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Synthesis and Characterization of Indium Compounds with Phosphinothiol Ligands. The Crystal and Molecular Structures of $[In\{2-(Ph_2P)C_6H_4S\}_3]$, $[In\{2-(Ph_2P)-6-(Me_3Si)C_6H_3S\}_2\{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S\}]$, and $[NMe_4][In\{PhP(C_6H_4S-2)_2\}_2]\cdot CH_3CN$

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The electrochemical oxidation of anodic indium metal in an acetonitrile solution of phosphinothiol ligands affords $[In\{2-(Ph_2P)C_6H_4S\}_3]$ (**1**), $[In\{2-(Ph_2P)-6-(Me_3Si)C_6H_3S)\}_2\{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S\}]$ (**2**), $[In\{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S\}_3]$ (**3**), and $[NMe_4][In\{PhP(C_6H_4S-2)_2\}_2]\cdot CH_3CN$ (**4**) complexes exhibiting distorted six-coordinate geometries based on $\{InS_3P_3\}$, $\{InS_3P_2O\}$, and $\{InS_4P_2\}$ cores, respectively. In all cases, the In−P bond distances are anomalously long, presumably as a consequence of steric crowding. The anion of **4** provides an unusual example of an In(III)−thiolate coordination complex ion. Crystal data: **1**, $C_{54}H_{42}InP_3S_3$, monoclinic, $P2_1/c$, $a = 16.6579(1)$ Å, $b = 12.6628(2)$ Å, $c = 22.5520(3)$ Å, $\beta = 96.42(1)°$, $V = 4727.15(1)$ Å^3, $Z = 4$, 6176 reflections, $R = 0.0579$; **2**, $C_{63}H_{66}InOP_3S_3Si_3$, monoclinic, $P2_1/c$, $a = 11.53090(10)$ Å, $b = 26.2505(3)$ Å, $c = 20.4206(2)$ Å, $\beta = 94.0870(10)°$, $V = 6165.43(11)$ Å^3, $Z = 4$, 10 699 reflections, $R = 0.0621$; **4**, $C_{42}H_{41}InN_2P_2S_4$, monoclinic, $P2(1)$, $a = 13.0052(2)$ Å, $b = 11.2240(2)$ Å, $c = 14.3070(3)$ Å, $\beta = 93.190(1)°$, $V = 2085.16(7)$ Å^3, $Z = 2$, 6651 reflections, $R = 0.0352$.

Introduction

The coordination chemistry of indium thiolates remains relatively unexplored with only a handful of compounds exhibiting In−S bonds having been structurally characterized.[1,2] Since the pronounced tendency of sulfur to bridge metal centers often produces insoluble polymers, one strategy for the synthesis of low molecular weight compounds exploits bulky substituents on the ligand to prevent the association process. This approach has proved successful in the preparation and structural characterization of dinuclear indium thiolates of the class $[Mes_2In(\mu\text{-}SR)]_2$ ($R = Bu^t$, $2\text{-}Bu^tC_6H_4$, or $SiPh_3$),[3] which show potential as precursors for the deposition of indium chalcogenides under MOCVD conditions. Monomeric three-coordinated indium thiolate complexes have also been obtained by Power using very bulky ligands such as $HS(2,4,6\text{-}Bu^t{}_3C_6H_2)$.[4] An alternative route to molecular species involves the saturation of the metal coordination sphere with other donor atoms in addition to the thiolate groups; in the specific case of multidentate mixed-donor ligands, complex stability is enhanced by the chelate effect. This technique has been exploited to prepare monomeric and binuclear indium compounds with pyridine-2-thione and its derivatives with lipophilic characteristics as potential sources of ^{111}In or ^{113}In γ emitters in medical imaging.[5] As a continuation of this work, we report the synthesis of indium phosphinoarenethiolate complexes, with ligands incorporating both thiolate sulfur and tertiary phosphorus atoms as donor sites. The synthesis involves an electrochemical procedure with the metal acting as the anode of a cell containing the ligand in an acetonitrile solution. This method has previously been employed in the preparation of homoleptic indium thiolate complexes[6] and more generally for complexes with ligands containing weakly acidic groups such as heterocyclic thiones and their derivatives.[7−11]

While coordination compounds of phosphinoarenethiol ligands have been reported previously by Dilworth and Zubieta, mainly with heavier transition metals, such as molybdenum,[12] techne-

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tium and rhenium,[13] ruthenium,[14] and rhodium and iridium,[15] materials with main group metals remain relatively unexplored, and indium compounds of such ligand types have not been reported to date.

Experimental Section

General Considerations. All manipulations were carried out under an inert atmosphere of dry nitrogen. Indium (Aldrich Chemie) was used as plates (ca. 2 × 2 cm). Syntheses of ligands were carried out using minor modifications of the standard literature procedures involving lithiation of benzenethiol,[16] using Schlenk techniques and dry solvents. Elemental analysis were performed in a Carlo-Erba EA 1108 microanalyzer. IR spectra were recorded in KBr disks using a Bruker IFS 66v spectrophotometer. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker AMX 300 MHz instrument using Cl_3CD as solvent, except for **4**, which was recorded in DMSO-d_6. ^{1}H NMR chemical shifts were determined against TMS as the internal standard. ^{31}P NMR chemical shifts were determined against 85% H_3PO_4. The FAB mass spectra were recorded on a Kratos MS-50TC spectrophotometer, using 3-nitrobenzyl alcohol (3-NOBA) as a matrix material.

Electrochemical Synthesis. The electrochemical procedure used in the synthesis of the complexes was similar to that described by Tuck.[17] The cell consisted of a metal anode suspended from a platinum wire in a solution of the corresponding thiol ligand (and ca. 20 mg of tetramethylammonium perchlorate as supporting electrolyte) in acetonitrile with a platinum cathode. The cells can be summarized as $Pt_{(-)}$/CH_3CN + RP-SH/$In_{(+)}$.

[In{2-(Ph$_2$P)C$_6$H$_4$S}$_3$] (1). Electrochemical oxidation of an indium anode in a solution of 2-(diphenylphosphinyl)benzenethiol, 2-(Ph$_2$P)-C$_6$H$_4$SH (0.330 g, 1.12 mmol), in acetonitrile (50 cm^3), at 8 V and 5 mA for 2 h caused 43 mg of indium to be dissolved, $E_f = 1.0$ mol F^{-1}. During the electrolysis hydrogen was evolved at the cathode, and after 1 h, white crystalline needles appeared on the electrodes and at the bottom of the vessel. The solid was filtered off, washed with acetonitrile and ether, and dried under vacuum (313 mg, 0.315 mmol, 84%). Anal. Calcd for $C_{54}H_{42}InP_3S_3$: C, 65.13; H, 4.22; S, 9.65. Found: C, 65.35; H, 4.33; S, 9.61. IR (KBr, cm^{-1}): 1573 (m), 1480 (m), 1438 (s), 1417 (m), 1121 (m), 1095 (m), 742 (s), 645 (s). ^{1}H NMR (CD$_3$Cl, ppm): δ 7.8−6.7 (m, 42 H). ^{31}P NMR (CD$_3$Cl, ppm): δ 40.1, 39.5, and 39.2.

[In{2-(Ph$_2$P)-6-(Me$_3$Si)C$_6$H$_3$S}$_2${2-(Ph$_2$PO)-6-(Me$_3$Si)C$_6$H$_3$S}] (2). A solution of acetonitrile (50 cm^3) containing 2-diphenylphosphino-6-trimethylsilylbenzenethiol (0.270 g, 0.75 mmol) was electrolyzed at 5 mA for 2 h, during which time 42 mg of indium metal was dissolved from the anode, $E_f = 0.98$ mol F^{-1}. The resulting microcrystalline product was washed with acetonitrile and ethyl ether and dried (285 mg, 0.232 mmol, 63%). Colorless crystals suitable for X-ray studies were obtained by recrystallization from methanol/chloroform and identified by elemental analysis. Anal. Calcd for $C_{63}H_{66}InOP_3S_3Si_3$: C, 61.17; H, 5.38; S, 7.83. Found: C, 61.22; H, 5.39; S, 7.42. IR (KBr, cm^{-1}): 1554 (m), 1481 (m), 1435 (m), 1353 (s), 1244 (m), 1128 (s), 1095 (w), 1039 (w), 850 (s), 741 (s), 692 (s). ^{1}H NMR (CD$_3$Cl, ppm): δ 7.8−6.4 (m, 39H), 0.10 (s, 9H), 0.30 (s, 9H), 0.40 (s, 9H). ^{31}P NMR (CD$_3$Cl, ppm): δ 40.9 and 43.7.

[In{2-(Ph$_2$PO)-6-(Me$_3$Si)C$_6$H$_3$S}$_3$] (3). In a procedure similar to that employed in the isolation of **2** (6 V, 5 mA, 2.0 h), 44 mg of indium dissolved in the presence of the ligand 2-(Ph$_2$PO)-6-(Me$_3$Si)C$_6$H$_3$SH (0.290 g, 0.56 mmol) in 50 cm^3 of acetonitrile, $E_f = 1.02$ mol F^{-1}. A white crystalline precipitate formed during the electrolysis at the anode, and hydrogen was evolved at the cathode. The solid was collected, washed with cool acetonitrile and diethyl ether, and dried under vacuum (260 mg, 0.207 mmol, 78%). Anal. Calcd for $C_{63}H_{66}InP_3S_3Si_3$: C, 60.10; H, 5.25; S, 7.63. Found: C, 60.28; H, 5.10; S, 7.20. IR (KBr, cm^{-1}): 1554 (m), 1484 (w), 1437 (m), 1355 (s), 1244 (m), 1132 (s), 1072 (m), 853 (s), 749 (m), 693 (m), 557 (s). ^{1}H NMR (CD$_3$Cl, ppm): δ 7.8−6.8 (m, 39 H), 0.10 (s, 9H), 0.20 (s, 9H), 0.40 (s, 9H). ^{31}P NMR (CD$_3$Cl, ppm): δ 49.8, 50.0, and 50.7.

Table 1. Summary of Crystallographic Data for the Compounds [In{2-(Ph$_2$P)C$_6$H$_4$S}$_3$] (**1**), [In{2-(Ph$_2$P)-6-(Me$_3$Si)C$_6$H$_3$S}$_2${2-(Ph$_2$PO)-6-(Me$_3$Si)C$_6$H$_3$S}] (**2**), and [NMe$_4$][In{PhP(C$_6$H$_4$S-2)$_2$}$_2$]·CH$_3$CN (**4**)

	1	**2**	**4**
empirical formula	$C_{54}H_{42}InP_3S_3$	$C_{63}H_{66}InOP_3S_3Si_3$	$C_{42}H_{41}InN_2P_2S_4$
fw	994.79	1227.34	878.77
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1$
unit cell dimens			
a, Å	16.6579(1)	11.53090(10)	13.0052(2)
b, Å	12.6628(2)	26.2505(3)	11.2240(2)
c, Å	22.5520(3)	20.4206(2)	14.3070(3)
β, deg	96.42(1)	94.087(10)	93.19(1)
vol, Å^3	4727.15(1)	6165.43(11)	2085.16(7)
Z	4	4	2
d_{calc}, g cm^{-3}	1.398	1.322	1.400
λ, Å (Mo Kα radiation)	0.71073	0.71073	0.71073
μ(Mo Kα), cm^{-1}	7.70	6.61	8.75
T, °C	25	−123	25
no. of reflns collected	19116	31098	10546
no. of indep reflns	6176	10699	6651
F(000)	2032	2544	900
R^a	0.0579	0.0621	0.0352
$R_w{}^b$	0.1392	0.1683	0.0869

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

[NMe$_4$][In{PhP(C$_6$H$_4$S-2)$_2$}$_2$]·CH$_3$CN (4). The electrochemical oxidation of indium in a solution of PPh(C$_6$H$_4$SH-2)$_2$ (0.17 g, 0.52 mmol) in acetonitrile (60 mL) containing tetramethylammonium perchlorate (20 mg) as supporting electrolyte for 2 h at 4 V and 5 mA resulted in the loss of 42 mg of indium from the anode, $E_f = 0.98$ mol F^{-1}. A white solid of an uncharacterized compound precipitated in the cell. Concentration of the solution yielded crystals of **4** suitable for X-ray diffraction as a minor product. Anal. Calcd for $C_{42}H_{41}N_2P_2S_4In$: C, 61.36; H, 5.11; N, 3.49; S, 7.98. Found: C, 60.85; H, 5.05; N, 3.32; S, 8.11. IR (KBr, cm^{-1}): 1574 (s), 1481 (s), 1436 (s), 1246 (m), 1127 (m), 1096 (s), 999 (m), 741 (s), 695 (m). ^{1}H NMR (DMSO-d_6, ppm): δ 7.6−6.8 (m, 26H), 3.1 (s, 12H). ^{31}P NMR (DMSO-d_6, ppm): δ 42.7.

X-ray Crystallography. Compounds **1** and **4** were studied on a Rigaku AFC6S equipped with a conventional scintillation counter, and compound **2** was studied on a Siemens Smart system with a CCD detector. Data collection of **2** was carried out at low temperature while that of **1** and **4** was carried out under ambient conditions, using graphite-monocromated Mo Kα radiation. The crystal parameters and other experimental details of the data collection are summarized in Table 1. A complete description of the details of the crystallographic methods is given in the Supporting Information. The structures were solved by direct methods.[18] Neutral atom scattering factors were taken from Cromer and Waber[19] and anomalous dispersion factors were taken from Cromer[20] for **1** and **4** and Creagh and McAuley for **2**.[21] All calculations were performed using the Texsan crystallographic sofware package[22] for **1** and **4** and the SHELXTL crystallographic sofware package[23] for

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

In−S(1)	2.518(2)	In−S(2)	2.550(2)
In−S(3)	2.557(2)	In−P(1)	2.963(2)
In−P(3)	2.728(2)	In−P(2)	2.812(2)
S(1)−C(11)	1.777(6)	P(1)−C(26)	1.812(8)
S(2)−C(41)	1.781(7)	P(1)−C(36)	1.821(7)
S(3)−C(71)	1.775(6)	P(1)−C(16)	1.804(7)
P(2)−C(46)	1.815(6)	P(2)−C(56)	1.820(7)
P(2)−C(66)	1.822(6)	P(3)−C(86)	1.817(6)
P(3)−C(76)	1.818(6)	P(3)−C(96)	1.825(6)
S(1)−In−S(2)	161.91(6)	S(1)−In−S(3)	95.50(5)
S(2)−In−S(3)	96.85(6)	S(1)−In−P(3)	106.15(6)
S(2)−In−P(3)	90.02(5)	S(3)−In−P(3)	73.60(5)
S(1)−In−P(2)	92.52(6)	S(2)−In−P(2)	72.26(5)
S(3)−In−P(2)	100.53(5)	P(3)−In−P(2)	160.77(5)
S(1)−In−P(1)	71.31(5)	S(2)−In−P(1)	100.22(6)
S(3)−In−P(1)	158.60(5)	P(3)−In−P(1)	93.50(5)
P(2)−In−P(1)	96.90(5)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

In(1)−O(1)	2.198(5)	In(1)−S(3)	2.531(2)
In(1)−S(2)	2.538(2)	In(1)−S(1)	2.556(2)
In(1)−P(3)	2.827(2)	In(1)−P(2)	2.840(2)
S(1)−C(14)	1.759(6)	S(2)−C(34)	1.766(6)
S(3)−C(60)	1.774(6)	P(1)−O(1)	1.468(5)
P(1)−C(13)	1.807(6)	P(1)−C(1)	1.809(6)
P(1)−C(7)	1.811(7)	P(2)−C(35	1.822(6)
P(2)−C(28)	1.829(6)	P(2)−C(22)	1.830(6)
P(3)−C(43)	1.827(6)	P(3)−C(55)	1.828(7)
P(3)−C(49)	1.828(7)	Si(1)−C(20)	1.861(7)
O(1)−In(1)−S(3)	99.72(13)	O(1)−In(1)−S(2)	93.47(13)
S(3)−In(1)−S(2)	163.03(6)	O(1)−In(1)−S(1)	86.71(13)
S(3)−In(1)−S(1)	100.19(5)	S(2)−In(1)−S(1)	91.13(5)
O(1)−In(1)−P(3)	76.03(13)	S(3)−ln(1)−P(3)	74.22(5)
S(2)−ln(1)−P(3)	98.94(5)	S(1)−ln(1)−P(3)	160.43(5)
O(1)−In(1)−P(2)	165.73(14)	S(3)−ln(1)−P(2)	93.26(5)
S(2)−ln(1)−P(2)	72.70(5)	S(1)−In(1)−P(2)	96.85(5)
P(3)−In(l)−P(2)	102.14(5)	C(14)−S(l)−In(1)	110.4(2)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **4**

In−S(2)	2.5578(11)	In−S(1)	2.5925(13)
In−S(4)	2.5949(9)	In−S(3)	2.6428(12)
In−P(2)	2.6779(11)	In−P(1)	2.7006(10)
P(1)−C(16)	1.818(5)	P(1)−C(26)	1.820(5)
P(1)−C(6)	1.837(4)	P(2)−C(56)	1.813(4)
P(2)−C(46)	1.823(5)	P(2)−C(36)	1.832(5)
S(1)−C(11)	1.761(5)	S(2)−C(21)	1.776(6)
S(3)−C(41)	1.776(4)	S(4)−C(51)	1.774(5)
S(2)−In−S(1)	99.01(4)	S(2)−In−S(4)	90.63(4)
S(1)−In−S(4)	99.02(5)	S(2)−In−S(3)	100.76(4)
S(1)−In−S(3)	151.22(5)	S(4)−In−S(3)	101.47(4)
S(2)−In−P(2)	163.96(4)	S(1)−In−P(2)	89.69(4)
S(4)−In−P(2)	74.63(3)	S(3)−In−P(2)	76.61(4)
S(2)−In−P(1)	75.61(4)	S(1)−In−P(1)	78.53(4)

2. No anomalies were encountered in the refinements of any of the structures. Atomic position parameters and isotropic temperature factors for the structures are presented in the Supporting Information. Selected bond lengths and angles for **1**, **2**, and **4** are listed in Tables 2−4, respectively.

Results and Discussion

The indium(III) phosphinothiolato complexes **1**−**3** are readily prepared in good yield by oxidation of an indium anode in a cell containing a solution of the ligand and tetramethylammonium perchlorate as supporting electrolyte, while compound **4** could be obtained only as a minor product. The air-stable compounds obtained in this fashion are crystalline solids soluble in chloroform (except **4**) and in other common organic solvents.

The electrochemical efficiency for the process, E_f, defined as the number of moles of metal dissolved per faraday of charge, was in all cases close to 1 mol F^{-1}. These values demonstrate that the anodic oxidation of the metal leads initially to In(I) species, which are further oxidized to In(III) in solution. This observation and the evolution of the hydrogen at the cathode are compatible with the following mechanism:

$$\text{cathode:}\quad \text{RP-SH} + e^- \rightarrow \text{RP-S}^- + {}^1\!/_2\text{H}_2$$

$$\text{anode:}\quad \text{In} + \text{RP-S}^- \rightarrow [\text{In(S-PR)}] + e^-$$

$$[\text{In(S-PR)}] + 2[\text{RP-SH}] \rightarrow [\text{In(S-PR)}_3] + \text{H}_2$$

where RP-SH stands for the neutral ligand. This behavior has previously been observed in other indium systems in which low-oxidation-state species are the initial electrochemical products.[6,24]

The IR spectrum of **1** shows the absence of a band which appears at 2943 cm^{-1} in the free ligand and is attributed to ν(S−H). This observation indicates that the ligand is in the anionic thiolate form in the complex. The spectrum also shows bands in the aromatic region characteristic of the coordinated phosphinothiol ligand. The room temperature ^{1}H NMR of **1** exhibits peaks in the aromatic region, and also the disappearance of the signal attributable to SH hydrogen which appears at δ 4.1 ppm in the free ligand as a doublet as a result of the coupling with the phosphorus atom. The ^{31}P spectra of the complex shows three separate signals at δ 40.1, 39.5, and 39.2 ppm, an observation which is consistent with the compound in solution adopting a *mer* disposition of the ligands in the octahedral environment around the metal. This is also the structure observed for the compound in the solid state (vide infra). The FAB mass spectrum of this compound does not show the molecular ion, and the highest *m*/*e* peak corresponds to $[\text{In}\{2\text{-}(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{S}\}_2]^+$ (*m*/*z* 701, 40%). The spectrum also shows the peaks associated with $[\text{In}\{2\text{-}(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{S}\}]^{2+}$ and $[2\text{-}(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{S}]^-$ at *m*/*z* 407 (9%) and *m*/*z* 293 (100%), respectively. The peak clusters display the appropriate isotope distributions.

To evaluate possible steric effects upon the indium−phosphinothiolate coordination geometry, anodic indium was oxidized in a solution of the sterically enhanced ligand 2-(diphenylphosphinyl)-6-(trimethylsilyl)benzenethiol in acetonitrile. The solid obtained was identified as $[\text{In}\{2\text{-}(\text{Ph}_2\text{P})\text{-}6\text{-}(\text{Me}_3\text{Si})\text{C}_6\text{H}_3\text{S}\}_2\text{-}\{2\text{-}(\text{PhPO})\text{-}6\text{-}(\text{Me}_3\text{Si})\text{C}_6\text{H}_3\text{S}\}]$ (**2**). X-ray studies confirmed the presence of both the bidentate phosphinothiolate and oxophosphinothiolate forms of the ligands (vide infra). The oxygen atom incorporated into the oxophosphinothiolate moiety most likely originates from oxygen dissolved in the solvent. Such facile oxidation of phosphine to phosphine oxides has been observed for similar complexes.[12] The IR spectrum of **2** is similar to that of **1** with an additional medium-intensity band at 1128 cm^{-1}, attributed to ν(P−O), and an intense band at 850 cm^{-1} characteristic of the Si−C group. The room temperature ^{1}H NMR of the complex shows signals from aromatic protons in the range δ 7.8−6.4 ppm and three separate signals at δ 0.1, 0.3, and 0.4 ppm assigned to the three nonequivalent trimethylsilyl groups. The ^{31}P NMR spectrum shows two signals for the phosphorus atoms at δ 40.9 and 43.7 ppm. Of the several

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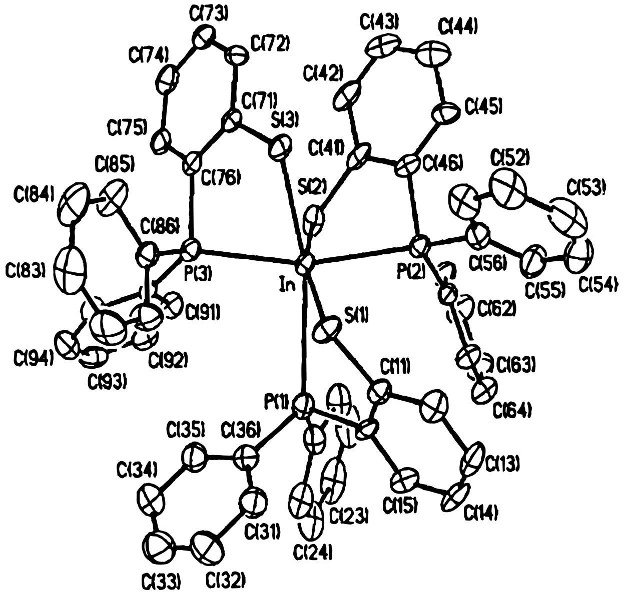

Figure 1. View of the structure of [In{2-(Ph_2P)C_6H_4S}$_3$] (**1**), showing the atom-labeling scheme and 50% thermal ellipsoids.

possible structures for the compound, the only one compatible with these data contains the indium atom coordinated to three sulfur atoms disposed in a meridional disposition and two phosphorus atoms trans to each other, a structure at variance with the solid state structure of this compound (vide infra). The FAB mass spectrum of this compound shows a peak at *m*/*z* 845 due to the [In{2-(Ph_2P)-6-(Me_3Si)C_6H_4S}$_2$]$^+$ ion (10%), formed by loss of the oxophosphinothiolate ligand, and also peaks associated with [In{2-(Ph_2P)-6-(Me_3Si)C_6H_4S}]$^{2+}$ at *m*/*z* 480 (4%) and [2-(Ph_2P)-6-(Me_3Si)C_6H_4S]$^-$ at *m*/*z* 365 (24%).

Compound **3** was obtained by oxidation of indium metal in a cell containing 2-(diphenylphosphinyl)-6-(trimethylsilyl)-benzenethiol. Attempts to obtain crystals suitable for X-ray studies were unsuccessful. Analytical data confirms the presence of an In(III) compound with three monoanionic ligands. The IR spectrum shows the characteristic bands of the coordinated ligand. Three signals for the trimethylsilyl groups at δ 0.1, 0.2, and 0.4 ppm in the ^{1}H NMR spectrum and three signals at δ 49.8, 50.0, and 50.7 ppm in the ^{31}P NMR again confirm a meridional disposition of the ligands in the octahedral arrangement around the metal in the solution phase. The FAB mass spectrum of this compound shows a peak at *m*/*z* 879 (53%), attributed to the [In{2-(PhPO)-6-(Me_3Si)C_6H_4S}$_2$]$^+$ ion, and also peaks associated with [In{2-(Ph_2PO)-6-(Me_3Si)C_6H_4S}]$^{2+}$ at *m*/*z* 496 (21%) and [2-(Ph_2PO)-6-(Me_3Si)C_6H_4S]$^-$ at *m*/*z* 381 (4%).

Compound **4** was obtained as a minor product in the oxidation of an indium anode in the presence of PhP(C_6H_4SH-2)$_2$. As the electrolysis proceeded, an amorphous and uncharacterizable solid precipitated in the cell. Concentration of the resulting solution resulted in the formation of a small amount of crystals containing the anionic species [In{PhP(C_6H_4SH-2)$_2$}$_2$]$^-$ and the cation tetramethylammonium. The absence of bands in the IR spectrum attributable to ν(SH) and the lack of signals for these hydrogen atoms in the ^{1}H NMR spectra in DMSO-d_6 confirm that the four thiol groups are deprotonated in the complex. The ^{1}H NMR shows the presence of the methyl groups from the tetramethylammonium cation at δ 3.1 ppm. The ^{31}P NMR shows one signal at δ 42.73 ppm, such that the phosphorus atoms are equivalent, an observation consistent with the structure of the compound in the solid state (vide infra).

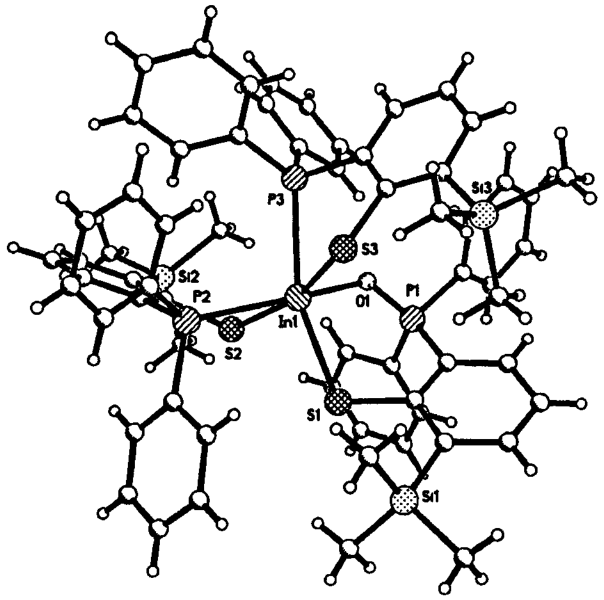

Figure 2. View of the structure of [In{2-(Ph_2P)-6-(Me_3Si)C_6H_3S}$_2${2-(Ph_2PO)-6-(Me_3Si)C_6H_3S}] (**2**), showing the atom-labeling scheme and 50% thermal ellipsoids.

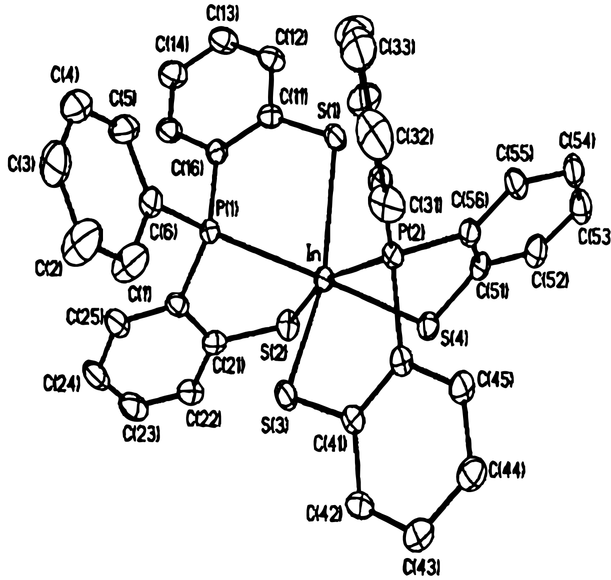

Figure 3. View of the structure of the anion [In{PhP(C_6H_4S-2)$_2$}$_2$]$^-$ of **4**, showing the atom-labeling scheme and 50% thermal ellipsoids.

Description of the Structures. The molecular structure of [In{2-(Ph_2P)C_6H_4S}$_3$] (**1**) is shown in Figure 1, together with the atomic numbering scheme adopted. Selected bond distances and angles are found in Table 2. In the case of compound **1**, the indium atom is coordinated to the phosphorus and sulfur donor atoms of three monoanionic chelating ligands. The environment around the indium can be described as possessing a distorted octahedral P_3S_3 core with an average value of 73.39(5)° for the chelate bite angles of the ligands. The angles defined by two trans atoms at the indium atom deviate considerably from the idealized value of 180° (161.91(6)°, 160.77(5)°, and 158.60(5)°). The arrangement of the sulfur and phosphorus atoms is such that the complex can be described as the *meridional* isomer, a disposition which is maintained in solution. This donor group arrangement has also been observed in other trischelate metal complexes involving this ligand, namely, [Re{2-(Ph_2P)C_6H_4S}$_3$], [Tc{2-(Ph_2P)C_6H_4S}$_3$],[13] Ir{2-(Ph_2P)-

Table 5. Selected Structural Parameters for In(III)−Thiolate Complexes

compound	coord no.	In−S, Å	In−X (X), Å	S−C, Å	M−S−C, deg	ref
$[In(SC_5H_2\text{-}2,4,6\text{-}Bu^t{}_3)_3]$	3	2.398(4)		1.81(1)	98.1(3)	4
$[Mes_2In(SBu^t)]_2$[a]	4	2.619(5)	2.107(8) (C)	*c*	*c*	3
$[Mes_2In(S\text{-amyl})]_2$	4	2.592(4)	2.22(1) (C)	*c*	*c*	3
$[Mes_2In(SSiPh_3)]_2$	4	2.621(1)	2.176(4) (C)	*c*	*c*	3
$[Mes_2In(SSiPh_3)]_3$	4	2.617(6)	2.12(1) (C)	*c*	*c*	3
$[In(SC_6H_2\text{-}2,4,6\text{-}(CF_3)_3)_3(OEt_2)]$	4	2.418	2.244(6) (O)	1.786(8)	104.1(3)	29
$[Ph_4P][BrIn(SPh)_3]$	4	2.450(4)	2.527(1) (Br)	1.75(3)	107.7(7)	2
$[In(SPh)_3(NC_5H_5)_2]$	5	2.458(5)	2.39(1) (N)	1.77(1)	104.9(7)	30
$[In\{(SCH_2CH_2)_3N\}]$	5	2.443(4) × 3 2.649(3) × 1	2.39(1) (N)	1.84(1)	95.7(2)	31
[In(TS-TACN)][b]	6	2.511(2)	2.397(4) (N)	*c*	*c*	32
$[In(SC_4H_4N)_3]$	6	2.531(2)	2.318(6) (N)	1.746(8)	81.5(3)	5
$[In(SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$	6	2.539(3)	2.31(1) (N)	1.76(1)	82.5(4)	5
$[In_2(OC_2H_5)_2(SC_5H_4N)_4]$	6	2.549(1)	2.296(4) (N)	1.733(4)	80.9(2)	5
$[In(PS)_3]$ (**1**)	6	2.542(3)	2.770(2) × 2 (P) 2.963(2) (P)	1.774(8)	98.5(3)	*d*
$[In(PS)_2(OPS)]$ (**2**)	6	2.542(3)	2.834(3) (P) 2.198 (O)	1.767(8)	107.2(3)	*d*
$[NMe_4][In(SPS)_2]$ (**4**)	6	2.582(1) × 3 2.643(1)	2.689(1) (P)	1.772(8)	104.5(4)	*d*

[a] Mes = 2,4,6-trimethylphenyl. [b] TS-TACN = 1,4,7-tris(2-mercaptoethyl)-1,4,7-triazacyclononane. [c] Not reported. [d] This work.

$C_6H_4S\}_3]$,[15] and $[Co\{2\text{-}(Ph_2P)C_6H_4S\}_3]$.[25] The three In−S bond distances are similar and fall in the range 2.518(2)−2.557(2) Å, with an average value of 2.541(2) Å. These values are similar to those found in indium complexes with heterocyclic thiones, e.g., $[In(pyt)_3]$, 2.531(3) Å, $[In(3\text{-}Me_3Sipyt)_3]$, 2.539(3) Å,[5a] and $[In(pymt)_3]$, 2.522(1) Å[26] (pyt = pyridine-2-thionato, pymt = pyrimidine-2-thionato). Curiously, the In−P(1) bond distance, 2.963(2) Å, is significantly longer than the other two In−P distances, 2.812(2) and 2.728(2) Å for In−P(2) and In−P(3), respectively. In the absence of additional structural data for In−P bond distances in octahedral indium complexes for comparison with **1**, it is tempting to conclude that steric crowding is responsible for the difference in these In−P bond lengths. The significantly shorter In−P distance of 2.603(7) Å reported for the four-coordinate $InI_3(PPh_3)$[27] would seem to support this analysis. The fact that the highest molecular peak in the mass spectrum corresponds to the $[In\{2\text{-}(Ph_2P)C_6H_4S\}_2]^+$ ion could be indicative of the weakness of the In−P(1) bond.

The structure of $[In\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}]$ (**2**), Figure 2, consists of discrete molecules with the indium atom in a distorted octahedral $[InOP_2S_3]$ environment, coordinated by two anionic bidentate 2-(diphenylphosphinyl)-6-(trimethylsilyl)benzenethiolate ligands bonding through their sulfur and phosphorus atoms and one bidentate anionic 2-(diphenylphosphinyl)-6-(trimethylsilyl)benzenethiolate ligand which coordinates through the oxygen and sulfur atoms. The phosphorus atoms exhibit a cis arrangement. The In−S distances 2.556(2), 2.538(2), and 2.531(2) Å and the In−P distances, 2.840(2) and 2.827(2) Å, Table 3, are similar to the corresponding distances found in **1**. The data reveal that the introduction of a trialkylsilyl group in the ligand has a negligible influence on the structural parameters of the compound. The In−O bond distance 2.198(5) Å is similar to that found in $[In(PT)_3]$ (PT = 1-oxopyridine-2-thionate anion), 2.203(5) Å average value, an In(III) compound with an octahedral $[InO_3S_3]$ core.[28]

The structural analysis of **4** reveals that the compound contains the anionic species $[In\{PhP(C_6H_4S)_2\}_2]^-$ and the cation $[NMe_4]^+$ incorporated from the background electrolyte. As shown in Figure 3, the complex anion consists of a distorted octahedral $[InP_2S_4]$ environment resulting from the coordination of an indium atom to two tridentate bis(2-mercaptophenyl)phenylphosphine ligands. The two sulfur donors and the phosphorus atom of each ligand adopt a *facial* arrangement, such that the phosphorus atoms are in the cis orientation. The In−S bond distances, Table 4, fall in the range 2.558(1)−2.643(1) Å, with an average value of 2.597(2) Å. The In−P bond distances 2.678(1) and 2.701(1) Å fall in the low range of values previously observed for compounds **1** and **3**.

The data summarized in Table 5 illustrate the remarkable structural versatility exhibited by In(III)−thiolate complexes, which display coordination numbers from three to six and often highly distorted geometries. Both the presence of sterically demanding groups and of auxiliary donor groups evidently influence the geometry adopted by this class of compounds. Not unexpectedly, bridging thiolate groups exhibit lengthened In−S distances which fall in the range 2.59−2.65 Å. Excluding such bridging types, there exists an apparent correlation of In−S bond distance with coordination number. Thus, as the coordination number increases from three to six, the average In−S bond distance increases monotonically with values of 2.398(3), 2.434(7), 2.493(4), and 2.542 Å observed for three, four, five, and six coordination, respectively.

While the compounds of this study in general exhibit unexceptional In−S distances for six coordination, the In−P distances are significantly longer than anticipated from the sums of the covalent radii of In(III) and phosphorus. The In−P distances would be expected to be on the order of 0.08−0.12 Å longer than the In−S distances in the corresponding complex, in the absence of other contributing factors. With the exception of **4**, which exhibits In−S distances of 2.582 and 2.643 Å and In−P distances of 2.689 Å, the other compounds of this study possess exceptionally elongated In−P bond distances. In fact,

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the 2.963(2) Å In−P bond length of **2** represents approximately 0.1−0.2 of a bond according to valence sum calculations, suggesting a negligible interaction between the metal and this donor group. The highly distorted geometries associated with all of the compounds of this study, in contrast to the more uniform bond length distributions exhibited by six-coordinate compounds with $\{InS_3N_3\}$ cores, suggest that the origin of this characteristic is steric, reflecting the constraints both of the chelate rings and of the sterically demanding phosphine groups.

Conclusions

The isolation of **1**−**4** demonstrates that electrochemical oxidation of In in the presence of thiolate ligands affords a facile method for the preparation of In−thiolates. With the exception of compound **4**, monophasic materials were obtained in high yield. Compounds **1**, **2**, and **4** represent the first structurally characterized compounds of In with mixed thiolate−sulfur/phosphine donors. The anomalously long In−P bond distances associated with these compounds appear to reflect steric constraints, as do the highly irregular geometries in general. A curious feature of the chemistry is the variance of the solution and solid state structures of **2**, an observation which may reflect the relative ease of bond breaking and rearrangement suggested by the anomalous In−P bond distances in the solid state. The electrochemical synthesis also affords the first example of a six-coordinate In(III)−thiolate complex anion in compound **4**. There is only one other structurally characterized example of an In−thiolate complex anion, the four-coordinate $[BrIn(SPh)_3]^-$ species. Since **4** could be prepared only by electrochemical methods, we are investigating these for the preparation of other complex ions of the In(III)−thiolate and Ga(III)−thiolate families.

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Supporting Information Available: Tables in CIF format providing atomic positional parameters, bond distances and angles, anisotropic thermal parameters and calculated hydrogen atoms positions for **1**, **2**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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