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The Crystal and Molecular Structure of γ-P_4S_6

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In Memory of Professor Hans Georg von Schnering

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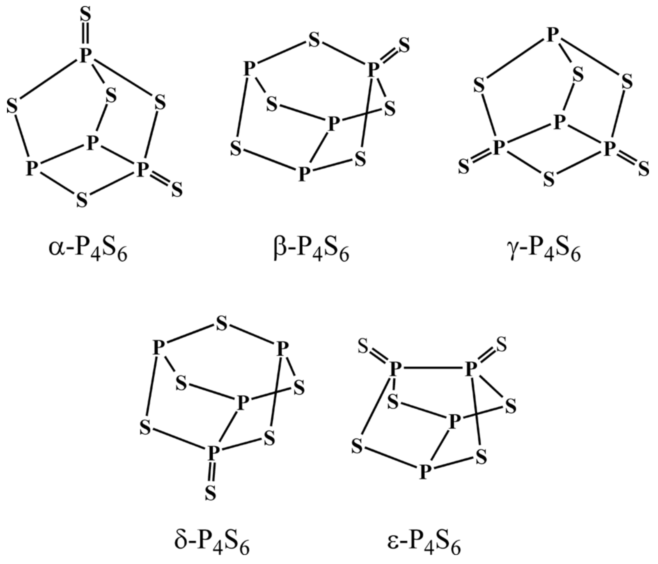
Abstract. The crystal and molecular structure of γ-P_4S_6 was determined from single-crystal X-ray diffraction. It crystallizes monoclinically in the space group $P2_1/m$ (No. 11) with $a = 6.627(3)$ Å, $b = 10.504(7)$ Å, $c = 6.878(3)$ Å, $\beta = 90.18(4)°$, $V = 478.8(4)$ Å^3, and $Z = 2$. The structure consists of cage-like P_4S_6 molecules with C_S symmetry arranged with the topology of a cubic close packing.

Introduction

In general the phosphorus sulfides consist of small cage-like molecules with the composition P_4S_n ($n = 3$–10). The structures of α-P_4S_3,[1] γ-P_4S_3,[1,2] α-P_4S_4,[3] α-P_4S_5,[4] β-P_4S_5,[5] β-P_4S_6,[6] α-P_4S_7,[4,7] β-P_4S_7,[8] P_4S_9-II,[9] P_4S_9-III,[10] and P_4S_{10}[4,7,11] were determined from single-crystal X-ray diffraction. Other phosphorus sulfides like P_4S_8 have been characterized by ^{31}P NMR spectroscopy.[12] They all have in common, that their molecular structures can be derived from the P_4 tetrahedron of white phosphorus by either insertion of sulfur atoms into P–P bonds or exocyclic addition to phosphorus atoms. Due to the possible combinations a large number of constitution isomers is suggested for each composition. Additionally, different crystal structures of the same molecule are conceivable. In the case of e.g. P_4S_6 five isomers are known, see Figure 1. Among these, only the crystal structure of β-P_4S_6 was determined by X-ray diffraction analysis.[6] On the contrary the structures of α-P_4S_6,[13] γ-P_4S_6,[14] δ-P_4S_6, and ε-P_4S_6[15] have been characterized only spectroscopically.


α-P_4S_6 β-P_4S_6 γ-P_4S_6

δ-P_4S_6 ε-P_4S_6

Figure 1. Known molecular structures of P_4S_6.[6,13–15]

γ-P_4S_6 has first been observed by *Jason* as a product in the oxidation of phosphorus by sulfur at low temperatures (< 100 °C) and in the sulfurization of α-P_4S_5 by triphenylarsenic sulfide.[14] Based on the signals in the corresponding solution ^{31}P NMR spectra he was able to assign a molecular structure. Herein, we confirm the molecular structure assigned by *Jason*, and in addition, present the crystal structure of γ-P_4S_6.

Results and Discussion

The crystal and molecular structure of γ-P_4S_6 was determined by single-crystal X-ray diffraction. The compound crystallizes as a pseudomerohedral twin in the monoclinic space group $P2_1/m$ (No. 11) with $a = 6.627(3)$ Å, $b = 10.504(7)$ Å, $c = 6.878(3)$ Å and $\beta = 90.18(4)°$. The monoclinic angle is very close to 90° and mimics a metrically orthorhombic cell. Analyzing the reflection data with XPREP[16] revealed that the true metric is monoclinic: whereas the internal R-value is poor for the higher symmetry ($R_{\text{int}} = 0.297$) it is very good for the lower symmetry ($R_{\text{int}} = 0.032$). In the monoclinic setting only the reflection condition for $2_1 \| b$ was fulfilled indicating the possible space groups $P2_1$ (No. 4) and $P2_1/m$ (No. 11). Due to pseudomerohedral twinning the E statistics ($|E^2-1| = 0.814$) were no real criterion for (non-)centrosymmetry. For this reason the structure solution was performed in the higher- and centrosymmetric space group $P2_1/m$ (No. 11). The structure solution using direct methods was successful and after a few refinement cycles a reasonable structural model was obtained. However, the R values were unusually high at this stage and

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pseudomerohedral twinning had to be taken into account. The possible twin laws were derived from symmetry reduction starting from the apparent Laue class 2/*m* 2/*m* 2/*m* and ending up with the true Laue class 2/*m*. Thus, a mirror plane perpendicular to the *a* axis could be used as a twin element in the refinement procedure. By doing this, the *R* values dropped significantly from $R_1 = 0.1311$ and wR_2 0.3174 to $R_1 = 0.0703$ and $wR_2 = 0.1758$ (for all data). Table 1 shows the results of the refinement for γ-P$_4$S$_6$. The atomic coordinates and anisotropic displacement parameters are listed in Table 2 and Table 3.

Table 1. Crystallographic data for γ-P$_4$S$_6$.[a)]

Compound	γ-P$_4$S$_6$
Formula Weight /g·mol^{-1}	316.24
Colour	yellow
Crystal system, space group	monoclinic, $P2_1/m$ (No.11)
Lattice constants	
a /Å	6.627(3)
b /Å	10.504(7)
c /Å	6.878(3)
β /°	90.18(4)
Volume *V* /Å^3	478.8(4)
Number of formula units *Z*	2
Calculated density ρ_{calc} /g·cm^{-3}	2.194
Temperature *T* /K	293(2)
Diffractometer	Stoe IPDS I
Wavelength λ /Å	0.71073 (Mo-K_a)
Absorption coeff. μ(Mo-K_a) /mm^{-1}	2.018
θ range of data collection /°	2.96–25.19
Index ranges	$-7 \leq h \leq 7$
	$-12 \leq k \leq 12$
	$-8 \leq l \leq 8$
Absorption correction	numerical, X-RED[17] and X-SHAPE[18]
No. of reflections collected	6288
(independent)	(905)
R_σ, R_{int}	0.0353, 0,0525
Completeness to θ = 25.19°	99.6 %
Structure solution	SIR92[19]
Structure refinement	SHELXL-97[20]
No. of refined parameters	53
No. of restraints	0
GooF	1.142
Twin law	–1 0 0, 0 1 0, 0 0 1
Batch scale factor BASF	0.138(4)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0604, 0.1705
R_1, wR_2 [all data]	0.0703, 0.1758
Largest diff. peak & hole /e·Å^{-3}	1.635 and –0.418

a) Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-423037**.**

Table 2. Atomic coordinates and equivalent isotropic displacement parameters U_{eq} [a)] (in Å^2) for γ-P$_4$S$_6$.

Atom	Wyck.	*x*	*y*	*z*	U_{eq}
P(1)	4*f*	0.2485(3)	0.1118(2)	0.2612(4)	0.040(1)
P(2)	2*e*	0.2046(5)	0.25	0.5084(5)	0.044(1)
P(3)	2*e*	0.6795(5)	0.25	0.3851(6)	0.053(1)
S(1)	4*f*	0.1055(3)	0.5460(2)	0.2492(4)	0.051(1)
S(2)	4*f*	0.5638(3)	0.0890(2)	0.2396(4)	0.053(1)
S(3)	2*e*	0.1533(6)	0.25	0.0562(6)	0.054(1)
S(4)	2*e*	0.4878(5)	0.25	0.6368(6)	0.053(1)

a) U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Anisotropic displacement parameters U^{ij} (in Å$^2 \times 10^3$) for γ-P$_4$S$_6$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P(1)	35(1)	39(1)	46(1)	–2(1)	–1(1)	–2(1)
P(2)	39(2)	41(2)	52(2)	0	5(1)	0
P(3)	30(2)	55(2)	74(3)	0	0(2)	0
S(1)	47(1)	43(1)	63(2)	0(1)	–8(1)	7(1)
S(2)	35(1)	48(1)	75(2)	–8(1)	3(1)	5(1)
S(3)	59(2)	45(2)	59(2)	0	–23(2)	0
S(4)	45(2)	58(2)	58(2)	0	–12(2)	0

As it is common for phosphorus sulfides the structure of γ-P$_4$S$_6$ consists of discrete cage-like molecules. The molecular structure can be derived from the P$_4$ tetrahedron of white phosphorus by introducing four bridging and two terminal sulfur atoms, see Figure 2. A single γ-P$_4$S$_6$ molecule exhibits only one symmetry element, a mirror plane through the atoms P(2), P(3), S(3) and S(4). Thus, the molecules are achiral and belong to the point group C_s. The intramolecular distances and angles in γ-P$_4$S$_6$ are summarized in Table 4. They are in good agreement with those in other phosphorus sulfides. The distance P(1)–P(2) is 2.255(4) Å. The exocyclic phosphorus sulfur distance *d*(P(1)–S(1)) = 1.912(3) Å is as expected shorter than the distances between phosphorus and bridging sulfur atoms which vary in the range from 2.071(5) Å to 2.151(6) Å.

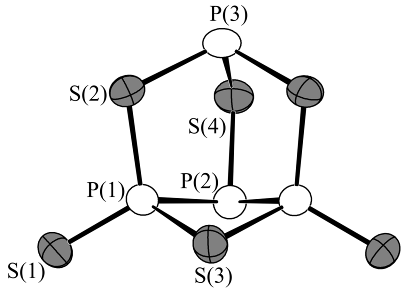

Figure 2. Single γ-P$_4$S$_6$ molecule. Ellipsoids are drawn at 75 % probability level.

Table 4. Selected interatomic distances (in Å) and angles (in °) in γ-P$_4$S$_6$.

P(1)–S(1)	1.912(3)	S(1)$^{\#1}$–P(1)–S(2)	112.9(1)
P(1)–S(2)	2.109(3)	S(1)$^{\#1}$–P(1)–S(3)	114.8(2)
P(1)–S(3)	2.118(4)	S(2)–P(1)–S(3)	108.9(2)
P(1)–P(2)	2.255(4)	S(1)$^{\#1}$–P(1)–P(2)	121.7(2)
P(2)–S(4)	2.071(5)	S(2)–P(1)–P(2)	104.8(2)
P(3)–S(2)	2.108(4)	S(3)–P(1)–P(2)	91.3(1)
P(3)–S(4)	2.151(6)	S(4)–P(2)–P(1)	101.7(2)
		P(1)–P(2)–P(1)$^{\#1}$	80.1(2)
		S(2)–P(3)–S(2)$^{\#1}$	106.7(2)
		S(2)–P(3)–S(4)	99.6(2)
		P(3)–S(2)–P(1)	103.6(1)
		P(1)$^{\#1}$–S(3)–P(1)	86.5(2)
		P(2)–S(4)–P(3)	101.1(2)

#1 symmetry transformation used to generate equivalent atoms: *x*, $-y+½$, *z*

Each unit cell contains two equivalent γ-P_4S_6 molecules related by a 2_1 screw axis along *b*. The shortest intermolecular distances are 3.58(3) Å for P(2)···P(3), 3.41(4) Å for P(2)···S(1) and 3.45(4) Å for S(1)···S(3). Hence, weak van der Waals forces are present between adjacent molecules. Figure 3 shows a section of the crystal structure of γ-P_4S_6 illustrating the molecular arrangement. Considering the cages to be almost spherical it is strongly related to a cubic closest packing of spheres. The symmetry relations are explained with the help of a Bärnighausen tree, see Figure 4. The low symmetry of the molecules enforces a reduction of the space group symmetry. Due to the non-ideal spherical shape of the molecules there are deviations from a perfect fcc packing resulting in a slight shift of the molecular centre from the ideal position and a significant distortion of the lattice. This finding is not surprising since α-P_4S_3, γ-P_4S_3, α-P_4Se_3 and α-As_4S_3 show quite similar deviations, albeit this time from a hexagonal packing of spheres.

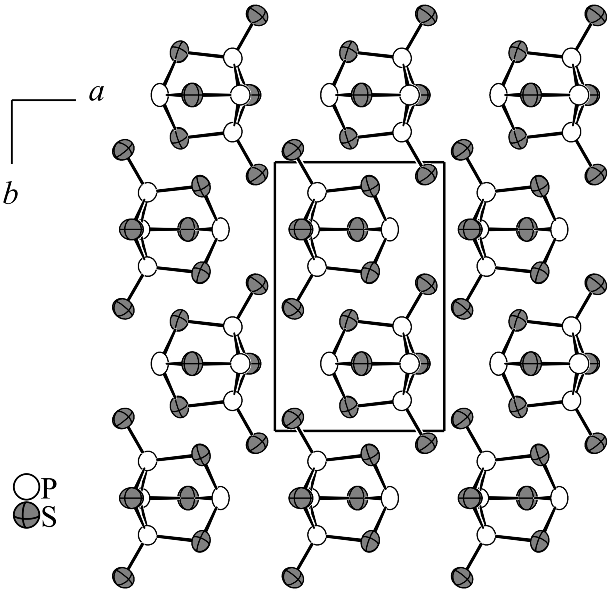

Figure 3. Section of the crystal structure of γ-P_4S_6 with view along *c*.

Note added in proof: In the meantime, the crystal structures of polymeric phosphorus polysulfides α-P_2S_7 and β-P_2S_7 were determined. They show a ratio of P:S < 4:10 and are the first well-characterized crystalline polymeric phosphorus polysulfides.[21]

Experimental Section

P_4S_3 was prepared by reaction of stoichiometric amounts of the elements, phosphorus (Hoechst, 99.999 %) and sulfur (Chempur, 99.999 %) in an evacuated silica ampoule at 300 °C and purified by recrystallization from toluene (Merck, p.A.). Commercial $FeCl_3$ (Fluka, >98 %) was purified by sublimation in a stream of chlorine gas at 250 °C.

Synthesis of γ-P_4S_6. Equimolar amounts of P_4S_3 and anhydrous $FeCl_3$ were dissolved in a 2:1 solvent mixture of dry carbon disulfide and chloroform. The reaction mixture was kept in a Schlenk flask under argon atmosphere for eight weeks. The solvent was then removed by slow evaporation under inert gas conditions at room temperature, yielding some crystals of γ-P_4S_6, together with larger amounts of unreacted starting materials. The air- and moisture-sensitive yellow crystals of γ-P_4S_6 were manipulated under argon atmosphere in a glovebox and a crystal suitable for the X-ray diffraction analysis was sealed in a glass capillary. The measurement was carried out on a STOE IPDS I diffractometer with λ = 0.71073 Å (Mo-K_α). Further details on the data collection are shown in Table 1.

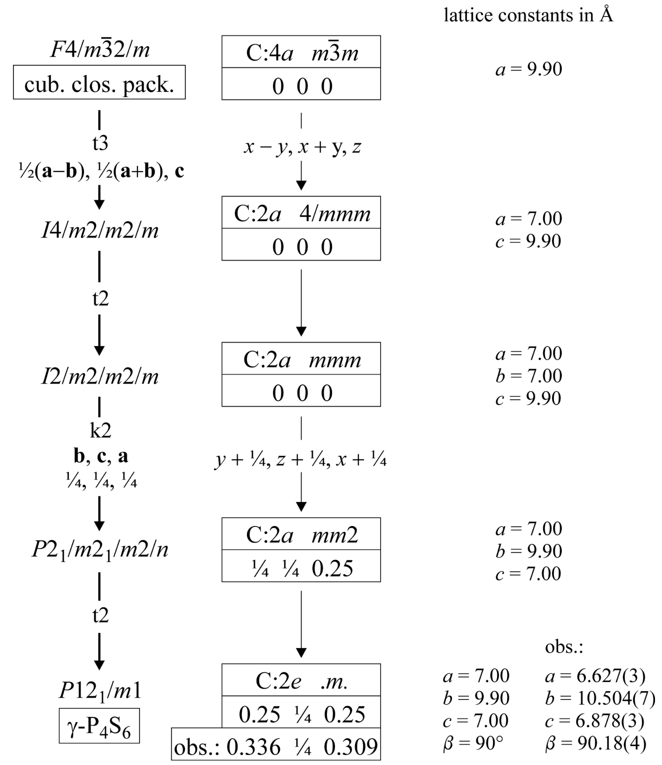

Figure 4. Bärnighausen tree relating a cubic closest packing of spheres with the molecular arrangement in γ-P_4S_6. Only the centre of the molecule (C) is displayed.

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