ligand. In addition, this structure and the structures for related thorium and samarium complexes indicate a strong tendency in the solid state for the CMP ligands to act as bidentate chelating ligands where steric factors permit.

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Supplementary Material Available: Listings of structure factors, hydrogen atom positional parameters, thermal parameters, and a least-squares plane (16 pages). Ordering information is given on any current masthead page.

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Crystal Structure Determination of Bis(tetraphenylphosphonium) Heptasulfide, $(Ph_4P)_2S_7$

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The S_7^{2-} anion has been obtained by the reaction of MoS_9^{2-} with an excess of the sodium salt of the diethyldithiocarbamate anion in acetonitrile solution. The tetraphenylphosphonium salt of S_7^{2-}, $(Ph_4P)_2S_7$ (I), crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ and lattice parameters $a = 11.041$ (3) Å, $b = 18.589$ (4) Å, $c = 12.040$ (3) Å, $\alpha = 74.58$ (3)°, $\beta = 69.05$ (3)°, $\gamma = 87.76$ (4)°, and $V = 2220.18$ Å^3. Diffraction data (Mo Kα radiation, $2\theta_{max} = 50°$) were collected with a Picker FACS-I automated diffractometer, and the structure was solved and refined by direct methods and full-matrix least-squares procedures to $R_F = 5.8\%$ and $R_{wF} = 8.7\%$ with use of 5102 unique reflections. The S_7^{2-} ion is found to be a right-handed nonbranched S(1)S(2)S(3)S(4)S(5)S(6)S(7) helix with very short terminal sulfur–sulfur bonds of 1.990 (2) and 1.995 (2) Å for S(1)–S(2) and S(6)–S(7), respectively. The internal bond distances are as follows (in Å): S(2)–S(3), 2.036 (2); S(3)–S(4), 2.062 (2); S(4)–S(5), 2.062 (2); S(5)–S(6), 2.037 (2). The torsion angles in the chain are as follows (in degrees): S(2)–S(3), 73.28 (10)°; S(3)–S(4), 74.41 (10)°; S(4)–S(5), 65.22 (10)°; S(5)–S(6), 79.86 (10)°. The $(Ph_4P)_2S_7$ salt dissolves in polar solvents to give blue solutions with adsorption bands at 610, 470, 345 (sh), and 304 nm.

Introduction

Various polysulfide anions have been characterized structurally to date in salts such as K_2S_2,[1] Na_2S_2,[1], BaS_3,[2] $BaS_4{\cdot}H_2O$,[3] Na_2S_4,[4] K_2S_5,[5] Tl_2S_5,[6] and Cs_2S_6.[7] The S_x^{2-} anions (x = 4–6) in these salts are doubly charged, nonbranched nonlinear sulfur chains. The preparation, certain properties, and lattice constants of the $C_3H_{12}N_2^{2+}S_7^{2-}$ salt have been reported[8] about 25 years ago; however, no other recent structural study of a heptasulfide or higher order polysulfide is available. In a attempt to replace the S_4^{2-} chelating ligands in the MoS_9^{2-} complex[9] by diethyldithiocarbamate ligands (in the presence of Ph_4PCl), we isolated an orange-red crystalline material, which was identified by elemental analysis as $(Ph_4P)_2S_7$. In this paper we report on the crystal and molecular structure of $(Ph_4P)_2S_7$, which contains the S_7^{2-} anion.

Experimental Section

Preparation of $(Ph_4P)_2S_7$. A 0.5- (0.9-mmol) of quantity of $(Et_4N)_2MoS_9$ and 0.6k g (1.8 mmol) of Ph_4PCl were added to ca. 50 mL of CH_3CN. To this heterogeneous solution was added 1.1 g (4.9 mmol) of sodium diethyldithiocarbamate trihydrate, and the mixture was heated for 15 min. The resulting deep green solution changed to brown after cooling to ambient temperature. Upon addition of ether, following filtration, crystalline unreacted $(Et_4N)_2MoS_9$ was deposited and removed by a subsequent filtration. The volume of the filtrate was reduced to dryness in vacuo, leaving an oily brown residue, which was then washed with two 10-mL portions of diethyl ether. The brown oil was dissolved in a minimum amount of CH_3CN (~30 mL), resulting in a blue solution to which diethyl ether was added (~20 mL) to initiate crystallization. When the solution stood for ca. 2 h, 0.15 g of analytically pure orange-red crystals was deposited and

Table I. Summary of Crystallographic Data and Data Collection Procedures

formula	$Ph_8P_2S_7$
fw	90$\underline{2}$
space group	$P\bar{1}$
a, Å	11.041 (3)
b, Å	18.589 (6)
c, Å	12.040 (3)
α, deg	74.58 (3)
β, deg	69.05 (3)
γ, deg	87.76 (4)
V, Å^3	2220.18
d_{calcd}, g/cm^3	1.35
d_{obsd},^{a} g/cm^3	1.35
Z	2
cryst size, mm	0.16 × 0.21 × 0.52
μ(Mo Kα), cm^{-1}	4.49
radiation	graphite monochromatized Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.710 73 Å)
scan type	θ–2θ
step size	0.12–0.16
no. of steps	7–15
max counting time, s	4
time/step, s	4
data collection range, deg	$3 < 2\theta < 50$
bkgd time, s	8
no. of unique data	5102
no. of data, $F_o^2 > 3\sigma(F_o^2)$	7251
p^b	0.06
cryst decay	negligible
no. of variables	514
R	0.058
R_w	0.087

[a] By flotation in a CCl_4/pentane mixture. [b] "Ignorance" factor, $\sigma^2(F^2) = (0.06F^2) + \sigma^2(F^2)$ (from counting statistics).

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Table II. Positional Parameters for the Sulfur Atoms in $(Ph_4P)_2S_7$

atom	x	y	z
S(1)	0.9332 (1)	0.29442 (8)	0.6561 (1)
S(2)	0.8634 (1)	0.23466 (8)	0.8325 (1)
S(3)	0.0094 (2)	0.20030 (8)	−0.1036 (1)
S(4)	0.9117 (1)	0.70888 (9)	0.0794 (1)
S(5)	0.9569 (2)	0.31364 (8)	0.0773 (1)
S(6)	0.9434 (1)	0.22604 (9)	0.2258 (1)
S(7)	1.0912 (2)	0.2312 (1)	0.2817 (2)

collected. Anal. Calcd for $C_{48}H_{40}P_2S_7$: C, 63.86; H, 4.43; P 6.87, S, 24.83. Found: C, 61.25, H, 4.45; P, 6.43, S, 24.28. Electronic spectrum obtained in CH_3CN on a Cary Model 119 spectrophotometer: 610, 470, 345 (sh), and 304 nm.

Collection and Reduction of X-ray Crystal Data. Preliminary cell parameters were obtained from precession photographs. A small orange crystal of $(Ph_4P)_2S_7$ (0.16 × 0.21 × 0.52 mm) was mounted on a goniometer head, which in turn was mounted on a Picker FACS-I four-circle computer-controlled diffractometer equipped with a scintillation counter and a pulse-height analyzer. Accurate cell dimensions and an orientation matrix were obtained from a least-squares refinement of the ω, χ, ϕ, and 2θ values from 12 carefully centered independent reflections.

Mo Kα radiation, which was graphite monochomatized ($2\theta_m$ = 12.50°), was used for data collection and cell dimension measurements. Intensity data were collected by using a θ–2θ step scan technique. The basic scan step of 0.10(2θ) was adjusted with angle to allow α_1–α_2 separation at high angles. Background measurements, 4 s at each end, were made at ±10 steps from the peak maximum. Three standard reflections were measured every 60 reflections and showed no fluctuation sgreater than ±5% during data collection.

Details concerning crystal characteristics and X-ray diffraction methodology are shown in Table I.

The raw data were corrected for Lorentz–polarization effects, and the estimated standard deviations (esd) were calculated on the basis of counting statistics. No absorption correction was applied to the data (μ = 4.49 cm^{-1}). The least-squares program minimizes the function $\sum w(|F_o| - |F_c|)^2$. The weighting function used gives zero weight to those reflections with $F^2 \leq 3\sigma(F^2)$ and $w = 1/\sigma^2(F)$ to all others.

Scattering factors of the neutral non-hydrogen atoms were taken from the tables of Doyle and Turner,[10] and real and imaginary dispersion corrections[11] were applied to all of them. The spherical hydrogen scattering factor tables of Stewart, Davidson, and Simpson[12] were used.

Structure Analysis and Refinement. The structure was solved by the multisolution tangent-refinement method[13] (MULTAN). Five sulfur atoms and the two phosphorus atoms were located this way, and a three-dimensional Patterson function map was used to verify the correctness of their positions. The remaining 2 sulfur atoms and 48 phenyl ring carbon atoms were located on subsequent Fourier syntheses following least-squares refinements of the input coordinates. The model was refined with isotropic temperature factors in the space group $P\bar{1}$ by a full-matrix least-squares program and gave a conventional R $(=\sum(|F_o| - F_o|)/\sum|F_3|)$ value of 0.079. At this point convergence was achieved, and the positional and thermal parameters were further refined with use of anisotropic temperature factors for all the non-hydrogen atoms. After six more cycles of anisotropic refinement the structure converged to R = 0.061 and weighted $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ = 0.090. Hydrogen atoms were placed at 0.95 Å from C atoms with an overall temperature factor of 5 Å^2. Further refinement, including the H atoms in the structure factor calculation but not refining on them, converged to a final R value of 0.058; the weighted R_w was 0.087. During the last cycle of refinement all parameter shifts were less than 10% of their esd's. The final difference Fourier map did not show any peaks with heights greater than 0.3 e/Å^3.

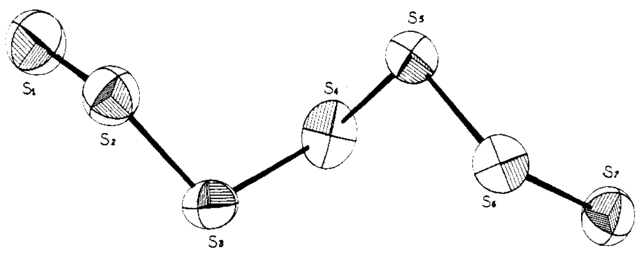

Figure 1. ORTEP-drawn representation of the S_7^{2-} anion and labeling scheme (C. K. Johnson, *Oak Ridge Natl. Lab.* [*Rep.*] *ORNL* (*U.S.*), **ORNL-3794** (1965)). Thermal ellipsoids represent 50% probability surfaces.

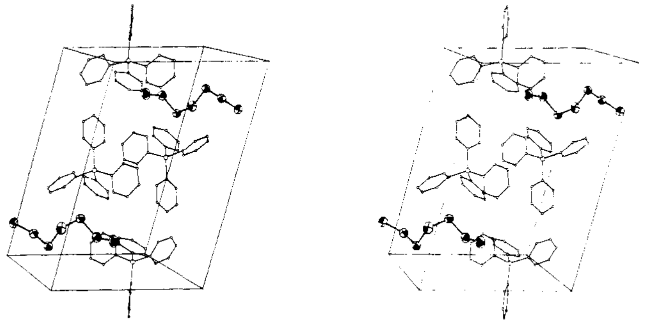

Figure 2. Unit cell packing arrangement drawn by ORTEP.

Table III. Bond Distances (Å), Angles (deg), and Dihedral Angles (deg) in the S_7^{2-} Ion

S(1)–S(2)	1.995 (2)	S(4)–S(5)	2.062 (2)
S(2)–S(3)	2.036 (2)	S(5)–S(6)	2.037 (2)
S(3)–S(4)	2.062 (2)	S(6)–S(7)	1.990 (2)
S(1)–S(2)–S(3)	111.30 (10)	S(4)–S(5)–S(6)	108.77 (10)
S(2)–S(3)–S(4)	108.59 (9)	S(5)–S(6)–S(7)	111.09 (11)
S(3)–S(4)–S(5)	106.75 (10)		
S(1)S(2)S(3)/S(2)S(3)S(4)	73.28 (10)		
S(2)S(3)S(4)/S(3)S(4)S(5)	74.41 (10)		
S(3)S(4)S(5)/S(4)S(5)S(6)	65.22 (10)		
S(4)S(5)S(6)/S(5)S(6)S(7)	79.86 (10)		

Positional parameters along with their esd's are shown in Table II.

Results and Discussion

Figure 1 shows a view of the S_7^{2-} anion together with the atom-labeling scheme. The packing of the ions in the crystal is shown in Figure 2. The bond distances, bond angles, and torsion angles along with the estimated standard deviations are reported in Table III.

The molecular structure of bis(tetraphenylphosphonium) heptasulfide consists of well-separated anions and cations. This investigation unambiguously demonstrates that the heptasulfide chain is a nonbranched and nonplanar, completely isolated polysulfur helix. The closest van der Waals distances are between each end of the heptasulfide chain and aromatic hydrogen atoms of the tetraphenylphosphonium cations, S(1)···H(44) and S(7)···H(83) being 2.887 and 2.857 Å, respectively.

The anion possesses no crystallographic symmetry; however, it does possess an approximate twofold symmetry, where the twofold axis is passing through the central S(4) atom bisecting the S(3)–S(4)–S(5) angle. This pseudo-twofold symmetry is apparent in the bond angles, distances, and thermal vibration parameters on either side of the S(4) atom. The torsion angles however do not show such a correlation. A pseudo-twofold symmetry also has been observed for the S_5^{2-} anion in the crystal structure of K_2S_5[5].

The polysulfide chain assumes a right-handed helix conformation with an average S–S–S angle of 109.3° very similar

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Table IV. Comparison of the Terminal S–S Distances and S–S–S Angles in the S_n^{2-} Polysulfides

polysulfide	$\overline{S_t\text{–}S}$, Å	$\overline{S_t\text{–}S\text{–}S}$, deg	ref
S_2^{2-}	2.13		1
S_3^{2-}	2.15	103	2
S_4^{2-}	2.074 (1)^a	109.76 (2)^a	4
S_5^{2-}	2.043 (4)^a	109.2 (1)^a	5
S_6^{2-}	2.01 (3)^a	109.6 (20)^a	7
S_7^{2-}	1.992 (2)^a	111.2 (1)^a	this work

[a] These are average values of the two S_t–S and S_t–S–S terminal distances and angles, respectively.

to the one observed in the S_6^{2-} helix[7] (108.8°).

The heptasulfide chain is characterized by relatively short terminal sulfur–sulfur bonds of 1.995 (2) and 1.990 (2) Å for S(1)–S(2) and S(6)–S(7), respectively. This shortening of the terminal S–S bonds indicates that the negative charge is primarily localized at the terminal S(1) and S(7) atoms and is in accord with the predictions made by Hordvik.[14] The terminal sulfur–sulfur bonds are the shortest that have been observed so far in polysulfide chains. According to Hordvik, the terminal sulfur atoms in a polysulfide chain will arrange themselves in such a way as to attain a minimum lone-pair repulsion and a maximum p_π–d_π bond overlap. On the basis of these hypotheses, the terminal S–S bonds should reach a minimum value of about 2.02 Å. This value is in reasonable agreement with our findings of 1.995 and 1.990 Å, respectively. The decreasing length for the S–S terminal bond lengths from S_3^{2-} (2.15 Å)[2] to S_7^{2-} (1.993 (2) Å) suggests that electron delocalization along the chain is less likely to occur in higher polysulfides. A comparison of terminal S–S distances and S–S–S angles of all S_n^{2-} species characterized thus far is shown in Table IV.

A S_i–S_j bond length-dihedral SS_iS_j/S_iS_jS angle relationship has been suggested by Hordvik and has been presented graphically as a curve. In the structure of S_7^{2-} the S(2)–S(3), S(4)–S(5), and S(5)–S(6) bond lengths can be predicted reasonably well from this curve from the values of the dihedral angles S(1)S(2)S(3)/S(2)S(3)S(4), S(3)S(4)S(5)/S(4)S(5)S(6), and S(4)S(5)S(6)/S(5)S(6)S(7) of 73.3 (1), 65.2 (1), and 78.9 (1)°, respectively. The S(2)S(3)S(4)/S(3)S(4)S(5) dihedral angle of 74.4 (1)° corresponds to an S(3)–S(4) bond length of ~2.04 Å (as obtained from the curve), which is shorter than the observed value of 2.062 (2) Å. This discrepancy cannot be explained; however, it could be the result of packing forces that open up the S(2)S(3)S(4)/S(3)S(4)S(5) dihedral angle to 74.4° from the expected value of ~66.0°.

Electronic Spectrum. The $(Ph_4P)_2S_7$ salt is readily soluble in aprotic donor solvents such as dimethylformamide (DMF) and CH_3CN. The intense blue CH_3CN solution shows absorptions at 304, 345 (sh), 470, and 610 nm. The blue color of the polysulfide anions in donor solvents such as DMF, dimethyl sulfoxide (Me_2SO), and CH_3CN has been the subject of considerable debate.[15] The 610–625-nm absorption, responsible for the blue color of these solutions, orginally was attributed by Lux et al.[16] to neutral S_x molecules ($x = 2$–4). At a later date Bonnaterre and Cauquis[17] suggested that the blue chromophore was the S_3^- ion. This suggestion also has been advanced by Gruen, McBeth, and Zielen[18] and appears to be compatible with ESR[20] and Raman[21] spectroscopic results. Additional support for the S_3^- anion as the blue chromophore is available in results of SCF–Xα–SW calculations by Cotton et al.,[15] who assigned the 620-nm absorption to the first allowed doublet–doublet transition within the S_3^- ion. The corresponding doublet–doublet transition in S_2^- is predicted to occur at 17 300–20 300 cm^{-1} (depending on structure parameters) and precludes the S_2^- ion as the chromophore responsible for the blue color. The suggestion that the blue color is caused by S_2^- has been advanced previously by Giggenbach.[19] To date, the common view among most investigators is that the cause of the blue color of polysulfide anions in donor solvents is the existence of the S_3^- ion.

It appears that the S_7^{2-} anion in DMF or CH_3CN solution exists in equilibrium with other sulfides, one of which is the S_3^- ion responsible for the 610-nm electronic absorption band.

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Registry No. $(Ph_4P)_2S_7$, 83615-66-1; $(Et_4N)_2MoS_9$, 76581-48-1; Ph_4PCl, 2001-45-8; sodium diethyldithiocarbamate, 148-18-5.

Supplementary Material Available: Listings of observed structure factors for $(Ph_4P)_2S_7$ and positional coordinates and thermal parameters for all atoms in the asymmetric unit (30 pages). Ordering information is given on any current masthead page.

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