# Syntheses and Characterization of the New Homoleptic Indium–Polysulfide Complexes [In$_2$S$_{27}$]$^{4-}$, [In$_2$S$_{14}$]$^{2-}$, and [In$_2$S$_{16}$]$^{2-}$

Sandeep S. Dhingra and Mercouri G. Kanatzidis*

Department of Chemistry and Center for Fundamental and Materials Research,
Michigan State University, East Lansing, Michigan 48824

The reaction of InCl$_3$ with K$_2$S$_5$ and Ph$_4$PCl in a 2:5:4 mole ratio in DMF afforded thin pale yellow crystals of (Ph$_4$P)$_4$[In$_2$S$_{27}$] (I). I crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a$ = 12.276(3) Å, $b$ = 21.849(8) Å, $c$ = 10.852(2) Å, $\alpha$ = 99.57(2)°, $\beta$ = 112.44(2)°, $\gamma$ = 79.28(3)°, $V$ = 2628(1) Å$^3$ (at –90 °C), and $Z$ = 1. The [In$_2$(S$_4$)$_2$(S$_6$)$_2$(S$_7$)]$^{4-}$ anion consists of In$^{3+}$ centers in trigonal bipyramidal coordination. Each In atom is chelated by two bidentate polysulfide S$_4{}^{2-}$ and S$_6{}^{2-}$ ligands forming a [In(S$_4$)(S$_6$)]$^-$ unit. Two [In(S$_4$)(S$_6$)]$^-$ units are bridged by an S$_7{}^{2-}$ chain forming a dimer. A similar reaction of InCl$_3$ with K$_2$S$_5$ and Ph$_4$PCl in a slightly different mole ratio of 1:2:1 in DMF afforded pale yellow crystals of (Ph$_4$P)$_2${[In$_2$S$_{14}$]$_{0.5}$[In$_2$S$_{16}$]$_{0.5}$} (II). II crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a$ = 10.906(2) Å, $b$ = 11.892(2) Å, $c$ = 21.554(3) Å, $\alpha$ = 89.81(1)°, $\beta$ = 97.46(1)°, $\gamma$ = 92.25(1)°, $V$ = 2769(1) Å$^3$ (at –80 °C), and $Z$ = 2. II is a cocrystallizate of [In$_2$S$_{14}$]$^{2-}$ and [In$_2$S$_{16}$]$^{2-}$ anions with equal occupancies. The two anions contain tetrahedral In$^{3+}$ centers. The In atoms are bridged by an S$^{2-}$ and an S$_5{}^{2-}$ ligand to form an eight-membered [In$_2$S(S$_5$)]$^{2+}$ ring core in an extreme cradle configuration. The remaining two coordination sites on each In atom are occupied by a S$_4{}^{2-}$ chelating ligand on one side and a S$_4{}^{2-}$ or a S$_6{}^{2-}$ chelating ligand disordered on the other. These complexes show no absorption peaks in the UV/vis region of the spectrum. The solid-state far-IR spectra of the compounds exhibit strong absorptions in the 500–100-cm$^{-1}$ region due to the S–S and M–S stretching vibrations. Thermal gravimetric analysis data for these compounds are reported.

## Introduction

To date, transition metal–polychalcogenide complexes have been extensively investigated, whereas corresponding complexes containing main group elements have been relatively little explored.[1-9] The few existing examples include [Bi$_2$S$_{34}$]$^{4-}$,[10] [Sn(S$_4$)$_2$(S$_6$)$_{0.6}$(S$_4$)$_{0.4}$]$^{2-}$,[11] [In$_2$Se$_{21}$]$^{4-}$,[12] [SnSe$_{12}$]$^{2-}$,[13] [PbSe$_8$]$^{2-}$,[14] [In$_2$Se$_{10}$]$^{2-}$,[15] and [M$_3$Se$_{15}$]$^{3-}$ [15] (M = In, Tl). Interest in this area derives from the relevance and possible significance of these complexes as model compounds for sulfided heterogeneous catalysts,[1] bioinorganic systems,[2] metal sulfur transport agents in geochemistry,[3] and low-temperature precursors to chalcogenide semiconductors.[4] As part of our systematic investigation of polychalcogenide chemistry of the late transition and main group metals,[12-15] and in an attempt to prepare the sulfur analogs of the recently reported indium–polyselenide complexes,[12,15] we investigated the corresponding indium polysulfide chemistry. Recently, we reported the synthesis of the mixed-ligand complexes [In(S$_4$)(S$_6$)X]$^{2-}$ [16] (X = Cl, Br). Here we report the synthesis, structures, and properties of the first *homoleptic* indium-polysulfide complexes: [In$_2$S$_{27}$]$^{4-}$, [In$_2$S$_{14}$]$^{2-}$, and [In$_2$S$_{16}$]$^{2-}$.

## 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; indium(I) chloride, 99.999% purity, indium(I) bromide, 99.999% purity, Cerac Inc., Milwaukee, WI; tetraphenylphosphonium chloride (Ph$_4$PCl), 98% purity, tetraphenylphosphonium bromide (Ph$_4$-PBr), 98% purity, Aldrich Chemical Co. Inc., Milwaukee, WI. Dimethylformamide (DMF), analytical reagent, was stored over 4A Linde molecular sieves for over 1 week and then distilled under reduced pressure at 25–30 °C. The first 50 mL was discarded. 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. Methanol (MeOH) anhydrous (E. M. Science, Gibbstown, NJ) was distilled after refluxing with CaH$_2$ for 8–12 h.

**Physicochemical Measurements.** Infrared spectra of the complexes were recorded as solids in a CsI matrix on a Nicolet 740 FT-IR spectrometer. Each sample was ground 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

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spectrophotometer. Thermal gravimetric analyses (TGA) of the compounds were recorded on either a Cahn TG system 121 or a Shimadzu TGA-50. The solid samples were heated from room temperature to 1000 °C at a rate of 5 °C/min under a steady flow of dry nitrogen. Quantitative microprobe analysis of the compounds was performed on a scanning electron microscope (SEM) JEOL JSM-35C equipped with a Tracor Northern TN 5500 X-ray microanalysis attachment, 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 charge that is developed on the sample under an electron beam. 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 four individual measurements on several different single crystals of each compound.

**Syntheses.** All experiments and syntheses were performed under nitrogen in a Vacuum Atmospheres Dri-Lab glovebox.

**Potassium Pentasulfide, $K_2S_5$.** A 30.757-g sample (0.959 mol) of finely powdered elemental sulfur was combined with 15.00 g (0.384 mol) of sliced potassium metal in a round-bottom flask equipped with a Teflon valve and a stirbar. A 150-mL volume of liquid ammonia was condensed into the flask at –78 °C (dry ice/acetone bath), and the mixture was stirred for a couple of hours until the potassium metal had dissolved completely. When a deep blue solution formed, the ammonia was removed by evaporation at room temperature (by allowing the cold bath to warm up slowly) under a steady flow of dry nitrogen. The resulting yellow-orange solid was dried in vacuo, flame dried, and ground to a fine powder in the glovebox. It was used without further characterization. The yellow-orange powder dissolves in DMF and acetonitrile resulting in deep blue-green solutions.

Preparation of $K_2S_4$ and $K_2S_6$ were accomplished by following the same procedure as for $K_2S_5$, by varying the stoichiometric ratios of potassium and sulfur.

**Tetrakis(tetraphenylphosphonium) Bis(tetrasulfido)bis(hexasulfido)-($\mu$-heptasulfido)diindate, $(Ph_4P)_4[In_2S_{27}]$ (I). Method A.** A 5-mL DMF solution of 0.100 g (0.452 mmol) of $InCl_3$ was added to a 15-mL DMF solution of 0.270 g (1.132 mmol) of $K_2S_5$ in the presence of 0.339 g (0.904 mmol) of $Ph_4PCl$. The mixture was stirred for 20 min. Filtration of the pale yellow solution to remove the KBr precipitate was followed by slow addition of ca. 10 mL of methanol and later ca. 20 mL of ether. Storage at room temperature for 2 weeks afforded very thin yellow platelets in 52% yield. A quantitative microprobe analysis performed on a number of crystals of I with EDS/SEM system gave an average composition of $InS_{14.04}P_{2.15}$.

**Method B.** In a Pyrex tube was added 0.050 g (0.226 mmol) of $InCl_3$, 0.184 g (0.680 mmol) of $K_2S_6$, and 0.170 g (0.454 mmol) of $Ph_4PCl$ and 0.5 mL of methanol. The mixture was frozen in liquid nitrogen and flame sealed under vacuum. The tube was subsequently heated to 110 °C for 10 days. The tube was opened in an inert-atmosphere glovebox, and large (~2–3 mm in size) yellow crystals were isolated by filtration and washed quickly with methanol, ethanol, and finally with ether, yield 58%. A quantitative microprobe analysis performed on a number of crystals of I with EDS/SEM system gave an average composition of $InS_{13.98}P_{2.05}$.

**Cocrystallizate of Bis(tetraphenylphosphonium) with Half-Occupancies of Bis(tetrasulfido)($\mu$-sulfido)($\mu$-pentasulfido)diindate and (Tetrasulfido)-(hexasulfido)($\mu$-sulfido)($\mu$-pentasulfido)diindate, $(Ph_4P)_2\{[In_2S_{14}]_{0.5}$-$[In_2S_{16}]_{0.5}\}$ (II).** To a solution of 0.216 g (1.132 mmol) of $K_2S_5$ and 0.170 g (0.454 mmol) of $Ph_4PCl$ in 15 mL of DMF was added dropwise a 5-mL DMF solution of 0.100 g (0.452 mmol) of $InCl_3$. The mixture was then stirred for ca. 20 min until its color became pale yellow. Following filtration (to remove KCl), 20 mL of ether was layered over it to cause crystallization. Upon standing at room temperature for 2 days, yellow platelets of II were formed and isolated by filtration, yield 48%. A quantitative microprobe analysis performed on a number of crystals of II with EDS/SEM system gave an average composition of $InS_{7.99}P_{1.17}$.

**X-ray Crystallographic Studies.** X-ray powder diffraction patterns were recorded with a Phillips XRG-3000 computer-controlled powder diffractometer. Ni-filtered, Cu-radiation was used. $d$-spacings (Å) for all materials were measured. The X-ray powder patterns obtained from both complexes matched well with those calculated from the atom coordinates obtained from the X-ray single-crystal diffraction studies, using the program POWD-10.[17] This confirmed the homogeneity and

**Table I.** Summary of Crystallographic Data for $(Ph_4P)_4[In_2S_{27}]$ (I) and $[Ph_4P]_2\{[In_2S_{14}]_{0.5}[In_2S_{16}]_{0.5}\}$ (II)

|  | I | II |
|---|---|---|
| formula | $C_{96}H_{80}P_4In_2S_{27}$ | $C_{48}H_{40}P_2In_2S_{15}$ |
| fw | 2452.96 | 1389.40 |
| cryst color | pale yellow | pale yellow |
| temp (°C) | –90 | –80 |
| $a$ (Å) | 12.276(3) | 10.906(2) |
| $b$ (Å) | 21.849(8) | 11.892(2) |
| $c$ (Å) | 10.852(2) | 21.554(3) |
| $\alpha$ (deg) | 99.57(2) | 89.81(1) |
| $\beta$ (deg) | 112.44(2) | 97.46(1) |
| $\gamma$ (deg) | 79.28(3) | 92.25(1) |
| $Z$; $V$ (Å$^3$) | 1; 2628(1) | 2; 2769.7(1) |
| space group | $P\bar{1}$ (No. 2) | $P\bar{1}$ (No. 2) |
| $D_{calc}$ (g cm$^{-3}$) | 1.55 | 1.66 |
| $\mu$ (cm$^{-1}$) | 10.51 (Mo K$\alpha$) | 128.7 (Cu K$\alpha$) |
| cryst size (mm) | 0.52, 0.29, 0.16 | 0.74, 0.24, 0.12 |
| $\lambda$; $2\theta_{max}$ (deg) | Mo$_{K\alpha_1}$; 50 | Cu$_{K\alpha_1}$; 114 |
| final $R/R_w$ (%)$^a$ | 9.5/12.0 | 7.6/8.6 |

$^a R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. $R_w = \{\Sigma[w(|F_o| - |F_c|)^2]/\Sigma[w|F_o|)^2]\}^{1/2}$.

the purity of the complexes, assuming no amorphous phases were present. Calculated and observed $d$-spacings (Å) for I and II are compiled in the supplementary material. The crystals of I and II were mounted on the tip of glass fibers with silicon grease and the data were collected at low temperature. The data for I were collected on a Rigaku AFC6S four-circle automated diffractometer with $\omega$–$2\theta$ scan technique and Mo K$\alpha$ radiation. The crystallographic data for II were collected on a Nicolet P3 four-circle automated diffractometer using a $\theta$–$2\theta$ step scan mode[18] and Cu K$\alpha$ radiation. Accurate unit cell dimensions were determined from the refined $2\theta$, $\omega$, $\phi$, and $\chi$ angles of 15–25 machine-centered reflections. The intensities of three check reflections were monitored every 100–150 reflections and did not show any appreciable decay over the data collection period. An empirical absorption correction, based on $\psi$ scans for 3 ($\chi \sim 90°$) reflections, was applied to the data of I. The structures were solved with direct methods and difference Fourier synthesis maps and refined with full-matrix least-square techniques using the TEXSAN crystallographic software package from Molecular Structure Corp. An additional absorption correction was applied before anisotropic refinement using DIFABS.[19] All calculations were performed on a VAXstation 3100/76 computer. For I and II all non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were calculated and included in the structure factor calculations but were not refined. All compounds consist of discrete, well-separated cations and anions. The $Ph_4P^+$ cations are ordered and have the usual tetrahedral structure.

The $[In_2S_{27}]^{4-}$ anion has a crystallographically imposed center of symmetry. This induces a positional disorder of the central S(14) atom of the bridging $S_7^{2-}$ chain resulting in half positional occupancy for S(14). S(11), the terminal atom, and S(12) of the bridging $S_7^{2-}$ chain are both positionally disordered over two sites of equal occupancy thus leading to two different conformations of the $S_7^{2-}$ chain in the solid state.

The structure of II has disorder in the $S_x^{2-}$ ligand chelating In(2). There are two different chain lengths $S_4^{2-}$ and $S_6^{2-}$ of the chelating polysulfide, respectively, sitting on the same crystallographic site. The $S_4^{2-}$ consists of S(11)S(12)S(13)S(14) atoms, whereas $S_6^{2-}$ consists of S(11)S(15)S(16)S(17)S(18)S(19) atoms. All atoms in these two different $S_x^{2-}$ chains were refined with half-occupancy except S(11). The complete data collection parameters and details of the structure solution and refinement for I and II are summarized in Table I. The final coordinates, temperature factors, and estimated standard deviations (esd's) of all atoms in the anions for both compounds are shown in Tables II and III.

## Results and Discussion

**Synthesis and Spectroscopic Studies.** This study demonstrates that $In/S_x^{2-}$ chemistry is quite different from that of $In/Se_x^{2-}$.[12,15] For example, the isolation of $(Ph_4P)_2[In(S_4)(S_6)X]$ (X

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**Table II.** Fractional Atomic Coordinates and $B_{eq}$ Values for $(Ph_4P)_4[In_2S_{27}]$ (I) with Their Estimated Standard Deviations in Parentheses

| atom | x | y | z | $B_{eq},^a$ Å$^2$ |
|---|---|---|---|---|
| In(1) | 0.5653(1) | 0.25088(7) | 0.4991(1) | 3.22(5) |
| S(1) | 0.7157(4) | 0.2028(2) | 0.7164(5) | 3.8(2) |
| S(2) | 0.6503(4) | 0.2509(2) | 0.8590(5) | 3.9(2) |
| S(3) | 0.6140(4) | 0.3419(2) | 0.8182(4) | 3.3(2) |
| S(4) | 0.4825(4) | 0.3400(2) | 0.6325(5) | 3.9(2) |
| S(5) | 0.4042(5) | 0.2949(4) | 0.2836(5) | 6.4(3) |
| S(6) | 0.4399(5) | 0.3803(4) | 0.2676(6) | 6.8(3) |
| S(7) | 0.5186(5) | 0.3653(3) | 0.1272(5) | 5.1(3) |
| S(8) | 0.6979(5) | 0.3431(3) | 0.2236(5) | 4.4(2) |
| S(9) | 0.7283(5) | 0.2524(3) | 0.2654(6) | 5.1(3) |
| S(10) | 0.7547(4) | 0.2528(3) | 0.4632(6) | 4.5(2) |
| S(11) | 0.436(2) | 0.164(1) | 0.417(2) | 8(1) |
| S(11') | 0.479(2) | 0.151(1) | 0.380(3) | 9(1) |
| S(12) | 0.538(2) | 0.090(1) | 0.412(1) | 7.8(9) |
| S(12') | 0.441(2) | 0.114(2) | 0.482(3) | 15(2) |
| S(13) | 0.5686(7) | 0.0615(6) | 0.5780(7) | 10.4(6) |
| S(14) | 0.426(1) | 0.016(1) | 0.557(2) | 9(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 III.** Fractional Atomic Coordinates and $B_{eq}$ Values for $[Ph_4P]_2\{[In_2S_{14}]_{0.5}[In_2S_{16}]_{0.5}\}$ (II) with Their Estimated Standard Deviations in Parentheses

| atom | x | y | z | $B_{eq},^a$ Å$^2$ |
|---|---|---|---|---|
| In(1) | 0.27513(8) | 0.24718(7) | 0.83377(4) | 2.53(4) |
| In(2) | 0.27475(9) | 0.27926(8) | 0.65531(4) | 3.16(4) |
| S(1) | 0.3884(3) | 0.4081(3) | 0.8938(1) | 2.8(1) |
| S(2) | 0.3141(4) | 0.3906(3) | 0.9767(1) | 3.9(2) |
| S(3) | 0.2879(3) | 0.2243(3) | 0.9892(1) | 3.8(1) |
| S(4) | 0.1502(3) | 0.1767(3) | 0.9170(2) | 3.2(1) |
| S(5) | 0.1467(3) | 0.2769(5) | 0.7378(2) | 6.4(2) |
| S(6) | 0.4162(4) | 0.0856(3) | 0.8415(2) | 4.3(2) |
| S(7) | 0.5021(4) | 0.1073(3) | 0.7643(2) | 4.7(2) |
| S(8) | 0.6216(4) | 0.2395(3) | 0.7835(2) | 5.0(2) |
| S(9) | 0.5207(3) | 0.3780(3) | 0.7659(1) | 3.0(1) |
| S(10) | 0.4771(4) | 0.3848(4) | 0.6713(2) | 4.8(2) |
| S(11) | 0.1640(4) | 0.3829(3) | 0.5657(2) | 4.4(2) |
| S(12) | 0.0627(8) | 0.230(1) | 0.5236(4) | 7.0(5) |
| S(13) | 0.203(1) | 0.127(1) | 0.5173(5) | 7.4(6) |
| S(14) | 0.267(1) | 0.0865(8) | 0.6109(4) | 5.9(5) |
| S(15) | 0.0095(7) | 0.2958(7) | 0.5510(3) | 3.8(3) |
| S(16) | 0.014(1) | 0.1873(8) | 0.4808(4) | 5.6(4) |
| S(17) | 0.102(1) | 0.0460(8) | 0.5140(4) | 6.0(4) |
| S(18) | 0.287(1) | 0.098(1) | 0.5196(5) | 5.8(5) |
| S(19) | 0.3512(8) | 0.1036(7) | 0.6113(4) | 4.0(4) |

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

$= Br, Cl$,[16] a mixed-ligand complex, is not paralleled by a synthesis of a Se analog. The synthesis $(Ph_4P)_2[In(S_4)(S_6)X]$ was accomplished from $InX_3$ and $K_2S_5$ (or a mixture of $K_2S_4$ and $K_2S_6$) in DMF in the presence of $Ph_4P^+$ according to eq 1. Under similar conditions using $K_2Se_5$ only $[In_2Se_{21}]^{4-}$ is obtained.

$$InX_3 + 2K_2S_5 + 2Ph_4PX \rightarrow$$
$$(Ph_4P)_2[In(S_4)(S_6)X] + 4KX \quad (1)$$
$$X = Br, Cl$$
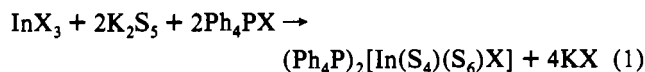
In order to form a homoleptic indium polysulfide, we increased the amount of polysulfide ligand according to eq 2. This afforded a new microcrystalline yellow compound in 52% yield.

$$2InCl_3 + 5K_2S_5 + 4Ph_4PCl \rightarrow$$
$$(Ph_4P)_4[In_2S_{27}] + 10KCl \quad (2)$$
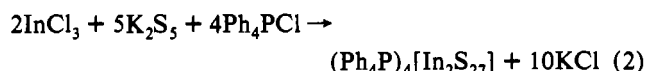
The addition of a small amount of methanol assisted in the growth of very thin platelets of I, but the crystal quality was

**Table IV.** Frequencies (cm$^{-1}$) of the Infrared Spectral Absorptions for $(Ph_4P)_4[In_2S_{27}]$ (I) and $[Ph_4P]_2\{[In_2S_{14}]_{0.5}.[In_2S_{16}]_{0.5}\}$ (II)

| complexes | freq (cm$^{-1}$) |
|---|---|
| $(Ph_4P)_4[In_2S_{27}]$ | 485 (s), 457 (m), 289 (s), 260 (m), 186 (m), 137 (w) |
| $[Ph_4P]_2\{[In_2S_{14}]_{0.5^-}$ $[In_2S_{16}]_{0.5}\}$ | 491 (m), 479 (w), 463 (m), 458 (w), 355 (s), 290 (s), 258 (m), 231 (m), 192 (w), 147 (w) |

insufficient for single-crystal X-ray diffraction. The failure to grow good crystals encouraged us to resort to hydro(methanol)thermal synthesis. The hydrothermal technique has been shown by us to be very promising for the growth of large single crystals of metal polychalcogenides.[20] The reaction of $InCl_3$ with $K_2S_6$ in the presence of $Ph_4P^+$ in methanol at 110 °C in an evacuated sealed Pyrex tube afforded large ($\sim$2–3 mm in size) crystals of I.

The reaction of $InCl_3$ with $K_2S_6$ and $Ph_4P^+$ in 1:2:1 molar ratio in DMF affords II according to eq 3. As will be seen below, $(Ph_4P)_2[In_2S(S_5)(S_4)_{1.5}(S_6)_{0.5}]$ is a cocrystallization of two similar but distinct complexes, $[In_2S_{14}]^{2-}$ and $[In_2S_{16}]^{2-}$.

$$InCl_3 + 2K_2S_5 + Ph_4PCl \xrightarrow{DMF}$$
$$^1/_2(Ph_4P)_2[In_2S(S_5)(S_4)_{1.5}(S_6)_{0.5}] + 4KCl \quad (3)$$
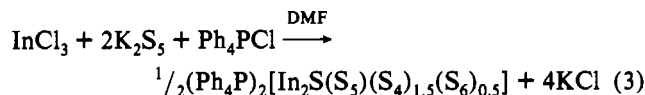
Note that the particular length of alkali polysulfide reagent has nothing to do with the polysulfide sizes found in the products. This is a common theme in polychalcogenide chemistry and is due to the fact that polychalcogenide solutions involve equilibria between multiple $S_x^{2-}$ species. Those that satisfy the metal coordination preference bind to the metal and leave the equilibrium cycle. This makes chemical reactions difficult to balance.

I and II give pale-yellow DMF solutions and have no characteristic absorption bands in the UV/vis spectrum. The absence of an absorption band around 650 nm suggests that the complexes do not dissociate in this solvent to form $S_x^-$ radical anions, which are responsible for this absorption.[12] Thus, the solution behavior of $[In_2S_{27}]^{4-}$, as judged by the UV/vis spectra, is in stark contrast to that of the structurally similar $[In_2Se_{21}]^{4-}$, which was found to release free $Se_x^{2-}$ in solution.[15]

In the far-IR region I and II exhibit spectral absorptions due to S–S and M–S stretching vibrations. Observed absorption frequencies of all complexes are given in Table IV. For both complexes two spectral absorptions are observed in the vicinity of 490 and 458 cm$^{-1}$. These bands can be assigned to S–S vibrations by comparison with the spectra of other known polysulfide complexes.[1] The $\nu$(S–S) absorptions in this region have been observed previously in various compounds, and some representative examples are $[Fe_2S_{12}]^{2-}$[21] at 474 cm$^{-1}$, $[Pd_2S_{28}]^{4-}$[22] at 482 and 453 cm$^{-1}$, $[Cu_3S_{18}]^{3-}$[23] at 468 and 455 cm$^{-1}$, $[Cu_2S_{20}]^{4-}$[23] at 484 and 456 cm$^{-1}$, and $[Bi_2S_{34}]^{2-}$[10] at 500, 465, 456, and 448 cm$^{-1}$. The far-IR spectra of I and II also show two additional strong bands around 290 and 260 cm$^{-1}$. These may be due to In–S stretching vibrations by comparison to the spectra reported for some indium halide complexes with trimethylphosphine sulfide and trimethylarsine sulfide,[24] which exhibit absorptions in the range 251–277 cm$^{-1}$.

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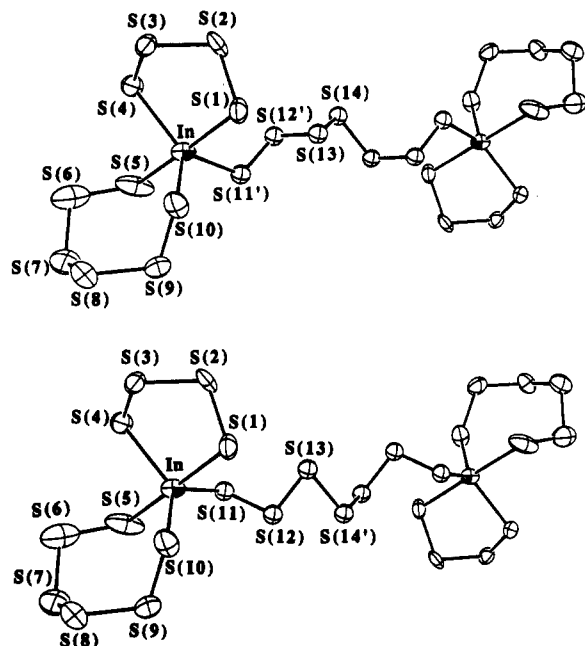(24) Robinson, W. T.; Wilkins, C. J.; Zeying, Z. *J. Chem. Soc., Dalton Trans.* **1988**, 2187–2192.

**Figure 1.** ORTEP representation of the two conformations of the $[In_2(S_4)_2(S_6)_2(S_7)]^{4-}$ anion in I with labeling scheme.
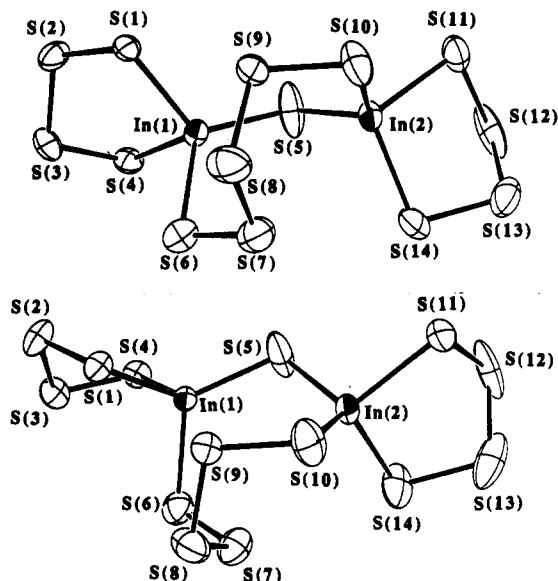


**Figure 2.** Two views of the $[In_2S(S_5)(S_4)_2]^{2-}$ anion in II with labeling scheme.

**Thermal Gravimetric Analysis Studies.** TGA examination of the thermolysis of I and II under flowing nitrogen shows that the compounds begin to lose weight at ∼260 and 270 °C, respectively. This onset temperature of initial weight loss is shared by $Ph_4P^+$ salts of polyselenide complexes,[15] and it is associated with the thermal stability of the $Ph_4P^+$ ion with respect to nucleophilic attack from the $S_x^{2-}$ ligands. Byproducts are $Ph_3PS$ and $Ph_2S$. I and II exhibit a plateau around 570 °C; however, the weight loss does not correspond to any known binary In/S phase. Even at 1000 °C, the highest temperature studied, the compounds continue to lose weight. The black residues obtained from I and II contained In/S in approximately 1:3 ratio, and the X-ray diffraction pattern could not be matched to any of the known phases. This thermal decomposition behavior contrasts that of the $(Ph_4P)_4[In_2Se_{21}]$ complex, which decomposes in well-defined steps to yield single-phase $\beta$-$In_2Se_3$.[15]

**Description of the Structures. Structure of $(Ph_4P)_4[In_2S_{27}]$ (I).** Figure 1 shows the structure of the $[In_2S_{27}]^{4-}$ anion. The structure consists of two $[In(S_4)(S_6)]^-$ units bridged by a $S_7^{2-}$

**Table V.** Selected Bond Distances (Å) in the $[In_2(S_7)(S_4)_2(S_6)_2]^{4-}$ Anion with Standard Deviations in Parentheses

| In(1)–S(1) | 2.619(5) | S(6)–S(7) | 2.051(8) |
|---|---|---|---|
| In(1)–S(4) | 2.523(5) | S(7)–S(8) | 2.045(8) |
| In(1)–S(5) | 2.610(6) | S(8)–S(9) | 2.041(8) |
| In(1)–S(10) | 2.510(5) | S(9)–S(10) | 2.046(8) |
| In(1)–S(11) | 2.52(2) | S–S(mean) | 2.045(5) |
| In(1)–S(11') | 2.53(2) | S(11)–S(12)$^a$ | 1.86(3) |
| In–S(mean) | 2.55(4) | S(11')–S(12')$^a$ | 1.72(4) |
| S(1)–S(2) | 2.057(7) | S(12)–S(13)$^a$ | 1.89(2) |
| S(2)–S(3) | 2.039(7) | S(12')–S(13)$^a$ | 1.83(3) |
| S(3)–S(4) | 2.044(7) | S(13)–S(14)$^a$ | 2.09(2) |
| S(5)–S(6) | 2.04(1) | S(13)–S(14')$^a$ | 2.06(2) |

$^a$ S–S distances within the disordered $S_x^{2-}$ chain.

**Table VI.** Selected Bond Angles (deg) in the $[In_2(S_7)(S_4)_2(S_6)_2]^{4-}$ Anion with Standard Deviations in Parentheses

| S(1)–In(1)–S(4) | 92.2(2) | In(1)–S(5)–S(6) | 109.1(3) |
|---|---|---|---|
| S(1)–In(1)–S(5) | 176.1(2) | In(1)–S(10)–S(9) | 112.3(3) |
| S(1)–In(1)–S(10) | 81.4(2) | In(1)–S(11)–S(12) | 106(1) |
| S(1)–In(1)–S(11) | 96.4(7) | In(1)–S(11')–S(12') | 112(2) |
| S(1)–In(1)–S(11') | 96.7(2) | S(1)–S(2)–S(3) | 104.7(3) |
| S(4)–In(1)–S(5) | 87.3(2) | S(2)–S(3)–S(4) | 103.7(3) |
| S(4)–In(1)–S(10) | 121.7(2) | S(5)–S(6)–S(7) | 106.3(4) |
| S(4)–In(1)–S(11) | 111.0(5) | S(6)–S(7)–S(8) | 108.1(3) |
| S(4)–In(1)–S(11') | 128.7(7) | S(7)–S(8)–S(9) | 107.6(3) |
| S(5)–In(1)–S(10) | 102.2(2) | S(8)–S(9)–S(10) | 103.8(3) |
| S(5)–In(1)–S(11) | 80.1(7) | S(11)–S(12)–S(13) | 102.3(9) |
| S(5)–In(1)–S(11') | 80.6(7) | S(11')–S(12')–S(13) | 110(1) |
| S(10)–In(1)–S(11) | 127.2(5) | S(12)–S(13)–S(14') | 107.7(7) |
| S(10)–In(1)–S(11') | 109.6(7) | S(12')–S(13)–S(14) | 104(1) |
| In(1)–S(1)–S(2) | 101.5(2) | S(13)–S(14)–S(13') | 105.6(7) |
| In(1)–S(4)–S(3) | 103.0(2) | | |

chain. Indium is chelated by an $S_4^{2-}$ and an $S_6^{2-}$ bidentate ligand and bound to an equatorially disposed terminal S atom of a "stretched" $S_7^{2-}$ chain. Thus, a more descriptive formula would be $[In_2(S_4)_2(S_6)_2(S_7)]^{4-}$. The coordination of indium is best described as trigonal bipyramid. Two axial sulfur atoms S(1) and S(5) and three equatorial atoms S(4), S(10), and S(11') compose the coordination sphere of indium. In view of the structures of $[In_2Se_{21}]^{4-}$ and $[In(S_4)(S_6)Br]^{2-}$ and that described here, it appears that five coordination in indium polychalcogenide chemistry is not only readily accessible but in many cases it may be preferred. The axial S(1)–In–S(5) angle is 176.1(2)°. The equatorial S–In–S angles average 119.9(2)°, and the In, S(4), S(10), and S(11') atoms do not deviate more than 0.011 Å from the corresponding least-squares plane. The equatorial In–S bonds are 0.94 Å shorter than the axial bonds as expected. The chelating $S_4^{2-}$ ligand which occupies an axial and an equatorial position adopts a half-chair conformation. Atoms S(2) and S(3) are 0.478 and 0.681 Å above and below the InS(1)S(4) plane, respectively. The bidentate $S_6^{2-}$ also occupies an axial and an equatorial position and has a similar conformation as found in $[In(S_4)(S_6)Br]^{2-}$. The occurrence of $S_6^{2-}$ ligands is uncommon. In the seven-membered $InS_6$ ring the S(5), S(7), S(8), and S(10) atoms lie on a least-squares plane and do not deviate more than 0.005 Å and the S(6) and S(9) atoms are symmetrically positioned 1.196 Å above and below the plane, respectively. The In atom is situated 0.434 Å above the plane. The same conformation has also been observed in the seven-membered $HgS_6$ ring of the $[Hg(S_6)_2]^{2-}$ complex.[25] The axial–equatorial chelation mode of the $S_6^{2-}$ ligand influences the S(5)–In–S(10) bond angle thus extending it more than 12° than that expected for trigonal-bipyramidal geometry. This is due to the large bite size of the $S_6^{2-}$ ligand and the relatively large size of the $InS_6$ ring.

$[In_2(S_4)_2(S_6)_2(S_7)]^{4-}$ has a crystallographically imposed center of symmetry situated halfway between the In- - -In vector. This induces a positional disorder of the central S(14) atom of the

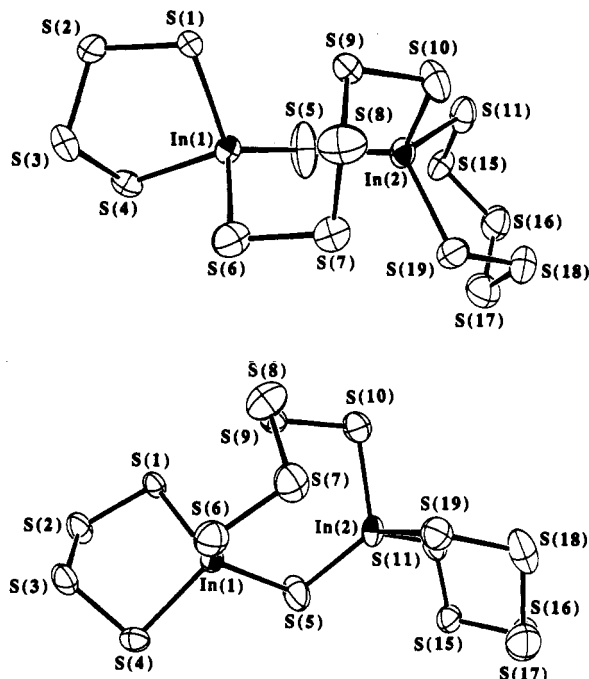(25) Müller, A.; Schimanski, J.; Schimanski, U. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 159–160.

**Figure 3.** Two views of the $[In_2S(S_5)(S_4)(S_6)]^{2-}$ anion in II with labeling scheme.

bridging $S_7^{2-}$ chain and results in two different conformations of the chain in the solid state with a half positional occupancy of the S(14) atom. The S(11) and S(12) atoms of the bridging $S_7^{2-}$ chain are disordered and positionally distributed over two sites of equal occupancy. Selected bond distances and angles are given in Tables V and VI. Due to the marginal quality of the data set and the extent of disorder the accuracy of the S- -S bond lengths in the $S_7^{2-}$ chain is low.

**Structure of $(Ph_4P)_2\{[In_2S_{14}]_{0.5}[In_2S_{16}]_{0.5}\}$ (II).** II is a cocrystallizate of the $[In_2S_{14}]^{2-}$ and $[In_2S_{16}]^{2-}$ anions with equal occupancies. The structures of these complexes are shown respectively in Figures 2 and 3. The two anions contain tetrahedral $In^{3+}$ coordination. The In atoms are bridged by an $S^{2-}$ and an $S_5^{2-}$ to form an eight-membered $[In_2S(S_5)]^{2+}$ ring core. This ring is similar in construction to the seven-membered heterocyclic ring found in $[(Cp)_2Hf]_2(O)(Se_4)^{26}$ (Cp = cyclopentadienyl). This heterocycle has an extreme cradle conformation with an approximate pseudo-$D_{2d}$ symmetry, and the conformation resembles that of $As_4S_4$ and $N_4S_4^{27}$ shown schematically as follows:
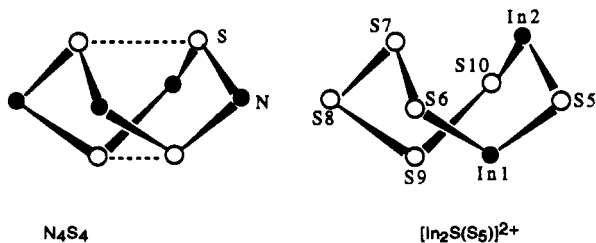


The S(5)S(6)S(8)S(10) atoms are situated on a least-squares plane and do not deviate more than 0.15 Å from it. The In(1) and S(9) atoms are positioned 1.257 and 1.176 Å below the plane, while In(2) and S(7) atoms are 1.147 and 1.146 Å above it, respectively. The bridging monosulfide S(5) atom has short In–S bond distances of 2.377 and 2.399 Å compared to the average In–S distance of 2.50(1) Å for those In–S bonds involving the polysulfide ligands. The average bond angle between the atoms in the eight-membered $[InSIn(S_5)]^{2+}$ ring is 108.3°. The

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**Table VII.** Selected Bond Distances (Å) in the Anions in $[Ph_4P]_2\{[In_2S_{14}]_{0.5}[In_2S_{16}]_{0.5}\}$ with Standard Deviations in Parentheses

| | | | |
|---|---|---|---|
| In(1)–S(1) | 2.505(3) | S(6)–S(7) | 2.024(5) |
| In(1)–S(4) | 2.513(3) | S(7)–S(8) | 2.011(6) |
| In(1)–S(5) | 2.377(4) | S(8)–S(9) | 2.025(5) |
| In(1)–S(6) | 2.500(4) | S(9)–S(10) | 2.034(5) |
| In(2)–S(5) | 2.399(4) | S(11)–S(12) | 2.23(1) |
| In(2)–S(10) | 2.481(4) | S(12)–S(13) | 2.01(2) |
| In(2)–S(11) | 2.490(4) | S(13)–S(14) | 2.11(2) |
| In(2)–S(14) | 2.480(10) | S(11)–S(15) | 1.94(1) |
| In(2)–S(19) | 2.513(9) | S(15)–S(16) | 2.00(1) |
| In–S(mean) | 2.47(5) | S(16)–S(17) | 2.05(1) |
| S(1)–S(2) | 2.064(4) | S(17)–S(18) | 2.08(2) |
| S(2)–S(3) | 2.009(5) | S(18)–S(19) | 2.01(1) |
| S(3)–S(4) | 2.081(5) | S–S(mean) | 2.04(6) |

**Table VIII.** Selected Bond Angles (deg) in the Anions in $[Ph_4P]_2\{[In_2S_{14}]_{0.5}[In_2S_{16}]_{0.5}\}$ with Standard Deviations in Parentheses

| | | | |
|---|---|---|---|
| S(1)–In(1)–S(4) | 98.0(1) | In(1)–S(6)–S(7) | 101.9(2) |
| S(1)–In(1)–S(5) | 121.2(2) | In(2)–S(10)–S(9) | 101.9(2) |
| S(1)–In(1)–S(6) | 107.4(1) | In(2)–S(11)–S(12) | 94.1(3) |
| S(4)–In(1)–S(5) | 111.2(1) | In(2)–S(11)–S(15) | 101.3(3) |
| S(4)–In(1)–S(6) | 95.3(1) | In(2)–S(14)–S(13) | 98.2(5) |
| S(5)–In(1)–S(6) | 118.6(2) | In(2)–S(19)–S(18) | 107.6(5) |
| S(5)–In(2)–S(10) | 118.9(1) | S(1)–S(2)–S(3) | 106.0(2) |
| S(5)–In(2)–S(11) | 107.3(1) | S(2)–S(3)–S(4) | 104.0(2) |
| S(5)–In(2)–S(14) | 107.6(3) | S(6)–S(7)–S(8) | 105.6(2) |
| S(5)–In(2)–S(19) | 123.0(2) | S(7)–S(8)–S(9) | 105.7(2) |
| S(10)–In(2)–S(11) | 101.5(1) | S(8)–S(9)–S(10) | 106.0(2) |
| S(10)–In(2)–S(14) | 118.4(3) | S(11)–S(12)–S(13) | 101.5(5) |
| S(10)–In(2)–S(19) | 96.8(2) | S(12)–S(13)–S(14) | 104.2(6) |
| S(11)–In(2)–S(14) | 100.6(2) | S(11)–S(15)–S(16) | 110.1(5) |
| S(11)–In(2)–S(19) | 106.9(2) | S(15)–S(16)–S(17) | 109.6(5) |
| In(1)–S(1)–S(2) | 99.4(1) | S(16)–S(17)–S(18) | 102.2(6) |
| In(1)–S(4)–S(3) | 93.0(1) | S(17)–S(18)–S(19) | 105.9(6) |
| In(1)–S(5)–In(2) | 108.0(2) | | |

remaining two coordination sites on In(1) atom are occupied by the $S_4^{2-}$ bidentate chelate. The five-membered $InS_4$ ring adopts an envelope conformation with S(3) lying 1.11 Å above the $InS(I)S(2)S(4)$ plane. The coordination sphere of the In(2) atom is completed by the $S_4^{2-}$ and the $S_6^{2-}$ bidentate ligands occupying the same crystallographic site. Another example of a polysulfide complex in which both $S_4^{2-}$ and $S_6^{2-}$ ligands are disordered about the same crystallographic site is found in $\{[Sn(S_6)(S_4)_2]_{0.6^-}[Sn(S_4)_3]_{0.4}\}^{2-}$.[11] The $S_4^{2-}$ ligand coordinated to In(2) adopts a half-chair conformation; atoms S(12) and S(13) are 0.388 and 0.876 Å above and below the $In(2)S(11)S(14)$ plane, respectively, as shown in Figure 2. In the seven-membered $InS_6$ ring, the S(11)S(16)S(17)S(19) atoms lie on a least-squares plane and do not deviate more than 0.06 Å; the S(18) and S(15) atoms are positioned 1.201 and 0.997 Å above and below the plane, respectively. The In atom is positioned 0.971 Å below the plane. Thus, the chelating $S_6^{2-}$ ligand is in a chair conformation as found previously in $[In(S_4)(S_6)Br]^{2-}$ and in I; however, in II the In atom exhibits a large deviation from the plane defined by S(11)S(16)S(17). Two different views of the seven-membered $InS_6$ ring of II are shown in Figure 3. Selected bond distances and angles are given in Tables VII and VIII.

**Comparison of the Structures.** I and II have no selenium analogs, but I resembles closely $(Ph_4P)_4[In_2(Se_4)_4(Se_5)]^{12}$ in both the coordination geometry and bonding mode of $In^{3+}$ centers. The $[In_2(Se_4)_4(Se_5)]^{4-}$ anion contains trigonal bipyramidal In atoms chelated by two bidentate $Se_4^{2-}$ ligands forming $[In(Se_4)_2]^-$ units which are bridged via the terminal atoms of a $Se_5^{2-}$ chain. The presence of longer chelating $S_x^{2-}$ ligands in I can be rationalized by the smaller size of S relative to Se thus requiring a longer chain to attain a similar bite size. This is also evident by observing the S–In–S angles for the chelating $S_4^{2-}$ bidentate in II, 98.0 and 100.6°, almost 10° smaller than expected leading to highly distorted tetrahedral geometry around the In atoms. The flexibility of the $S_6^{2-}$ ligand to tune its "bite" size is evident

by the fact that it has now been found to participate in a chelating fashion in tetrahedral, trigonal bipyramidal (on both the axial–equatorial and the equatorial–equatorial positions), and octahedral coordination.[11] In retrospect, the $[In(S_4)(S_6)X]^{2-}$ (X = Br, Cl) anions can be considered as chemical and structural intermediates to the dimeric $[In_2(S_4)_2(S_6)_2(S_7)]^{4-}$.

The dimeric structure of $[In_2(S_4)_2(S_6)_2(S_7)]^{4-}$ also resembles that of $[Bi_2(S_7)_4(S_6)]^{4-}$,[10] which is composed of two highly distorted square-pyramidal $[Bi(S_7)_2]^-$ units bridged by a $S_6^{2-}$ chain. On the basis of the structure of $[In_2(S_4)_2(S_6)_2(S_7)]^{4-}$ and the arguments presented above, it can be rationalized that the presence of a larger $S_7^{2-}$ chelate in $[Bi_2(S_7)_4(S_6)]^{4-}$ and an even larger $S_9^{2-}$ chelate in $[Au(S_9)]^-$[28] is consistent with the correspondingly larger sizes (than $In^{3+}$) of the $Bi^{3+}$ and $Au^+$ ions. The latter two cations demand a larger bite-size, which is better provided by the large $S_x^{2-}$ ligands. From the results reported here and our previous $In/S_x$ and $In/Se_x$ work, a previously less appreciated property of $In^{3+}$ has emerged as a dominant feature: its ability and perhaps tendency to expand its coordination sphere to five when surrounded by chalcogenide atoms. It should be noted that the great majority of known In/chalcogenides are extended solids and contain tetrahedral indium.

When studying $In/Q_x^{2-}$ chemistry, we may consider potential similarities with $Fe/Q_x^{2-}$ chemistry. Since $Fe^{3+}$ and $In^{3+}$ have similar ionic radii, one may wonder why the dimeric complex $[In_2S_2(S_5)_2]^{2-}$, isostructural to $[Fe_2S_2(S_5)_2]^{2-}$,[21] was not observed. The iron complex also has been crystallized with $Ph_4P^+$, and therefore, crystal packing effects cannot be responsible for not crystallizing $(Ph_4P)_2[In_2S_2(S_5)_2]$. Most likely, the stability of the $[Fe_2S_2]^{2+}$ core is electronically driven by the weak but significant $d^5$–$d^5$ attractive interactions in this core. The absence

of such interactions in the $d^{10}$ $In^{3+}$ analog could destabilize a $[In_2S_2]^{2+}$ core via $In^{3+}$- -$In^{3+}$ repulsions. This repulsive force is somewhat dissipated in $[In_2Se_2(Se_4)_2]^{2-}$ [15] due to the larger size of the $[In_2Se_2]^{2+}$ ring. Even if $[In_2S_2(S_5)_2]^{2-}$ were stabilized in a crystalline lattice, it might be metastable in polar solutions.

## Conclusion

In summary, the reactions of pentasulfide anion, $S_5^{2-}$, with $In^{3+}$ in the presence of tetraphenylphosphonium cation in DMF, in varying molar ratios, affords several new homoleptic $In^{3+}$ polysulfide anions: $[In_2S_{27}]^{4-}$, $[In_2S_{14}]^{2-}$, and $[In_2S_{16}]^{2-}$. The latter two anions are found cocrystallized and contain unique structural features such as the unusual $[In_2S(S_5)]^{2+}$ ring core. The $In/S_x$ system exhibits certain similarities with the $In/Se_x$ system in regard to stabilizing five-coordinate $In^{3+}$ centers. I and II have no selenium analogs, reaffirming the fact that often the $Q_x^{2-}$ species (Q = S, Se, Te) have their own distinctly different coordination chemistry. Similar investigations with other quaternary ammonium and phosphonium cations in different stoichiometries could uncover additional new structural $In/S_x$ chemistry.

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