Syntheses and Characterization of the First Thallium Polysulfide Anions

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The reaction of potassium tetrasulfide with thallium chloride in dimethylformamide (DMF) was investigated. The addition of the cations Ph_4P^+, Et_4N^+, and Me_4N^+ to this reaction afforded six new soluble thallium(I) polysulfide complexes, α-$(Ph_4P)_2[Tl_2(S_4)_2]$ (I), β-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$ (II), β'-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$ (III) γ-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot DMF$ (IV), $(Et_4N)_2[Tl_2(S_4)_2]$ (V), and $(Me_4N)_2[Tl_2(S_4)_2]$ (VI). Compound I (pale yellow platelets) crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with unit cell dimensions $a = 9.907(3)$ Å, $b = 11.014(3)$ Å, $c = 12.794(4)$ Å, $\alpha = 71.05(3)°$, $\beta = 87.33(3)°$, $\gamma = 68.79(2)°$, $V = 1227(1)$ Å^3 (at 23 °C), and $Z = 1$. Single-crystal X-ray diffraction studies show that compounds II and III are isostructural and crystallize in the monoclinic space group $P2_1/c$ (No. 14). The unit cell dimensions of the pale orange crystals of II are $a = 10.815(3)$ Å, $b = 14.486(5)$ Å, $c = 18.281(5)$ Å, $\beta = 97.29(3)°$, $V = 2841(1)$Å^3 (at 23 °C), and $Z = 2$, and the unit cell dimensions of the deep red crystals of III are $a = 10.810(5)$ Å, $b = 14.480(8)$ Å, $c = 18.294(7)$ Å, $\beta = 97.37(3)°$, $V = 2839(2)$ Å^3 (at 23 °C), and $Z = 2$. Compound IV (orange crystals) crystallizes in the monoclinic space group $C2/c$ (No. 15) with unit cell dimensions $a = 26.324(6)$ Å, $b = 9.269(10)$ Å, $c = 24.062(5)$ Å, $\beta = 117.36(1)°$, $V = 5213(4)$ Å^3 (at −120 °C), and $Z = 4$. Compound V (orange crystals) crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with unit cell dimensions $a = 11.880(10)$ Å, $b = 17.202(6)$ Å, $c = 7.200(6)$ Å, $\beta = 97.29(3)°$, $V = 1457(2)$ Å^3 (at −100 °C), and $Z = 2$. Compound VI (pale orange platelets) crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with unit cell dimensions $a = 6.160(3)$ Å, $b = 9.683(6)$ Å, $c = 10.160(5)$ Å, $\alpha = 66.05(4)°$, $\beta = 84.88(4)°$, $\gamma - 80.64(4)°$, $V = 546(1)$ Å^3 (at −100 °C), and $Z = 1$. Surprisingly, all the complexes (I–VI) stabilize the same $[Tl_2(S_4)_2]^{2-}$ anions. Despite their different colors II and III are structurally identical. The anion features two trigonal pyramidal Tl^+ centers each chelated by a tetrasulfide ligand and the third coordination site is satisfied by bonding a terminal sulfur atom of another TlS_4 unit, forming a dimer. This bonding mode of the S_4^{2-} ligands results in a new condensed inorganic ring system with a central, strictly planar, four-membered Tl_2S_2 rhombic unit and two five-membered TlS_4 rings in an envelope configuration. The envelope configuration of the five membered TlS_4 ring in the $[Tl_2(S_4)_2]^{2-}$ anions results in either the boat–boat or the chair–chair conformation. The reaction of potassium tetrasulfide with thallium chloride in acetonitrile afforded orange red crystals of $K_{0.68}Tl_{1.32}S_5$ (VII). Compound (VII) crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19) with unit cell dimensions of $a = 6.630(4)$ Å, $b = 16.989(6)$ Å, $c = 6.499(2)$ Å, $V = 727(1)$ Å^3, and $Z = 4$. Compound VII is isostructural to the known K_2S_5 and Tl_2S_5 and consists of a S_5^{2-} chain with Tl^+ and K^+ as charge-compensating cations. VII can be considered as a solid solution of the two known compounds. All complexes show similar UV/vis spectra in DMF with two absorptions at ∼432 and ∼617 nm. The solid-state far-IR spectra of all compounds exhibit strong absorptions in the 500–100-cm^{-1} region due to the S–S and M–S stretching frequencies; tentative assignments are reported.

Introduction

In recent years the synthesis, characterization, and reactivity of soluble metal polychalcogenides has become an active area of research.[1] These complexes have been studied as model compounds for industrial heterogeneous catalysts,[2] biological systems,[3] and metal sulfur transport agents in geochemistry.[4] This class of compounds have exhibited a remarkably diverse structural chemistry which derives from the tendency of the chalcogens to catenate and to bind simultaneously to multiple metal centers. As a result, a number of polychalcogenide complexes with transition metals have been isolated and structurally characterized.[1–4] In contrast, the preparation of soluble polychalcogenide compounds containing main-group elements has not been pursued to any considerable extent.[5] In our initial investigation of polychalcogenide chemistry of the main-group IIIA metals we successfully isolated and structurally characterized a number of new complexes: $[Ga_2Se_2(Se_5)_2]^{2-}$,[6] $[In_2(Se_4)_4(Se_5)]^{4-}$,[7,8] $[In_2Se_2(Se_4)_2]^{2-}$,[8] $[M_3Se_3(Se_4)_3]^{3-}$ [8] (M = In, Tl), $[Tl_4Se_4(Se_2)_2(Se_4)_2]^{4-}$,[9] $[In(S_4)(S_6)X]^{2-}$ [10] (X = Br, Cl), $[In_2(S_4)_2(S_6)_2(S_7)]^{4-}$,[10] $[In_2S(S_5)(S_4)_2]^{2-}$,[10] and $[In_2S(S_5)(S_4)(S_6)]^{2-}$.[10] To further explore main-group chemistry and in an attempt to prepare the sulfur analog of the thallium polyselenide complexes, we investigated the corresponding thallium polysulfide chemistry. In addition, Tl is attractive for study because of its inert 6s^2 lone pair of electrons which may or may not be manifested structurally in a given compound. Whether the lone pair is stereochemically active or not affects both the lattice structure and the properties of the resulting compounds. This issue is related to the larger question of stereochemical activity of a lone pair in

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compounds with s^2 configuration. In this paper we present the syntheses, structural characterization and solution properties of some new thallium polysulfide complexes: α-$(Ph_4P)_2[Tl_2(S_4)_2]$, β-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$, β'-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$, γ-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot DMF$, $(Et_4N)_2[Tl_2(S_4)_2]$, $(Me_4N)_2[Tl_2(S_4)_2]$, and $K_{0.68}Tl_{1.32}S_5$.

Experimental Section

Reagents. The chemicals in this research were used as obtained commercially: sulfur, 99.999% purity, American Smelting and Refining Co., Denver, CO; potassium metal, analytical reagent, Mallinckrodt Inc., Paris, KY; thallium(I) chloride, 99.999% purity, Cerac Inc. Milwaukee, WI; tetraphenylphosphonium chloride (Ph_4PCl), 98% purity, tetraethylammonium bromide (Et_4NBr), 98% purity, and tetramethylammonium chloride (Me_4NCl), 98% purity, Aldrich Chemical Company Inc., Milwaukee, WI. Dimethylformamide (DMF), analytical reagent, was stored over 4A Linde molecular sieves for over a weak and then distilled under reduced pressure at 25–30 °C. The first 50 mL was discarded. Acetonitrile (analytical reagent, Mallinckrodt Inc., Paris, KY) was distilled after refluxing with calcium hydride for 8 h. Diethyl ether (ACS anhydrous, Columbus Chemical Industries Inc., Columbus, WI) was distilled after refluxing with sodium/potassium alloy, with benzophenone and triethylene glycol–dimethyl ether for 12 h.

Caution! Extra precautions must be taken in these reactions to handle all thallium salts and complexes, as Tl is *very toxic* and appropriate waste disposal is absolutely essential.

Physicochemical Studies. Infrared spectra of the complexes were recorded as solids in a CsI matrix on a Nicolet 740 FT-IR spectrometer. Each sample was ground along with CsI to a fine powder and a translucent pellet was made by applying ~15 000 psi pressure to the mixture. The spectra were recorded in the far-IR region (500–100 cm^{-1}). UV/vis spectra of the complexes were measured on a Hitachi U-2000 spectrophotometer. Quantitative microprobe analysis of the compounds was performed on a JEOL JSM-35C scanning electron microscope (SEM) equipped with an X-ray microanalysis attachment from Tracor Northern, Model TN 5500, for energy dispersive spectroscopy (EDS). Single crystals of each sample were mounted on an aluminum stub using conductive carbon paint for adhesion to the stub as well as to dissipate the charge that is developed on the sample under an electron beam. Energy dispersive spectra were obtained using the following experimental set-up: X-ray detector position, 55 mm; working distance, 39 mm; accelerating voltage, 20 kV; take-off angle, 27°; beam current, 200 pA; Accumulation time, 60 s; detector window, Beryllium. A standardless quantitative (SQ analysis) program was used to analyze the X-ray spectra obtained. The analysis could not be used for the atoms below atomic number 11 (sodium) due to the absorption of the low-energy X-rays by the Be window of the detector. The analyses reported here are an average of three to four individual measurements on several different single crystals of each compound.

Syntheses. All the experiments and syntheses were performed under dry nitrogen in a Vacuum Atmospheres Dri-Lab glovebox. All the syntheses were carried out in the dark by wrapping the reaction flasks with aluminum foil, and the flasks were also stored in the dark during crystal growth. The isolated compounds were always kept under a nitrogen atmosphere, away from light.

α-Bis(tetraphenylphosphonium) Bis(tetrasulfido)dithallate(I), α-$(Ph_4P)_2[Tl_2(S_4)_2]$ (I). A 0.200-g (0.834-mmol) sample of TlCl was added to a 80-mL DMF solution containing 0.172 g (0.833 mmol) of K_2S_4 and 0.313 g (0.835 mmol) of Ph_4PCl. The mixture was stirred for ca. 6 h, and the resulting blue solution was filtered to remove KCl. To the filtrate was added 60 mL of ether to incipient crystallization. When this mixture was allowed to stand for 24 h, pale yellow single crystals of α-$(Ph_4P)_2[Tl_2(S_4)_2]$ (I) were formed. They were isolated by filtration and washed with ether; yield 52%. A quantitative microprobe analysis performed on a number of crystals of I with the EDS/SEM system gave an average composition of $Tl_{1.0}S_{4.12}P_{1.02}$.

β-Bis(tetraphenylphosphonium) Bis(tetrasulfido)dithallate(I)–Bis(dimethylformamide), $(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$ (II). A 0.200-g (0.834-mmol) sample of TlCl was added to a 80-mL DMF solution containing 0.172 g (0.833 mmol) of K_2S_4 and 0.313 g (0.835 mmol) of Ph_4PCl. The mixture was stirred for ca. 6 h, and the resulting blue solution was filtered to remove KCl. To the filtrate was added 60 mL of ether to cause crystallization. When this mixture was allowed to stand for 3 days, pale orange crystals of β-$(Ph_4P)_2[Tl_2(S_4)_2\cdot 2DMF$ (II) were formed. They were isolated by filtration and washed with ether; yield 42%. A quantitative microprobe analysis performed on a number of crystals of II with the EDS/SEM system gave an average composition of $Tl_{1.0}S_{4.06}P_{1.06}$.

β'-Bis(tetraphenylphosphonium) Bis(tetrasulfido)dithallate(I)–Bis(dimethylformamide), $(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$ (III). A 0.200-g (0.834 mmol) sample of TlCl was added to a 80-mL DMF solution containing 0.172 g (0.833 mmol) of K_2S_4 and 0.313 g (0.835 mmol) of Ph_4PCl. The mixture was stirred for ca. 6 h, and the resulting blue solution was filtered to remove KCl. To the filtrate was added 60 mL of ether to cause crystallization. When the mixture was allowed to stand for 3 days, deep red crystals of β'-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$ (III) were formed. They were isolated by filtration and washed with ether; yield 38%. A quantitative microprobe analysis performed on a number of crystals of III with the EDS/SEM system gave an average composition of $Tl_{1.0}S_{4.09}P_{1.10}$.

γ-Bis(tetraphenylphosphonium) Bis(tetrasulfido)dithallate(I)–Dimethylformamide, $(Ph_4P)_2[Tl_2(S_4)_2]\cdot DMF$ (IV). A 0.200-g (0.834-mmol) sample of TlCl was added to a 40-mL DMF solution containing 0.172 g (0.833 mmol) of K_2S_4 and 0.313 g (0.835 mmol) of Ph_4PCl. The mixture was stirred for ca. 6 hrs and the resulting blue solution was filtered to remove KCl. To the filtrate was added 60 mL of ether. When the mixture was allowed to stand for 3 days, pale orange crystals of γ-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot DMF$ (IV) were formed. They were isolated by filtration and washed with ether; yield 62%. A quantitative microprobe analysis performed on a number of crystals of IV with the EDS/SEM system gave an average composition of $Tl_{1.0}S_{4.14}P_{0.98}$.

Bis(tetraethylammonium) Bis(tetrasulfido)dithallate(I), $(Et_4N)_2[Tl_2(S_4)_2]$ (V). A 0.200-g (0.834-mmol) sample of TlCl was added to a 80-mL DMF solution containing 0.172 g (0.833 mmol) of K_2S_4 and 0.175 g (0.833 mmol) of Et_4NBr. The mixture was stirred for ca. 6 h, and the resulting blue solution was filtered to remove KCl. To the filtrate was added 60 mL of ether. When the mixture was allowed to stand for 3 days, pale orange crystals of $(Et_4N)_2[Tl_2(S_4)_2]$ (V) were formed. They were isolated by filtration and washed with ether; yield 70%. A quantitative microprobe analysis performed on a number of crystals of V with the EDS/SEM system gave an average composition of $Tl_{1.0}S_{4.02}$.

Bis(tetramethylammonium) Bis(tetrasulfido)dithallate(I), $(Me_4N)_2[Tl_2(S_4)_2]$ (VI). A 0.200-g (0.834-mmol) sample of TlCl was added to a 80-mL DMF solution containing 0.172 g (0.833 mmol) of K_2S_4 and 0.091 g (0.831 mmol) of Me_4NCl. The mixture was stirred for ca. 6 h, and the resulting blue solution was filtered to remove KCl. To the filtrate was added 60 mL of ether. When the mixture was allowed to stand for 3 days, pale orange crystals of $(Me_4N)_2[Tl_2(S_4)_2]$ (VI) were formed. They were isolated by filtration and washed with ether; yield 74%. A quantitative microprobe analysis performed on a number of crystals of VI with the EDS/SEM system gave an average composition of $Tl_{1.0}S_{4.38}$.

Potassium Thallium Pentasulfide, $K_{0.68}Tl_{1.32}S_5$ (VII). A 0.200-g (0.834-mmol) sample of TlCl was added to a 80-mL acetonitrile solution containing 0.172 g (0.833 mmol) of K_2S_4. The mixture was stirred for ca. 6 h, and the resulting blue solution was filtered. To the filtrate was added 60 mL of ether. When the mixture was allowed to stand for 4 days, orange crystals of $K_{0.68}Tl_{1.32}S_5$ (VII) were formed. They were isolated by filtration and washed with ether; yield 58%. A quantitative microprobe analysis performed on a number of crystals of VII with the EDS/SEM system gave an average composition of $K_{0.87}Tl_{1.0}S_{5.02}$.

X-ray Crystallographic Studies. X-ray powder diffraction patterns were recorded with a Phillips XRγ-3000 computer-controlled powder diffractometer. Ni-filtered, Cu-radiation was used. The *d*-spacings (Å) for all materials were measured. The X-ray powder patterns obtained from the complexes were in good agreement with those calculated, from the atom coordinates obtained from the X-ray single-crystal diffraction studies, using the program POWD-10.[11] This confirmed the homogeneity and the purity of the complexes, assuming to amorphous phases were present. Calculated and observed *d*-spacings (Å) for all the compounds are compiled in the supplementary material. All complexes are very air and moisture sensitive; thus the crystals of I–III were mounted inside glass capillaries and sealed, whereas the crystals of IV–VII were mounted on the tip of a glass fiber with silicon grease and the data were collected at low temperature (−100 to −120 °C). The crystallographic data for I, III, and VI were collected on a Nicolet P3 four-circle automated

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Table I. Summary of Crystallographic Data for α-$(Ph_4P)_2[Tl_2(S_4)_2]$ (I), β-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot2DMF$ (II), and β′-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot2DMF$ (III)

	I	II	III
formula	$C_{48}H_{40}P_2Tl_2S_8$	$C_{54}H_{54}P_2N_2O_2Tl_2S_8$	$C_{54}H_{54}P_2N_2O_2Tl_2S_8$
fw	1344.06	1490.24	1490.24
cryst color	yellow	orange	deep-red
temp, °C	23	23	23
a, Å	9.907(3)	10.815(3)	10.810(5)
b, Å	11.014(3)	14.486(5)	14.480(8)
c, Å	12.794(4)	18.281(5)	18.294(7)
α, deg	71.05(3)	90.00	90.00
β, deg	87.33(3)	97.29(3)	97.37(3)
γ, deg	68.79(2)	90.00	90.00
Z, *V*, $Å^3$	1; 1227(1)	2; 2841(1)	2; 2839(2)
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
D_{calc}, g cm^{-3}	1.82	1.74	1.74
μ, cm^{-1} (Mo Kα)	70.52	60.99	61.13
cryst size, mm	0.16, 0.32, 0.50	0.18, 0.30, 0.40	0.38, 0.43, 0.31
$2\theta_{max}$, deg	45	40	43
no. of data collcd	3538	3076	4017
no. of data with $I > 3\sigma(I)$	2341	1461	1821
no. of variables	271	196	196
min/max abs cor	0.392/0.998	0.475/1.000	0.847/0.998
final R/R_w, %	5.0/5.5	7.7/9.7	4.4/4.8

diffractometer using a θ–2θ step scan mode[12] and Mo Kα radiation. The data for the rest of the complexes were collected on Rigaku AFC6S four-circle automated diffractometer with ω–2θ scan technique and Mo Kα radiation. Accurate unit cell dimensions were determined from the 2θ, ω, φ, and χ angles of 15–25 machine-centered reflections. The intensities of three check reflections were monitored every 100–150 reflections. The data for II showed 7% decay in their intensities over the data collection period; thus a decay correction was applied to the complete data set. An empirical absorption correction was applied to the data of all complexes based on ψ scans for three (χ∼90°) reflections. The structures were solved with direct methods and differences Fourier synthesis maps and refined with full-matrix least-squares techniques. An additional absorption correction was applied before anisotropic refinement using DIFABS.[13] The structures of I–IV were solved with direct methods using SHELXS-86[14] and were refined with the SDP[15] package of crystallographic programs, using a VAXstation 2000 computer. The structures of V–VII were solved with direct methods using the TEXSAN crystallographic software package from Molecular Structure Corp., using a VAXstation 3100/76 computer. In I, V, and VI all non-hydrogen atoms were refined anisotropically. In II and III all atoms of the anion, the phosphorous atom of the cation, and the atoms of DMF were refined anisotropically. The carbon atoms of the cation were refined isotropically. For IV all non-hydrogen atoms, except the atoms of DMF, were refined anisotropically. The hydrogen atom positions were calculated and included in the structure factor calculations but were not refined. All structures consist of discrete, well-separated cations and anions. In VII only the Tl atoms were refined anisotropically; the potassium and the sulfur atoms were refined isotropically.

In IV the DMF molecule has an unusual disorder, with the nitrogen and oxygen atoms situated on a crystallographic C_2 axis with half-occupancies. Due to the C_2 axis, the carbon atoms of this molecule are positionally disordered over two sites with half-occupancy, thus giving rise to two different orientations of the DMF molecule in the crystal lattice.

All examined crystals of VI were found to be twinned with two or three platelets stuck together along the flat face. The data was collected on

Table II. Summary of Crystallographic Data for γ-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot DMF$ (IV), $(Et_4N)_2[Tl_2(S_4)_2]$ (V) and $(Me_4N)_2[Tl_2(S_4)_2]$ (VI)

	IV	V	VI
formula	$C_{51}H_{47}P_2NOTl_2S_8$	$C_{16}H_{40}N_2Tl_2S_8$	$C_8H_{24}N_2Tl_2S_8$
fw	1417.15	925.78	813.57
cryst color	orange	orange	pale orange
temp, °C	−120	−100	−100
a, Å	26.324(6)	11.880(10)	6.160(3)
b, Å	9.269(10)	17.202(6)	9.683(6)
c, Å	24.062(5)	7.200(6)	10.160(5)
α, deg	90.00	90.00	66.05(4)
β, deg	117.36(1)	97.29(3)	84.88(4)
γ, deg	90.00	90.00	80.64(4)
Z, *V*, $Å^3$	4; 5213(4)	2; 1457(2)	2; 546(1)
space group	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
D_{calc}, g cm^{-3}	1.80	2.11	2.47
μ, cm^{-1} (Mo Kα)	66.434	117.20	156.10
cryst size, mm	0.16, 0.22, 0.40	0.10, 0.21, 0.57	0.04, 0.20, 0.36
$2\theta_{max}$(°)	50	40	60
no. of data collcd	5151	1550	3542
no. of data with $I > 3\sigma(I)$	3267	1120	2397
no. of variables	287	127	91
min/max abs cor	0.616/1.000	0.263/1.000	0.033/1.000
final R/R_w, %	3.6/4.6	2.3/3.7	16.2/21.3

Table III. Summary of Crystallographic Data for $K_{0.68}Tl_{1.32}S_5$ (VII)

formula	$K_{0.68}Tl_{1.32}S_5$	space group	$P2_12_12_1$ (No. 19)
fw	456.69	d_{calc}, g cm^{-3}	4.162
cryst color	deep-red	μ, cm^{-1} (Mo Kα)	311.53
temp, °C	−100	cryst size, mm	0.16, 0.21, 0.31
a, Å	6.630(4)	$2\theta_{max}$, deg	50
b, Å	16.989(6)	no. of data collcd	823
c, Å	6.499(2)	no. of data with $I > 3\sigma(I)$	563
α, deg	90.00	no. of variables	44
β, deg	90.00	min/max abs cor	0.563/1.000
γ, deg	90.00	final R/R_w, %	7.5/9.4
Z; *V*, $Å^3$	4; 727(1)		

the major component of a twinned crystal. The minor twin had relatively weak diffraction intensity in the axial photographs. Our attempts to refine the structure did not give good results due to this problem.

In $K_{0.68}Tl_{1.32}S_5$ (VII) a thallium and potassium atom are disordered over the same crystallographic site and the occupancies of Tl(2) and K(2) were estimated as 0.5 and 0.5. They were then refined with the restriction that the sum of their occupancies be equal to unity. This refinement resulted in occupancies of 0.32 and 0.68, respectively. Thus, this compound represents a solid solution of K_2S_5 and Tl_2S_5.

The complete data collection parameters and details of the structure solution and refinement for compounds I–VII are summarized in Tables I–III. The final coordinates, temperature factors and their estimated standard deviations (esd's) of all non-hydrogen atoms for the compounds, are shown in Tables IV–X.

Results and Discussion

Syntheses and Spectroscopic Studies. Prior to this work no thallium polysulfide complex had been reported. The syntheses of complexes I–VI are readily accomplished by a common reaction between TlCl and K_2S_4, in a 1:1 molar ratio in the presence of different quaternary phosphonium or quaternary ammonium cations in DMF as represented by eq 1.

$$2TlCl + 2K_2S_4 + 2R_4EX \xrightarrow[DMF]{} (R_4E)_2[Tl_2(S_4)_2] + 2KCl + 2KX \quad (1)$$

$$R = Ph, E = P; R = Me, Et, E = N; X = Cl, Br$$

Initially, the reactions between TlCl and K_2S_4 were run in a 1:2 ratio in order to get a polysulfide complex analogous to the known polyselenide $[Tl_3Se_3(Se_4)_3]^{3-}$,[1,8] where we had observed an unusual two-electron oxidation of Tl^+ to Tl^{3+}. Instead, we isolated the $[Tl_2(S_4)_2]^{2-}$ anion, which was contaminated with some $(R_4E)_2S_x$ crystals. Subsequently, we adjusted the TlCl:K_2S_4 ratio

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Table IV. Fractional Atomic Coordinates and B_{eq} Values for α-$(Ph_4P)_2[Tl_2(S_4)_2]$ with Their Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq},[a] Å^2
Tl(1)	0.30760(8)	−0.00291(7)	0.45678(5)	5.72(2)
S(1)	0.4731(4)	−0.1529(4)	0.3200(3)	5.00(9)
S(2)	0.4878(4)	0.3314(4)	0.5495(3)	5.9(1)
S(3)	0.3462(5)	0.3354(4)	0.4360(4)	6.3(1)
S(4)	0.4646(5)	0.1891(4)	0.3633(3)	6.2(1)
P	0.0482(3)	−0.2180(3)	0.8713(3)	3.29(7)
C(1)	−0.050(1)	1.051(1)	0.2068(9)	3.2(3)
C(2)	0.079(1)	0.941(1)	0.252(1)	4.1(3)
C(3)	0.081(2)	0.814(1)	0.325(1)	6.5(5)
C(4)	−0.055(2)	0.802(1)	0.352(1)	5.7(4)
C(5)	−0.184(1)	0.908(1)	0.305(1)	5.2(4)
C(6)	−0.184(1)	1.035(1)	0.233(1)	4.6(3)
C(7)	0.120(1)	0.201(1)	0.0666(9)	3.2(3)
C(8)	0.130(1)	0.219(1)	−0.045(1)	4.3(3)
C(9)	0.259(1)	0.207(1)	−0.094(1)	5.5(4)
C(10)	0.385(1)	0.169(1)	−0.027(1)	5.2(4)
C(11)	0.379(1)	0.152(1)	0.084(1)	4.9(4)
C(12)	0.249(1)	0.167(1)	0.133(1)	3.9(3)
C(13)	0.073(1)	0.684(1)	0.7808(9)	3.5(3)
C(14)	0.181(1)	0.685(1)	0.706(1)	4.9(4)
C(15)	0.208(2)	0.607(1)	0.637(1)	5.8(4)
C(16)	0.125(2)	0.526(1)	0.640(1)	5.5(4)
C(17)	0.019(1)	0.524(1)	0.713(1)	5.3(4)
C(18)	−0.007(1)	0.600(1)	0.786(1)	4.6(3)
C(19)	0.192(1)	0.698(1)	−0.022(1)	3.5(3)
C(20)	0.226(1)	0.771(1)	0.038(1)	5.0(4)
C(21)	0.330(1)	0.699(2)	0.129(1)	5.7(4)
C(22)	0.397(1)	0.560(2)	0.159(1)	6.1(5)
C(23)	0.366(2)	0.486(2)	0.100(1)	6.4(5)
C(24)	0.264(1)	0.556(1)	0.010(1)	5.1(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

to a 1:1 ratio and obtained $(R_4E)_2[Tl_2(S_4)_2]$ as a single phase product, in high yield. The results reported here show that the $[Tl_2(S_4)_2]^{2-}$ anion displays considerable stability in the solid state and crystallization tendency. Slight variations of the composition of K_2S_x ($x = 4$–6) did not affect the final product.

Often the structure of metal polychalcogenide complexes is highly influenced by the nature of the counterions. This has been seen in the Ag/Se_x^{2-},[16] Cu/S_x^{2-},[17] and Mo/S_x^{2-} [18] systems, to name a few. This dependence on counterion was probed but not observed in this study as the same $[Tl_2(S_4)_2]^{2-}$ complex was isolated with three different cations (Ph_4P^+, Et_4N^+, and Me_4N^+) from DMF.

It is interesting to note that complexes I–IV are isolated from the same stoichiometric ratio of $Tl^+/S_4^{2-}/Ph_4P^+$. The $[Tl_2(S_4)_2]^{2-}$ anion has crystallized in four different crystal systems or colors depending on its conformation and the amount of solvent included in the crystal lattice. The pale yellow platelets of I are obtained within 6–8 h after reaction. Once I is isolated by filtration, the solution upon further standing at room temperature for 2 days affords a mixture of orange crystals of II and deep red crystals of III. The different crystal colors suggested to us that we were dealing with two different compounds. Surprisingly, single-crystal X-ray diffraction analyses of II and III found they were isostructural with essentially no discernible structural differences in the two compounds. The difference in colors is perhaps due to some impurities acting as dopants. In order to be sure that III was not a different compound, we performed the crystal structure analysis on two different dark red crystals obtained from different batches with nearly identical results.

Table V. Fractional Atomic Coordinates and B_{eq} Values for β-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$ with the Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq},[a] Å^2
Tl	1.1214(2)	0.5743(1)	−0.0576(1)	4.4(1)
S(1)	1.078(1)	0.451(1)	−0.1793(6)	5.6(7)
S(2)	0.978(1)	0.3619(9)	−0.1222(7)	4.9(7)
S(3)	1.098(1)	0.3070(9)	−0.0389(7)	6.2(8)
S(4)	1.143(1)	0.410(1)	0.0347(6)	4.6(6)
P(1)	1.4856(9)	0.5146(7)	−0.2474(6)	2.1(5)
O(1)	0.732(4)	0.395(3)	0.478(2)	8(3)
N(1)	0.900(5)	0.426(4)	0.563(3)	7(3)
C(1)	1.366(3)	0.594(2)	−0.236(2)	1.4(7)
C(2)	1.252(3)	0.587(3)	−0.288(2)	3.4(9)
C(3)	1.160(4)	0.660(3)	−0.280(2)	5(1)
C(4)	1.181(3)	0.723(3)	−0.231(2)	3.3(9)
C(5)	1.289(4)	0.725(3)	−0.181(3)	5(1)
C(6)	1.380(3)	0.660(3)	−0.188(2)	2.3(8)
C(7)	1.614(3)	0.582(2)	−0.265(2)	1.4(6)
C(8)	1.734(3)	0.572(3)	−0.226(2)	2.2(7)
C(9)	1.834(3)	0.627(3)	−0.237(2)	3.4(9)
C(10)	1.813(3)	0.699(3)	−0.290(2)	2.6(8)
C(11)	1.691(3)	0.712(2)	−0.329(2)	2.4(8)
C(12)	1.592(3)	0.655(2)	−0.318(2)	2.3(8)
C(13)	1.440(3)	0.437(2)	−0.322(2)	1.6(7)
C(14)	1.349(3)	0.376(3)	−0.317(2)	3.0(9)
C(15)	1.320(3)	0.310(3)	−0.376(2)	3.4(9)
C(16)	1.373(4)	0.310(3)	−0.438(3)	4.0(9)
C(17)	1.461(4)	0.379(3)	−0.447(2)	4(1)
C(18)	1.497(3)	0.444(3)	−0.387(2)	3.1(9)
C(19)	1.520(3)	0.445(2)	−0.165(2)	2.1(8)
C(20)	1.453(3)	0.458(2)	−0.107(2)	1.8(8)
C(21)	1.475(4)	0.398(3)	−0.046(2)	4(1)
C(22)	1.566(4)	0.339(3)	−0.043(3)	5(1)
C(23)	1.638(3)	0.321(3)	−0.105(2)	3(1)
C(24)	1.614(3)	0.374(2)	−0.166(2)	2.2(8)
C(25)	0.836(7)	0.370(4)	0.518(4)	7(4)
C(26)	1.030(6)	0.389(4)	0.595(3)	11(4)
C(27)	0.858(5)	0.515(5)	0.579(4)	10(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

I seems to be a metastable compound as it is the first to crystallize out of solution. It has been observed to slowly convert to II and III upon standing in solution over a period of 2 weeks. IV was obtained as a single phase product when the reaction was carried out in 40 mL of DMF, that is half the usual amount of solvent employed in the other reactions.

Complexes I–VI are extremely air, moisture, and light sensitive even in the solid state. The solutions of $(R_4E)_2[Tl_2(S_4)_2]$ in DMF are deep greenish blue and are air sensitive.

Since the $[Tl_2(S_4)_2]^{2-}$ anion was the only complex isolated from DMF, we changed our approach and used acetonitrile as solvent. The reaction of TlCl, K_2S_4, and Me_4NCl in acetonitrile resulted in a different than anticipated complex, $K_{0.68}Tl_{1.32}S_5$ (VII), and was subsequently prepared by mixing TlCl and K_2S_5 according to eq 2.

$$0.68TlCl + 1.32K_2S_5 \xrightarrow{CH_3CN} K_{0.68}Tl_{1.32}S_5 \qquad (2)$$

VII is a solid solution between K_2S_5[19] and Tl_2S_5[20] to which it is isostructural. The single crystals of VII by EDS/SEM microprobe analysis showed a slight variation of the K to Tl ratio and a more appropriate representation of the formula for this compound is $K_xTl_{2-x}S_5$ ($x = 0.35$–0.75).

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Table VI. Fractional Atomic Coordinates and B_{eq} Values for β'-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot2DMF$ with Their Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Tl	0.12148(7)	0.07437(5)	0.44236(4)	4.77(1)
S(1)	0.0780(5)	−0.0506(4)	0.3204(3)	5.9(1)
S(2)	−0.0223(4)	−0.1374(4)	0.3771(3)	5.4(1)
S(3)	0.0988(5)	−0.1932(3)	0.4611(3)	5.9(1)
S(4)	0.1422(5)	−0.0897(4)	0.5357(2)	5.4(1)
P	0.4865(4)	0.0142(3)	0.2521(2)	2.33(8)
C(1)	0.383(1)	0.583(1)	0.2646(7)	2.1(3)
C(2)	0.402(1)	0.652(1)	0.3175(8)	3.1(3)
C(3)	0.308(1)	0.710(1)	0.3298(8)	3.2(3)
C(4)	0.188(1)	0.700(1)	0.2894(8)	3.2(3)
C(5)	0.169(1)	0.630(1)	0.2381(8)	3.4(3)
C(6)	0.264(1)	0.572(1)	0.2234(7)	2.9(3)
C(7)	0.481(1)	0.4439(9)	0.1672(7)	2.0(3)
C(8)	0.388(1)	0.379(1)	0.1648(8)	2.9(3)
C(9)	0.363(2)	0.322(1)	0.1026(9)	4.0(4)
C(10)	0.430(2)	0.331(1)	0.0449(9)	3.8(4)
C(11)	0.524(2)	0.396(1)	0.0475(9)	3.8(4)
C(12)	0.554(1)	0.453(1)	0.1092(8)	3.1(3)
C(13)	0.443(1)	0.564(1)	0.6760(7)	2.9(3)
C(14)	0.497(1)	0.556(1)	0.6116(8)	3.4(3)
C(15)	0.463(2)	0.618(1)	0.5541(9)	4.1(4)
C(16)	0.372(2)	0.684(1)	0.5619(9)	3.8(3)
C(17)	0.319(2)	0.689(1)	0.6252(9)	4.1(4)
C(18)	0.352(1)	0.630(1)	0.6835(8)	3.2(3)
C(19)	0.363(1)	0.4056(9)	0.7609(7)	2.1(3)
C(20)	0.253(1)	0.408(1)	0.7128(8)	3.1(3)
C(21)	0.166(2)	0.341(1)	0.7210(9)	4.1(4)
C(22)	0.182(2)	0.275(1)	0.7712(9)	4.1(4)
C(23)	0.293(2)	0.271(1)	0.8212(9)	4.5(4)
C(24)	0.385(1)	0.336(1)	0.8149(8)	3.2(3)
N	0.107(1)	0.426(1)	0.4380(7)	5.4(3)
O	0.272(1)	0.393(1)	0.5234(9)	8.9(5)
C(31)	0.145(2)	0.515(2)	0.422(2)	10.5(8)
C(32)	−0.010(2)	0.396(2)	0.404(1)	10.1(8)
C(33)	0.171(2)	0.377(1)	0.486(1)	7.0(6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table VII. Fractional Atomic Coordinates and B_{eq} Values for γ-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot DMF$ with Their Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Tl	0.24124(1)	0.98529(4)	−0.00437(2)	2.44(1)
S(1)	0.2169(1)	0.9588(3)	−0.1318(1)	3.4(1)
S(2)	0.2962(1)	0.7597(3)	0.1439(1)	2.7(1)
S(3)	0.3631(1)	0.8034(3)	0.1252(1)	2.6(1)
S(4)	0.3318(1)	0.7718(2)	0.0302(1)	2.13(9)
P(1)	0.1261(1)	1.1038(2)	0.1018(1)	1.54(8)
O(1)	1.0000	0.328(2)	3/4	8.8(4)
N(1)	1.0000	0.094(1)	3/4	4.0(3)
C(1)	0.1065(3)	0.919(1)	0.1002(4)	1.7(3)
C(2)	0.0558(3)	0.875(1)	0.0999(4)	1.9(3)
C(3)	0.0417(4)	0.731(1)	0.0940(5)	2.5(4)
C(4)	0.0773(4)	0.629(1)	0.0883(4)	2.2(3)
C(5)	0.1281(4)	0.672(1)	0.0886(4)	2.1(4)
C(6)	0.1432(3)	0.816(1)	0.0962(4)	2.1(3)
C(7)	0.2009(3)	1.117(1)	0.1572(4)	1.6(3)
C(8)	0.2204(3)	1.054(1)	0.2164(4)	2.4(3)
C(9)	0.2768(4)	1.063(1)	0.2571(4)	2.7(4)
C(10)	0.3152(4)	1.127(1)	0.2421(5)	3.2(4)
C(11)	0.2970(4)	1.187(1)	0.1837(5)	2.9(4)
C(12)	0.2399(4)	1.183(1)	0.1418(5)	2.5(4)
C(13)	0.1137(3)	1.1595(9)	0.0251(3)	1.3(3)
C(14)	0.1209(4)	1.303(1)	0.0138(5)	2.3(4)
C(15)	0.1155(4)	1.345(1)	−0.0429(5)	2.6(4)
C(16)	0.1028(4)	1.244(1)	−0.0898(4)	2.6(4)
C(17)	0.0954(4)	1.102(1)	−0.0791(4)	2.5(4)
C(18)	0.1005(3)	1.059(1)	−0.0230(4)	1.9(3)
C(19)	0.0830(3)	1.2157(8)	0.1253(4)	1.7(3)
C(20)	0.1040(4)	1.277(1)	0.1844(4)	2.0(4)
C(21)	0.0687(4)	1.357(1)	0.1992(4)	2.2(3)
C(22)	0.0129(4)	1.379(1)	0.1582(5)	2.5(4)
C(23)	−0.0087(4)	1.320(1)	0.0989(4)	2.4(4)
C(24)	0.0260(4)	1.238(1)	0.0816(4)	1.9(3)
C(25)	0.975(1)	0.223(3)	0.756(1)	6.3(7)
C(26)	1.053(1)	0.060(3)	0.746(1)	5.0(6)
C(27)	0.971(1)	−0.033(3)	0.759(1)	6.2(7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table VIII. Fractional Atomic Coordinates and B_{eq} Values for $(Et_4N)_2[Tl_2(S_4)_2]$ with Their Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Tl(1)	0.09115(4)	0.02951(2)	0.28027(6)	2.06(3)
S(1)	0.2826(3)	0.0517(2)	0.5739(5)	2.9(2)
S(2)	0.1976(3)	0.0482(2)	0.8009(5)	2.6(2)
S(3)	0.0872(3)	0.1408(2)	0.7730(4)	2.3(1)
S(4)	−0.0319(3)	0.1145(2)	0.5438(4)	2.0(1)
N(1)	0.6696(8)	0.1832(5)	0.821(1)	1.5(4)
C(1)	0.661(1)	0.1314(6)	0.647(2)	2.1(6)
C(2)	0.563(1)	0.1475(7)	0.493(2)	3.0(6)
C(3)	0.773(1)	0.1549(7)	0.950(2)	2.1(6)
C(4)	0.798(1)	0.2003(7)	1.133(2)	2.9(6)
C(5)	0.681(1)	0.2672(6)	0.769(2)	2.0(6)
C(6)	0.784(1)	0.2876(7)	0.679(2)	2.7(6)
C(7)	0.562(1)	0.1761(7)	0.912(2)	2.0(6)
C(8)	0.532(1)	0.0949(7)	0.972(2)	2.6(6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

The UV/vis spectrum of all complexes in DMF and acetonitrile solution show similar spectra with two absorptions at ~432 and ~617 nm. The spectra of I in the two solvents are shown in Figure 1, as representative examples, and are similar to the spectra observed for $(Ph_4P)_2S_x$ or K_2S_4. This indicates that all complexes dissociate in DMF solution and give rise to S_x^{2-} species. These absorptions have been observed previously in various polysulfides solutions and had been studied extensively.[21] The UV/vis, Raman, and resonance Raman spectroscopic studies on polysulfides in liquid ammonia or polar solvents such as DMF suggest that different S_x^{2-} ligands are in equilibrium with the radical anion $S_3^{\bullet-}$ and other species such as $S_2^{\bullet-}$.[21] These studies have concluded that the absorption at ~620 nm is due to the presence of the $S_3^{\bullet-}$ species which also confers the blue color to these solutions and the band at ~450 nm is due to the $S_2^{\bullet-}$ species. All the complexes I–VII dissociate in DMF as depicted in eq 3. This is not entirely surprising if we consider that monovalent metal ions do not usually form complexes with high stability constants.

$$[Tl_2(S_4)_2]^{2-} \Leftrightarrow 2[Tl(DMF)_x]^+ + 2S_4^{2-} \qquad (3a)$$

$$2S_4^{2-} \Leftrightarrow S_3^{\bullet-} + S_2^{\bullet-} + S_3^{2-} \qquad (3b)$$

In the far-IR region all complexes reported here exhibit a complicated set of spectral absorptions characteristic of S–S and M–S stretching vibrations as shown in Figures 2 and 3. Observed absorption frequencies of all the complexes are given in Table XI. Compounds II and III exhibit identical spectra. All complexes show three spectral absorptions in the vicinity of 487, 460 and 448 cm^{-1}. Complexes V–VII show an additional absorption at 533 cm^{-1}. These bands can be assigned to S–S vibrations by comparison with the spectra of other known polysulfide complexes.[2] For example, the ν_{S-S} stretching vibrations in this region has been observed previously in various polysulfides and some representative examples are $[Fe_2S_{12}]^{2-}$ [22] at 474 cm^{-1}, $[Pd_2S_{28}]^{4-}$ [23] at 482 and 453 cm^{-1}, $[Cu_3S_{18}]^{3-}$ [17] at 468 and 455

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Table IX. Fractional Atomic Coordinates and B_{eq} Values for $(Me_4N)_2[Tl_2(S_4)_2]$ with Their Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq},[a] Å^2
Tl(1)	0.2374(4)	0.0793(3)	0.4315(3)	1.8(1)
S(1)	0.521(3)	0.061(2)	0.199(2)	3(1)
S(2)	0.531(3)	0.291(2)	0.131(2)	3(1)
S(3)	0.764(3)	0.314(2)	0.249(2)	3(1)
S(4)	0.622(3)	0.259(2)	0.454(2)	3(1)
N(1)	0.978(6)	0.296(5)	0.783(4)	1.1(7)
C(1)	0.88(1)	0.154(7)	0.815(7)	2(1)
C(2)	1.111(9)	0.275(6)	0.925(6)	2(1)
C(3)	1.13(1)	0.330(7)	0.657(7)	3(1)
C(4)	0.80(1)	0.432(7)	0.751(7)	2(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table X. Fractional Atomic Coordinates and B_{eq} Values for $K_{0.68}Tl_{1.32}S_5$ with Their Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq},[a] Å^2
Tl(1)	0.9031(4)	0.0134(1)	0.8716(4)	2.6(1)
Tl(2)	1.258(3)	0.160(1)	0.583(2)	1.7(5)
K(2)	1.25(1)	0.148(3)	0.551(8)	3(1)
S(1)	1.244(2)	0.3395(7)	0.455(2)	0.1(2)
S(2)	1.327(2)	0.3492(7)	0.761(2)	0.5(2)
S(3)	1.107(2)	0.3010(6)	0.947(2)	0.3(2)
S(4)	0.861(2)	0.3766(7)	0.923(2)	0.3(2)
S(5)	0.924(2)	0.4777(6)	1.081(2)	0.4(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

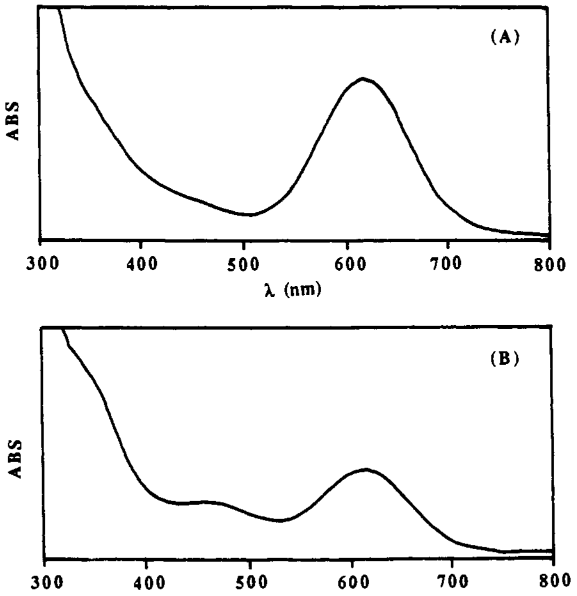

Figure 1. Typical UV/vis spectra of α-$(Ph_4P)_2[Tl_2(S_4)_2]$ in (A) DMF solution and (B) acetonitrile solution.

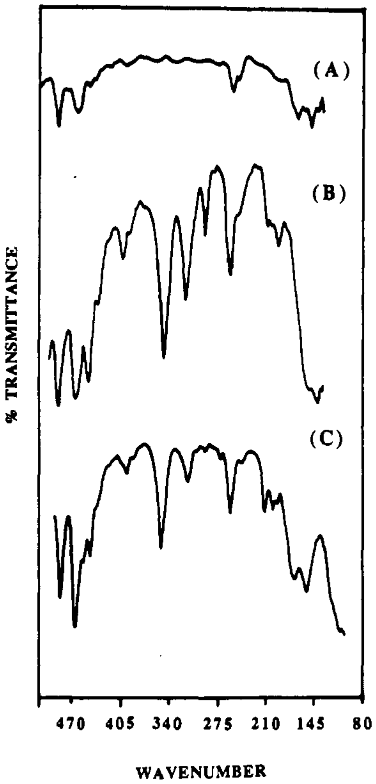

Figure 2. Far-IR spectra (CsI pellet) of (A) α-$(Ph_4P)_2[Tl_2(S_4)_2]$, (B) β- and β'-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$ and (C) γ-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot DMF$.

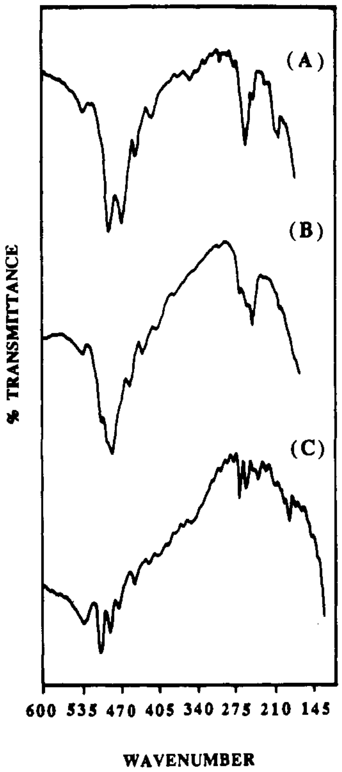

Figure 3. Far-IR spectra of (A) $(Et_4N)_2[Tl_2(S_4)_2]$, (B) $(Me_4N)_2[Tl_2(S_4)_2]$, and (C) $K_{0.68}Tl_{1.32}S_5$.

cm^{-1}, $[Cu_2S_{20}]^{4-}$ [17] at 484 and 456 cm^{-1}, and $[Bi_2S_{34}]^{2-}$ [24] at 500, 465, 456, and 448 cm^{-1}. An additional strong band around 257 cm^{-1} is observed in all Tl^+/S_x^{2-} complexes. This is a possible candidate for the Tl–S stretching frequency. The three strong absorptions in II, III, and VI around 400, 350, and 317 cm^{-1} are due to the DMF molecules in the crystal lattice.

Our initial attempts to make a Tl^{3+} polysulfide complex analogous to the thallium polyselenide, $[Tl_3Se_3(Se_4)_3]^{3-}$ [8] were unsuccessful. In the Tl^+/Se_x^{2-} system, we had observed two

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Table XI. Frequencies (cm^{-1}) of the Spectral Absorptions of I–VII

complexes	frequencies, cm^{-1}									
α-$(Ph_4P)_2[Tl_2(S_4)_2]$ (I)	489 (s)	462 (s)	446 (w)	254 (m)	167 (w)	150 (w)				
β-(II) and β'-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$ (III)	487 (s)	465 (s)	448 (m)	401 (m)	347 (s)	318 (s)	292 (s)	257 (s)	194 (w)	140 (w)
γ-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot DMF$ (VI)	485 (s)	464 (s)	446 (w)	396 (w)	350 (s)	316 (m)	259 (s)	210 (m)	171 (s)	155 (s)
$(Et_4N)_2[Tl_2(S_4)_2]$ (V)	535 (w)	489 (s)	466 (s)	445 (w)	417 (w)	257 (s)	246 (w)	202 (m)	147 (w)	
$(Me_4N)_2[Tl_2(S_4)_2]$ (VI)	534 (w)	502 (w)	484 (s)	454 (w)	432 (w)	266 (w)	254 (m)	246 (s)	200 (w)	
$K_{0.68}Tl_{1.32}S_5$ (VII)	533 (w)	503 (m)	488 (s)	474 (w)	447 (w)	267 (m)	257 (m)	238 (w)	184 (m)	

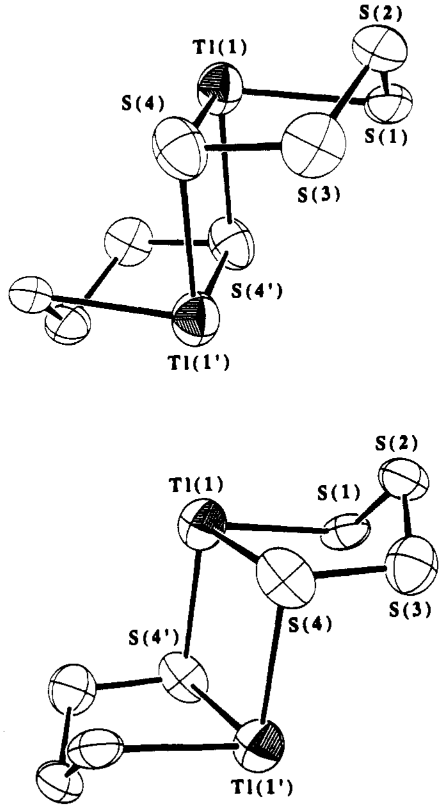

Figure 4. ORTEP representation of two views of the $[Tl_2(S_4)_2]^{2-}$ anion in I with labeling scheme.

electron oxidation of Tl^+ to Tl^{3+}. Thus far, we have not encountered any Tl^+ polyselenide complexes but the results reported here show that redox chemistry is not favorable with the polysulfide ligands. This sharp contrast in S_x^{2-} vs. Se_x^{2-} chemistry bears considerable resemblance to the Au/Se_x^{2-} system which also displays Au^+/Au^{3+} behavior with Se_x^{2-} but not with S_x^{2-}. In the gold system, only short Se_x^{2-} chains (e.g. $x \leq 3$) stabilize Au^+ complexes.[27,28]

Description of the Structures

Structure of α-$(Ph_4P)_2[Tl_2(S_4)_2]$ (I). Figure 4 shows the structure of the $[Tl_2(S_4)_2]^{2-}$ anion in I. The anion is assembled from two TlS_4 five-membered rings. It features two trigonal pyramidal Tl^+ centers each chelated by a tetrasulfide ligand, and the third coordination site is satisfied by coordination to one of the terminal sulfur atom of another TlS_4 unit, forming a dimer. This bonding mode of the S_4^{2-} ligands results in a condensed inorganic ring system with a central, strictly planar, four-membered Tl_2S_2 ring and two five-membered rings of TlS_4. The Tl_2S_2 rhombus, has a center of inversion halfway between the Tl- -Tl vector (4.047Å). It is in approximately a square geometry with slightly longer Tl–S(4) bond distances of 2.981(3) and 2.944(3) Å (average Tl–S bond is 2.926 Å in I and S(4)–Tl–S(4) and Tl–S(4)–Tl angles of 93.84(7) and 86.16(7)°, respectively. The chelating S_4^{2-} ligands adopt an envelope configuration. In the five-membered TlS_4 metallacycle, the TlS(1)S(3)S(4) atoms lie on a least-squares plane and do not deviate more than 0.084 Å; the S(2) atom is tipped away from the central four membered Tl_2S_2 ring. The overall geometry of the $[Tl_2(S_4)_2]^{2-}$ anion could thus be considered as two metallocyclic "chairs" fused together along their square "backs". Selected bond distances and angles for the anion in I are given in Table XII. The position of the S(2) atoms results in a so-called chair–chair conformation for the $[Tl_2(S_4)_2]^{2-}$ anion.

Structure of β-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$ (II). The $[Tl_2(S_4)_2]^{2-}$ anion in II is similar to that in I, and it is shown in Figure 5. The difference between these two anions lies in their conformation. The central Tl_2S_2 rhombus in this anion is almost in a square geometry with slightly longer Tl–S(4) bond distances of 2.90(1) and 2.95(1) Å (average Tl–S bond is 2.90 Å in I and S(4)–Tl–S(4′) and Tl–S(4)–Tl′ angles of 89.2(3)° and 90.8(3)°, respectively. The chelating S_4^{2-} ligands adopt an envelope configuration in the five-membered TlS_4 ring with TlS(1)S(3)S(4) atoms lying on a least-squares plane and do not deviate more than 0.069 Å. However, the S(2) atom is tipped toward the central four membered ring by 1.138 Å. The position of the S(2) atoms results in the so-called boat, boat conformation for the $[Tl_2(S_4)_2]^{2-}$ anion in II. The overall geometry of the $[Tl_2(S_4)_2]^{2-}$ anion could be thus considered as two metallocyclic "boats" fused together along their square "backs". A comparison of some selected bond distances and angles for the anion in II are given in Table XII. Due to crystal decay during the single-crystal X-ray data collection the standard deviations on the bond distances and angles are high. II has two noninteracting DMF molecules cocrystallized in the crystal lattice.

Structure of β'-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$ (III). The anion of III is identical to that of II, as the two compounds are isostructural. A comparison of some selected bond distances and angles for the anion in III are given in Table XII. The only reason this compound is differentiated here from II is its different color.

Structure of γ-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$ (IV). The anion moiety of IV is similar to that of II as it contains a similar structural unit as $[Tl_2(S_4)_2]^{2-}$ in the same boat, boat conformation. Figure 6 shows the structure of the $[Tl_2(S_4)_2]^{2-}$ anion in IV. The chelating S_4^{2-} ligands adopt an envelope configuration in the five-membered TlS_4 ring with TlS(1)S(3)S(4) atoms lying on a least-squares plane and do not deviate more than 0.08 Å, and the S(2) atom is tipped toward the central four-membered ring by 1.066 Å. IV has one DMF molecule co-crystallized in the crystal lattice and is disordered as mentioned earlier. A comparison of some selected bond distances and angles for the anion in IV are given in Table XII.

Structure of $(Et_4N)_2[Tl_2(S_4)_2]$ (V). The anion moiety of V is similar to that of II as it contains a similar structural unit as $[Tl_2(S_4)_2]^{2-}$ and is also in the same boat–boat conformation. Figure 6 shows the structure of the $[Tl_2(S_4)_2]^{2-}$ anion in V. The chelating S_4^{2-} ligands adopt an envelope configuration in the five-membered TlS_4 ring with TlS(1)S(3)S(4) atoms lying on a least-squares plane and do not deviate more than 0.012 Å, and the S(2) atom is tipped toward the central four membered ring by 1.091 Å. A comparison of some selected bond distances and angles for the anion in V are given in Table XII.

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Table XII. Comparison of Selected Bond Distances (Å) and Bond Angles (deg) of the $[Tl_2(S_4)_2]^{2-}$ Anion in I–V with Standard Deviations Given in Parentheses

	I	II	III	IV	V
Tl–Tl′	4.047	4.17	4.168	4.381	4.204
Tl–S(1)	2.852(2)	2.85(1)	2.860(1)	2.840(3)	2.903(5)
Tl–S(4)	2.981(3)	2.90(1)	2.917(1)	2.942(3)	2.943(4)
Tl–S(4′)	2.944(3)	2.95(1)	2.940(1)	2.909(3)	2.914(3)
Tl–S (mean)	2.926	2.92	2.906	2.897	2.920
S(1)–S(2)	2.045(4)	2.05(2)	2.028(2)	2.053(4)	2.040(5)
S(2)–S(3)	2.044(4)	2.03(2)	2.055(2)	2.048(4)	2.056(4)
S(3)–S(4)	2.084(4)	2.03(2)	2.039(2)	2.065(3)	2.066(5)
S–S (mean)	2.058	2.032	2.041	2.055	2.054
S(1)–Tl–S(4)	85.32(7)	86.1(4)	86.13(3)	84.30(7)	82.8(1)
S(1)–Tl–S(4′)	87.14(7)	95.3(4)	95.03(3)	89.91(7)	90.4(1)
S(4)–Tl–S(4′)	93.84(7)	89.2(3)	89.25(3)	83.05(8)	88.3(1)
Tl–S(4)–Tl′	86.2(1)	90.8(3)	90.75(3)	96.95(8)	91.7(1)
Tl–S(1)–S(2)	88.8(1)	92.4(5)	92.42(5)	100.3(1)	98.8(2)
Tl–S(4)–S(3)	95.8(1)	102.9(5)	102.3(1)	103.8(1)	106.1(2)
Tl–S(4′)–S(3′)	100.0(1)	89.8(5)	90.04(5)	94.4(1)	91.1(1)
S(1)–S(2)–S(3)	107.2(1)	107.3(7)	106.9(1)	105.6(2)	106.3(2)
S(2)–S(3)–S(4)	106.4(2)	106.5(7)	106.5(1)	105.6(1)	105.3(2)

Structure of $(Me_4N)_2[Tl_2(S_4)_2]$ (VI). The anion moiety of VI is similar to that of I as it contains a similar structural unit as $[Tl_2(S_4)_2]^{2-}$ in the chair–chair conformation. The chelating S_4^{2-} ligands adopt an envelope configuration in the five-membered TlS_4 ring with TlS(1)S(3)S(4) atoms lying on a least-squares plane and do not deviate more than 0.27 Å, and the S(2) atom is tipped away from the central four-membered ring by 1.25 Å. Due to the poor quality of this structure no meaningful metric parameters could be obtained.

Structure of $K_{0.68}Tl_{1.32}S_5$ (VII). VII is a three dimensional array of discrete S_5^{2-} chains with Tl^+ and K^+ ions (as shown in the packing diagram in Figure 7). The S_5^{2-} chain has five covalently linked sulfur atoms in an unbranched and nonplanar, helical conformation. The anion possesses no crystallographic symmetry; however, it does have an approximate 2-fold symmetry, passing through the central S(3) atom bisecting the S(2)–S(3)–S(4) angle, as shown in Figure 8. The polysulfide chain assumes a right-handed helix conformation with an average S–S–S angle of 108.1°. The Tl^+ and K^+ ions have several contacts with the individual sulfur atoms of the chain, and it is observed that the closest contacts of ca. 3.2 Å occur between the terminal S atoms with their nearest neighboring cations. A comprehensive list of the bond distances and bond angles in the anion as well as the cation/anion contacts are compiled in Table XIII.

Comparison of the Structures

The $[Tl_2(S_4)_2]^{2-}$ anion was found to crystallize in six different environments and in two different conformations. In α-$(Ph_4P)_2[Tl_2(S_4)_2]$ (I) and $(Me_4N)_2[Tl_2(S_4)_2]$ (VI) it prefers the chair–chair conformation and it is pale-orange to yellow in color. In β-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$ (II), β'-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot DMF$, (III) γ-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot DMF$ (IV), and $(Et_4N)_2[Tl_2(S_4)_2]$ (V) it adopts the boat–boat conformation and it appears orange to dark orange. There appears to be a mild correlation between color and conformation, but there seems to be no correlation between the Tl–Tl distances in these dimers and their respective conformations. The Tl–Tl distance in the α-form is the shortest 4.047(1) Å while it is the longest in the Et_4N^+ salt at 4.381(1) Å. This short distance is also reflected in the Tl–S(4)–Tl′ angle which is only 86.2(1)° in the α-form while it opens up to 96.95(8)° in the Et_4N^+ salt. Thus the origin of the different colors remains, at this stage, a mystery.

The structures of compounds I–VI suggest that in the solid state the $[Tl_2(S_4)_2]^{2-}$ anion has considerable stability, as it crystallizes in six different crystal morphologies depending on the conformation of the anion, the extent of solvent in the crystal lattice, and the countercation employed. This was a little surprising at first, as often the monovalent metals have exhibited a rich structural diversity with polychalcogenide ligands e.g. Cu/S_x^{2-},[17] Ag/S_x^{2-},[25] Ag/Se_x^{2-},[16] and Au/Se_x^{2-} [26] systems. The stability of the $[Tl_2(S_4)_2]^{2-}$ anion can be rationalized if we ascribe the Tl^+ a tetrahedral coordination environment, comprising of three sulfur atoms and the inert electron pair. The inert electron pair dictates this molecular arrangement as in this overall geometry of the anion the lone pair of the two Tl^+ are the farthest apart. The long Tl–Tl distances in these complexes (4.047(1) Å being the shortest) rule out any d^{10}–d^{10} interactions.[27] In fact, any other structural modification would be hindered due to the Coulombic repulsions from the electron pair which are rather diffused in space. The influence of the inert electron pair on the structure of the anion is also evident through the inspection of the S–Tl–S angles, which are ca. 88.4° (see Table XII). This effect is consistent with the predictions based on the valence shell electron pair repulsion (VSEPR) theory.

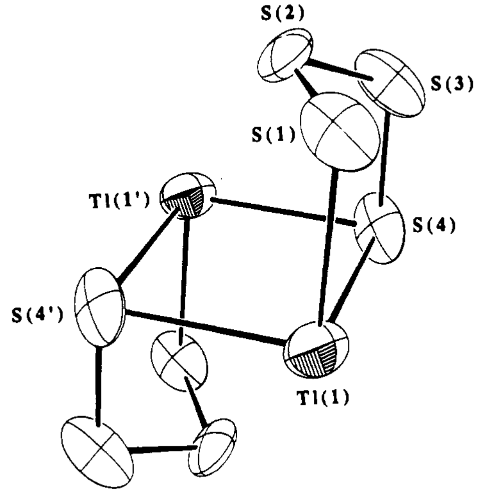

Figure 5. ORTEP representation of the $[Tl_2(S_4)_2]^{2-}$ anion in β- and β'-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$ with labeling scheme.

The coupling mode of the two five-membered TlS_4 rings in the $[Tl_2(S_4)_2]^{2-}$ anion resembles that of $[Re_2(CO)_6(Q_4)_2]^{2-}$ (Q = S[30a], Se[30b]) and $[Mn_2(CO)_6(Se_4)_2]^{2-}$.[1c] These compounds contain two Q_4^{2-} ligands (Q = S, Se) bridging as well as chelating the

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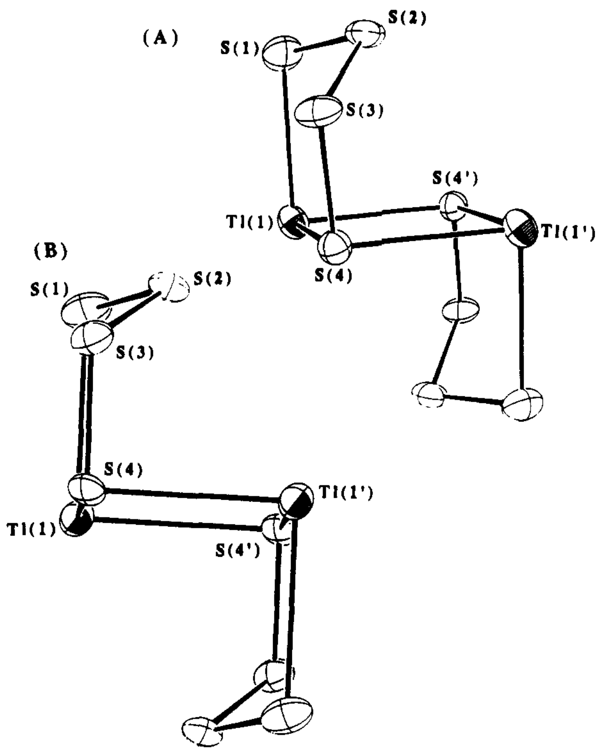

Figure 6. ORTEP representation of the $[Tl_2(S_4)_2]^{2-}$ anion (A) in γ-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot DMF$ and (B) in $(Et_4N)_2[Tl_2(S_4)_2]$ with labeling scheme.

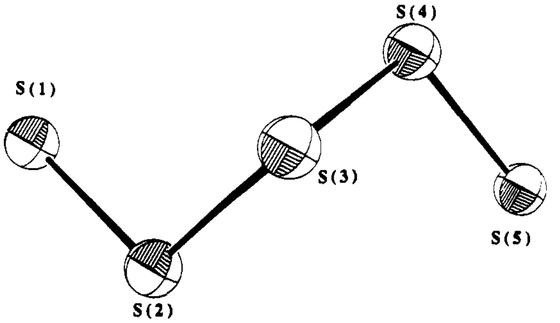

Figure 7. ORTEP representation of the S_5^{2-} anion in $K_{0.68}Tl_{1.32}S_5$ with labeling scheme.

two Re and Mn atoms. If we omit the three CO ligands the structures are very similar to the $[Tl_2(S_4)_2]^{2-}$ anion with the $[Re_2(S_4)_2]^{2-}$ fragment adopting the boat–boat conformation, whereas $[Re_2(Se_4)_2]^{2-}$ and $[Mn_2(Se_4)_2]^{2-}$ adopt the chair–chair conformation. The $[Tl_2(S_4)_2]^{2-}$ anion also bears close resemblance to $[Ag_2(S_5)_2]^{2-}$,[25] which consists of two S_5^{2-} ligands bridging and chelating symmetrically the two trigonal planar Ag^+ atoms. To the best of our knowledge complexes I–VI are the first molecular thallium polysulfides known to date.

The structure of VII is isotypic to a number of compounds such as K_2S_5,[19] Tl_2S_5,[20] Rb_2S_5,[31] and Cs_2S_5.[32] The most noteworthy difference between this compound and the $[Tl_2(S_4)_2]^{2-}$ anion is the significantly longer Tl–S bonds in the former. This derives from the considerably lower degree of covalent bonding in VII than is present in the $[Tl_2(S_4)_2]^{2-}$ anions. In fact, the Tl–S bonds in VII can be mostly described as ionic. Unlike in $[Tl_2(S_4)_2]^{2-}$, Tl^+ in VII does not display a stereochemically active s^2 lone pair, but it behaves more like an alkali-metal ion. The right-handed helical conformation of the S_5^{2-} anion has been observed in all the isotypic compounds and in various other polysulfide chain lengths e.g. S_6^{2-},[33] S_7^{2-},[34] and S_8^{2-}.[35] It has been suggested by Hordvik[36] that the S–S bond lengths vary according to the dihedral angle, being a maximum (ca. 2.10 Å) for a *cis* planar disulfide and a minimum (ca. 2.03 Å) when the dihedral angle is 90°. Our results agree with the expected values for the S–S bonds ca. 2.07 Å for a dihedral angles ca. 70°. However, we do not see any significant shortening of the terminal S–S bonds as observed in the K_2S_5 structure but found a rather high standard deviation in the bond distances and angles, similar to those observed in the Tl_2S_5 structure.

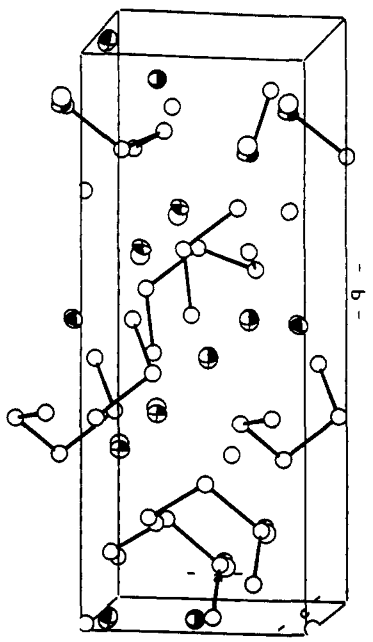

Figure 8. ORTEP representation of the unit cell of $K_{0.68}Tl_{1.32}S_5$.

Table XIII. Selected Bond Distances (Å) and Bond Angles (deg) for $K_{0.68}Tl_{1.32}S_5$ (VII) with Standard Deviations Given in Parentheses

S(1)–S(2)	2.07(2)	S(1)–S(2)–S(3)	110.0(7)
S(2)–S(3)	2.07(2)	S(2)–S(3)–S(4)	105.6(6)
S(3)–S(4)	2.07(2)	S(3)–S(4)–S(5)	108.6(7)
S(4)–S(5)	2.04(1)		

S(1)S(2)S(3)/S(2)S(3)S(4)	68.86
S(2)S(3)S(4)/S(3)S(4)S(5)	73.16

Tl(1)–S(1)	3.43(1)	Tl(2)–S(4)	3.41(2)
Tl(1)–S(1)	3.30(1)	Tl(2)–S(4)	3.34(1)
Tl(1)–S(2)	3.37(1)	Tl(2)–S(5)	3.37(1)
Tl(1)–S(2)	3.28(1)	Tl(2)–S(5)	3.47(1)
Tl(1)–S(4)	3.39(1)	K(2)–S(1)	3.30(5)
Tl(1)–S(5)	3.20(1)	K(2)–S(1)	3.40(6)
Tl(1)–S(5)	3.47(1)	K(2)–S(1)	3.25(6)
Tl(1)–S(5)	3.22(1)	K(2)–S(2)	3.49(6)
Tl(2)–S(1)	3.15(2)	K(2)–S(4)	3.19(5)
Tl(2)–S(1)	3.23(2)	K(2)–S(5)	3.39(6)
Tl(2)–S(2)	3.44(2)	K(2)–S(5)	3.23(5)
Tl(1)–Tl(1)	3.858(4)	Tl(1)–K(2)	3.87(6)
Tl(1)–Tl(2)	3.90(2)	Tl(1)–K(2)	3.74(6)
Tl(1)–Tl(2)	3.94(2)	K(2)–K(2)	4.83(8)

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In summary, the reactions of the tetrasulfide anion, S_4^{2-}, with Tl^+ in the presence of different quaternary phosphonium or quaternary ammonium cations in DMF, affords several new compounds: α-$(Ph_4P)_2[Tl_2(S_4)_2]$, β-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$, β'-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$, γ-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot DMF$, $(Et_4N)_2[Tl_2(S_4)_2]$, and $(Me_4N)_2[Tl_2(S_4)_2]$ all of which contain the $[Tl_2(S_4)_2]^{2-}$ anion in one of two different conformations: chair–chair for I and VI and boat–boat for the rest. The influence of the inert electron pair of the Tl^+ on the structure is profound. The $[Tl_2(S_4)_2]^{2-}$ does not retain its structural integrity in polar solvents such DMF and CH_3CN. This study has indicated that the Tl^+ does not posses sufficient reducing power to reduce polysulfides, and thus the Tl/S_x^{2-} chemistry does not parallel that of the Tl/Se_x^{2-} chemistry, which favors Tl^{3+} chemistry. The reaction of thallium chloride and potassium tetrasulfide in acetonitrile afforded $K_{0.68}Tl_{1.32}S_5$, a solid solution of K_2S_5 and Tl_2S_5.

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Supplementary Material Available: Tables of the anisotropic and isotropic thermal parameters of all non-hydrogen atoms, bond distances, bond angles, and experimental and calculated powder X-ray diffraction patterns for α-$(Ph_4P)_2[Tl_2(S_4)_2]$ (I), β-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$ (II), β'-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot 2DMF$ (III), γ-$(Ph_4P)_2[Tl_2(S_4)_2]\cdot DMF$ (IV), $(Et_4N)_2[Tl_2(S_4)_2]$ (V), $(Me_4N)_2[Tl_2(S_4)_2]$ (VI), and $K_{0.68}Tl_{1.32}S_5$ (VII), and hydrogen atom parameters for III, V, and VI (53 pages). Ordering information is given on any current masthead page.