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Synthesis and Crystal Structure of UP_2S_6

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The new ternary phase UP_2S_6 has been prepared and structurally characterized. The compound is isostructural with ZrP_2S_6 and ThP_2S_6 but is different from TiP_2S_6 . The structure has been determined by a single crystal X-ray diffraction technique. UP_2S_6 crystallizes in the tetragonal system ($C_{4h}^2-P4_2/m$, $a=6.797(7)$ Å, $c=9.738(12)$ Å) with two formula units in the unit cell. The structure can be described in terms of U^{4+} and $\text{P}_2\text{S}_6^{4-}$ ions. This hexathiohypodiphosphate anion ($\text{P}_2\text{S}_6^{4-}$) has ideally staggered conformation. The U^{4+} cation is coordinated by 8 sulfur atoms in a slightly distorted dodecahedral geometry (42m). The distribution of sulfur atoms is very well optimized for this geometry.

Introduction

For metals with oxidation number 4, the compounds $[\text{M}^{4+}][\text{P}_2\text{S}_6^{4-}]$ ($M=\text{Ti},^1 \text{Zr}$, and Th^2) represent new structural ty-

pes unrelated to the known hexathiohypodiphosphates of divalent metals ($[\text{M}^{2+}]_2[\text{P}_2\text{S}_6^{4-}]$). Attempts to prepare 8-12 μm IR-transmitting new phases in the metal/P/S system were made to investigate the effect of a highly oxidized metal

Table 1. Summary of Crystal Data, Intensity Collection, and Refinement for UP_2S_6

Molecular weight	492.36
a^a (Å)	6.797(7)
c^a (Å)	9.738(12)
V (Å ³)	449.88
Z	2
Space group	$\text{C}_{2h}^2\text{-P4}_2/\text{m}$
Density (calc, g/cm ³)	2.19
Crystal volume (mm ³)	2.1×10^{-4}
Crystal shape (mm)	needle bound by {100} {110} approx. dims. $0.024 \times 0.024 \times 0.44$
Radiation	graphite monochromated Mo $\text{K}\alpha_1$ ($\lambda(\text{K}\alpha_1)=0.70930$ (Å))
Linear absorption coefficient (cm ⁻¹)	187.1
Transmission factors	0.644-0.680
Detector aperture (mm)	3 horizontal, 1.8 vertical 17.3 cm from crystal
Take-off angle (deg)	3.5
Scan type	θ -2 θ
Scan range (deg)	0.8 below $\text{K}\alpha_1$ to 0.8 above $\text{K}\alpha_2$
Scan speed (deg/min)	2.0
$\lambda^{-1} \sin\theta$, limits (Å ⁻¹)	0.0492-0.7049
Background counts	1/4 of scan range on each side of reflection
p -factor	0.03
Number of unique data including $F_o^2 \leq 0$	697
Number of unique data with $F_o^2 > 3\sigma(F_o^2)$	504
Number of variables	24
$R(F^2)$	0.064
$R_w(F^2)$	0.080
$R(\text{on } F \text{ for } F_o^2 > 3\sigma(F_o^2))$	0.033
Error in observation of unit weight, e^2	1.17

^aObtained from refinement constrained so that $\alpha=\beta=\gamma=90^\circ$.

atoms. These attempts afforded a new compound, UP_2S_6 , which is isostructural with ZrP_2S_6 and ThP_2S_6 .² In this structure the metal atom is coordinated by eight sulfur atoms in a dodecahedral geometry.

Experimental

Synthesis. Single crystals of UP_2S_6 were initially isolated from a direct combination of the elemental powders of U (Johnson Matthey, 99.7%), P (AESAR, 99.999%), and S (Aldrich 99.999%) mixed in a 1:3:9 mole ratio in a quartz tube. The tube was evacuated to $\sim 10^{-5}$ Torr, sealed, heated at 700°C for 10 days, and then cooled slowly. Small needle-shaped dark red crystals formed. Qualitative chemical analysis with the microprobe of a scanning electron microscope confirmed the presence of all three elements in the crystal. Subsequent experiments demonstrated that single crystals of UP_2S_6 could be obtained in high yield from the reaction of the

Table 2. Positional Parameters and Equivalent Isotropic Thermal Parameters for UP_2S_6

Atom	x	y	z	Beq (Å ²) ^a
U	0	0	1/4	0.45(1)
P	0.0620(4)	0.3485(4)	1/2	0.57(5)
S(1)	0.1714(4)	0.1817(4)	0	0.62(5)
S(2)	0.2192(3)	0.3210(3)	0.3270(2)	0.86(4)

^aBeq = $(8\pi^2/3) \sum_i U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$ **Table 3.** Anisotropic Thermal Parameters^{a,b} for UP_2S_6

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	52(3)	52(3)	66(2)	0	0	0
P	85(12)	48(12)	82(12)	-1(10)	0	0
S(1)	84(11)	69(11)	81(11)	1(10)	0	0
S(2)	128(8)	95(8)	105(9)	-26(7)	43(7)	-22(7)

^aORTEP II, Type 8, ^bAll U_{ij} values given here are multiplied by 10^4 .

elements U, P, and S in a 1:2:6 mole ratio heated in a furnace having a temperature gradient of 700/750°C for 10 days. The addition of a small amount of I_2 as a transport agent resulted in the growth of rod-shaped crystals up to 2 mm in length at the cool end of the tube.

Crystallographic Studies. Preliminary examinations revealed that the crystals of UP_2S_6 possess 4/m Laue symmetry. The systematic absence $(00l, l=2n+1)$ is indicative of the space groups $\text{C}_{2h}^2\text{-P4}_2/\text{m}$ and $\text{C}_{2h}^3\text{-P4}_2$. The unit cell parameters were determined from least-squares analysis of the setting angles of 25 reflections automatically centered in the range $23.0^\circ < 2\theta$ ($\text{Mo K}\alpha_1$) $< 37.0^\circ$ on an Enraf-Nonius CAD4 X-ray diffractometer.

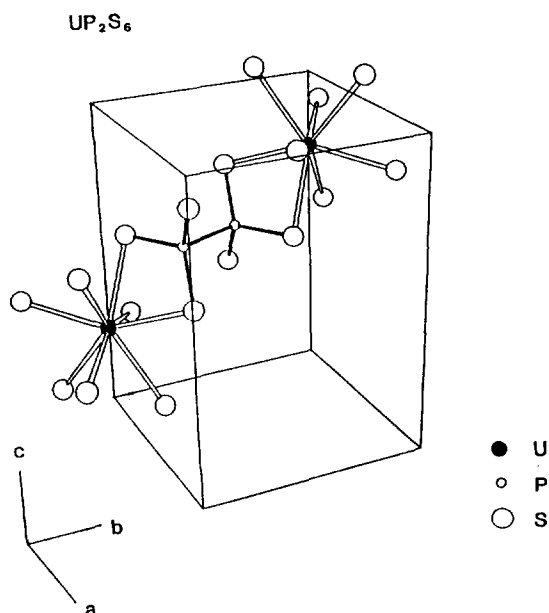
Intensity data were collected on a needle-shaped crystal with the θ -2 θ scan technique. During data collection, six standard reflections measured every three hours showed no significant variation in intensity throughout the data collection. Additional relevant crystal data and details of data collection are given in Table 1.

All calculations were carried out with the use of programs and methods described elsewhere.³ Conventional atomic scattering factors were used and anomalous dispersion corrections were applied.⁴ The reflection data were corrected for absorption with the use of the analytical method.⁵ As a satisfactory residual of 0.051 is obtained from averaging the absorption corrected data in $\text{P4}_2/\text{m}$, this space group is preferred. The structure was solved by the heavy atom method. The initial position for the U atom was determined from a Patterson synthesis and the P and S atoms were located in the subsequent electron density synthesis. The final anisotropic refinement on F_o^2 , based on 24 variables and 697 observations, resulted in an R index on F^2 of 0.064. Other residuals are $R_w(F^2)=0.080$, where the weights were derived from counting statistics and a value of p of 0.03. The conventional R index for the 504 data with $F_o^2 > 3\sigma(F_o^2)$ is 0.033. The final difference electron density map revealed no features greater than 10.5% of the height of a P atom.

Table 2 lists fractional coordinates and equivalent isotropic

Table 4. Selected Bond Distances (Å) and Angles (deg) for UP_2S_6

U-4S(2)	2.747(2)	P-P	2.226(6)
U-4S(1)	2.968(2)	P-2S(2)	2.004(3)
2S(1)-U-S(1)	69.78(9)	P-S(1)	2.047(4)
4S(1)-U-S(1)	132.28(5)	2S(1)-P-S(2)	112.1(1)
4S(1)-U-S(2)	71.37(6)	S(2)-P-S(2)	114.4(2)
4S(1)-U-S(2)	71.93(7)	P-P-S(1)	103.8(2)
4S(1)-U-S(2)	140.13(6)	2P-P-S(2)	106.8(1)
4S(1)-U-S(2)	82.08(7)		
2S(2)-U-S(2)	148.30(9)		
4S(2)-U-S(2)	94.28(2)		

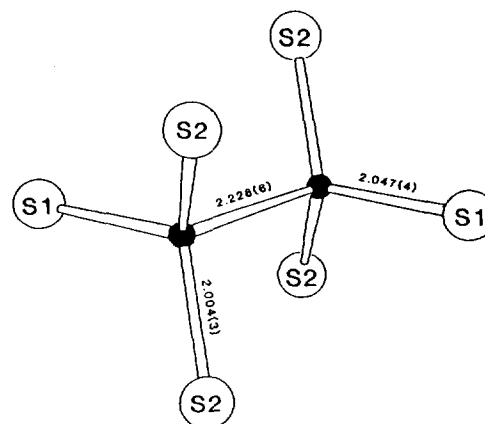
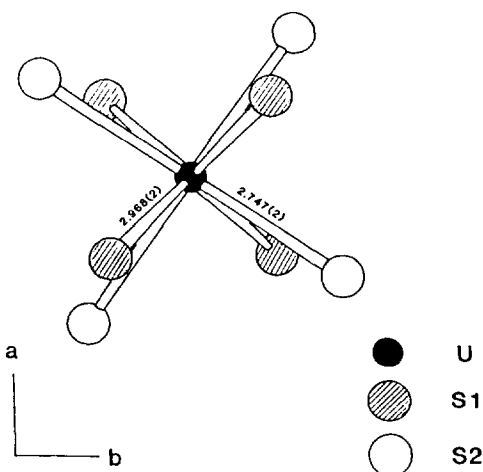
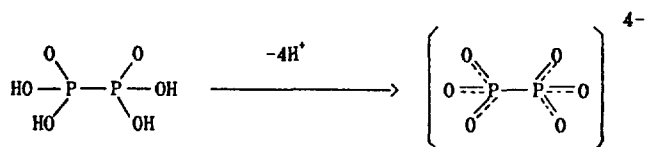
**Figure 1.** Perspective view of UP_2S_6 structure. U atoms are filled circles; P atoms are small open circles; S atoms are large open circles. Bonds in the $\text{P}_2\text{S}_6^{4-}$ anion are darkened for clarity.

thermal parameters. Anisotropic thermal parameters are given in Table 3.

Results and Discussion

The results of the single crystal study of UP_2S_6 demonstrate the existence of another phase of MP_2S_6 isomorphous with ZrP_2S_6 and ThP_2S_6 .² The structure of UP_2S_6 is described in terms of bond distances and angles in Table 4. The structure of this compound consists of the packing of U^{4+} and $\text{P}_2\text{S}_6^{4-}$ ions. A view of the structure is given in Figure 1.

In the $\text{P}_2\text{S}_6^{4-}$ anion shown in Figure 2, the phosphorus atom is surrounded tetrahedrally by three sulfur atoms and one additional phosphorus atom. This $\text{P}_2\text{S}_6^{4-}$ anion has crystallographically imposed $\bar{1}$ symmetry but shows approximate $3m$ molecular symmetry. This anion is typical of $\text{P}_2\text{Q}_6^{4-}$ anions ($\text{Q}=\text{S}, \text{Se}$)^{6,7} and has an ideally staggered conformation. This $\text{P}_2\text{S}_6^{4-}$ ion can be classified as a salt of hypothetical thiohypodiphosphoric acid ($\text{H}_4\text{P}_2\text{S}_6$). When the hypodiphosphoric acid ($\text{H}_4\text{P}_2\text{O}_6$) loses four protons, the hypodiphosphate anion is described by resonance structures:

**Figure 2.** View of the staggered conformation of the $\text{P}_2\text{S}_6^{4-}$ anion in UP_2S_6 showing bond distances in Å.**Figure 3.** Dodecahedral coordination about U down [001] in UP_2S_6 , showing bond distances in Å. The U atom is a filled circle; S(1) atoms are shaded circles; S(2) atoms are open circles.

The thio- and seleno-hypodiphosphoric acids have not been reported. However, the $\text{P}_2\text{S}_6^{4-}$ and $\text{P}_2\text{Se}_6^{4-}$ anions should be regarded as sulfur and selenium analogues of the $\text{P}_2\text{O}_6^{4-}$ anion. This can be justified by the fact that the average P-S distance (2.02(2) Å) is between the single bond distance (2.14 Å) and the double bond distance (1.91 Å). The bond distance between P-P (2.226(6) Å) is typical of single P-P bond length. Brec *et al.* pointed that the PS_3 groups appear as rigid entities and the P-P distances vary to accommodate the various metal sizes.⁸ However this trend has not been observed in the MP_2S_6 system where M is Ti, Zr, Th, or U. The S-P-S bond angles are greater than the P-P-S bond angles. This can be explained by the steric repulsion of the large sulfur atoms bound to the same phosphorus atom.

The U^{4+} cation is coordinated by four sulfur atoms (S(2))

Table 5. Comparison of Parameters for Dodecahedral Coordination

	$(M-L_1)/(M-L_2)$	$(L_1-M-L_1)/2$ (°)	$(L_2-M-L_2)/2$ (°)
Optimum $\bar{4}2m$ dodecahedron ^a	1.05	35.2	73.5
ZrP_2S_6 ^b	1.11	34.4	75.0
ThP_2S_6 ^b	1.07	34.8	73.7
UP_2S_6	1.08	34.9	74.2

^aReference 11, ^bReference 2.**Table 6.** The Ratio of Volume per Sulfur and the Ionic Radius^a of Each Metal in the MP_2S_6 System ($M=\text{Ti, Zr, Th, and U}$)

Compound	Ionic radius	Volume/sulfur ($\text{\AA}^3$)
TiP_2S_6 ^b	0.68	36.19
ZrP_2S_6 ^c	0.79	35.31
ThP_2S_6 ^c	1.02	39.06
UP_2S_6	0.97	37.49

^aReference 10, ^bReference 1, ^cReference 2.

at 2.747(2) $\text{\AA}$ and four sulfur atoms (S(1)) at 2.968(2) $\text{\AA}$ (Figure 3). The US_8 group has crystallographically imposed 4 symmetry but shows approximate dodecahedral $\bar{4}2m$ molecular symmetry, which is not unusual for U^{4+} .⁹ The average distance between U and S is 2.86(16) $\text{\AA}$. This is comparable to the sum of the ionic radii of each element (2.84 $\text{\AA}$).¹⁰

The two usual geometries for coordination number eight are the square antiprism and the dodecahedron. Detailed analysis⁹ of the energetics of metal-ligand and ligand-ligand interactions suggested that there will be little difference between the energies of the square antiprismatic and the dodecahedral arrangements. Therefore the choice between them is usually determined by other factors such as the chelating effect, energies of partially filled inner shell, and orbital hybridizations.⁹ At present there is no satisfactory method to predict the geometry the metal ion will adopt.

Hoard and Silverton have investigated the optimum arrangement of ligands in an isolated dodecahedron.^{11,12} To minimize the electrostatic repulsion energy between ligands, they determined the parameters for the most favorable shape of the dodecahedron. They found that the ratio of the two different distances between metal-ligand ($M-L_1$)/($M-L_2$) and the angles L_1-M-L_1 and L_2-M-L_2 for an optimum ligand arrangement. The parameters for this optimum arrangement are compared in Table 5 with the experimentally determined values for the MP_2S_6 system ($M=\text{Zr, Th, and U}$). Those of the ThP_2S_6 and UP_2S_6 are very close to the optimum values, which means the MS_8 groups have a favorable arrangement of sulfur atoms.

Comparing the ratios of the volume per sulfur for TiP_2S_6 and MP_2S_6 ($M=\text{Zr, Th, and U}$) along with the ionic radius of each element¹³ in Table 6, one can find that this ratio decreases from TiP_2S_6 to ZrP_2S_6 although the ionic radius increases. The compound TiP_2S_6 also has $\text{P}_2\text{S}_6^{4-}$ anions. However, the Ti metal is coordinated by only six sulfur atoms in a slightly distorted octahedral arrangement. The reason that TiP_2S_6 and MP_2S_6 ($M=\text{Zr, Th, and U}$) adopt different structures could be explained by the sizes of the metal atoms. The Ti^{4+} cation is not sufficiently large to accommodate eight sulfur atoms without undue crowding. Therefore, even if we assume the dodecahedral geometry of sulfur atoms around a Ti^{4+} cation, the repulsive energy between sulfur atoms would surpass the stabilization energy of the dodecahedral geometry. Thus, there are relatively few eight coordinated complexes known for the first row transition metals (i.e., $\text{Ti}(\text{S}_2\text{CNR}_2)_4$ ¹⁴).

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