiometry. Two independent Sn sites were included in the model. During the refinement of the structural model, it became obvious that one of the Sn sites was not occupied, and it was deduced that the correct formation of the compound was as SnP_2S_6.

Refinement of the stoichiometric SnP_2S_6 structure in the space group $R\bar{3}$ proceeded in a straightforward fashion to a value of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.0192$ and $\omega R = \Sigma\omega(|F_o| - |F_c|)^2/\Sigma|F_o|^2 = 0.0254$ with $\omega^{-1} = \sigma^2(F) + 0.0014F^2$ and a goodness of fit = 0.66. Extinction corrections were also included. However, a large residual electron peak (2.54 e $Å^{-3}$) remained at the vacant Sn site. Thus further refinement was pursued with partial occupancy of the second Sn site. The refinement of this second metal ion site was not particularly robust, and it proved impossible to refine more than one of the three independent parameters for the atom; the z coordinate, the isotropic temperature factor, and the site occupancy. Hence, the site was fixed in individual cycles of refinement. A minimum R value was obtained with a site occupancy of 0.008. This yielded $R = 0.0158$ and $\omega R = 0.0207$ and a goodness of fit of 0.75. The improvement in the fit of the model to the data was deemed significant. Final positional and equivalent isotropic thermal parameters are given in Table 1.

Results and Discussion

Structure Description. The structure is closely related to the rhombohedral $M_2P_2S_6$ layer structures. One-third of the octahedral holes between alternating pairs of sulfur layers are occupied by pairs of P atoms (thus defining the $P_2S_6^{4-}$ anions). The other two-thirds of the octahedral holes are occupied by the M(II) ions. In the stoichiometric version SnP_2S_6, one-third of the octahedral holes are occupied by the Sn(IV) ions. The other one-third of the holes are vacant. The coordination of Sn^{4+} by the $P_2S_6^{4-}$ group is shown in Figure 1. Bond distances and angles are given in Table 2. The Sn−S bonds average 2.582(9) Å, but the Sn atom is displaced toward one of the hexagonal S layers, so that one set of Sn−S bonds is shorter (2.573(2) Å) than the other set (2.590(2) Å). This is the source of the polarity of the SnP_2S_6 structure. A similar disparity of the P−S bonds are observed with P(1)−S(1) = 2.025(1) Å and P(2)−S(2) = 2.034(2) Å, although this may not be a statistically significant difference.

The second (partially occupied) octahedral hole is slightly larger, with an average Sn−S distance of 2.64(4) Å. The crystallographic data cannot be used to answer the question of the nature of the Sn atoms at this site. One possibility is simple disorder of Sn(IV) ions in the structure. This seems unlikely because of the strong electrostatic repulsion between the two highly charged cations. A second option is replacement of Sn(IV) ions by pairs of Sn(II) ions. The larger radius of the Sn(II) ions argues against this option. However, this option may explain the inability to satisfactorily refine the position of the atom at this site, since the nonspherical Sn(II) ions would be disordered.

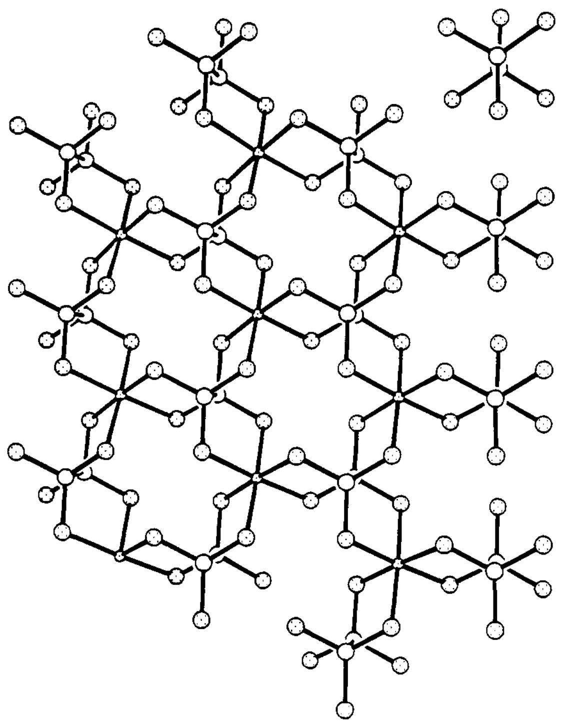

Figure 1. SnP_2S_6 viewed along the stacking axis, essentially parallel to the P−P bond axis. The vacant octahedral holes can be seen. The symmetry of the $P_2S_6^{4-}$ remains D_{3d} (see text).

Table 2. Bond Lengths (Å) and Distances (deg)

Sn−S(1)	2.573(2)	Sn−S(2)	2.590(2)
Sn(1)−S(1)	2.622(32)	Sn(1)−S(2)	2.648(33)
S(1)−P(1)	2.025(2)	P(1)−P(2)	2.210(3)
S(2)−P(2)	2.034(2)	S(1)−Sn−S(1)	83.6(1)
S(1)−Sn−S(2)	94.6(1)	S(1)−Sn−S(2)	177.4(1)
S(1)−Sn(1)−S(2)	178.5(5)	S(1)−Sn(1)−S(1)	86.0(13)
S(2)−Sn(1)−S(1)	94.4(1)	S(2)−Sn(1)−S(1)	95.5(1)
S(2)−Sn(1)−S(2)	84.2(13)	Sn(1)−S(1)−P(1)	102.1(5)
Sn(1)−S(1)−Sn	83.6(6)	P(1)−S(1)−Sn	104.1(1)
S(1)−P(1)−P(2)	105.0(1)	S(1)−P(1)−S(1)	113.6(1)
P(2)−P(1)−S(1)	105.0(1)	P(1)−P(2)−S(2)	106.0(1)
S(2)−P(2)−S(2)	112.7(1)		

The absence of one-half the metal ions with respect to the parent $M_2P_2X_6$ structure results in S atoms which are two-coordinate instead of three-coordinate (Figure 1). The symmetry of the $P_2S_6^{4-}$ remains essentially D_{3d}. Hence, as in the parent structure, the infrared band at 570 cm^{-1} ($\nu_d(PS_3)$) remains a single band. Conversely, in the three-dimensional $Sn_2P_2S_6$ material, where the symmetry at the $P_2S_6^{4-}$ is reduced to C/m, this band is observed as a multiplet.[11]

Conclusion

In this paper we report the first example of a layered metal hexathiohypodiphosphate where the metal ion is tetrapositive. This is significant since all of the known

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[11] Kliche, G. *J. Solid State Chem.* **1984**, *51*, 118.

layered metal hexathiohypodiphosphates contain dipositive metal ions or a combination of monopositive, tripositive, and vacancies. The other importance aspect of this structure is the distortion at the Sn^{4+} site which results in nonlinear-optical behavior, namely, second harmonic generation. The layered nature of the material suggests that intercalation chemistry might be used to modify the nonlinear properties of the host material. Such studies are currently underway.

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Supplementary Material Available: Crystal structure data and figure (4 pages); observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

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