Two New Carbon-Free Indium(III) Asymmetric Chelates – Synthesis and X-ray Crystal Structures of [In{$Ph_2P(O)NP(S)Ph_2$-*O,S*}$_3$]·3/4 C_6H_6 and [InCl{$Ph_2P(S)NP(Se)Ph_2$-*S,Se*}$_2$]

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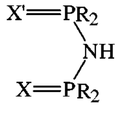
The ligands $[Ph_2(S)PNHP(X)Ph_2]^-$ (X = O, Se) react with $InCl_3$ in a 3:1 ratio to give a tris-chelate [In{$Ph_2P(O)NP(S)Ph_2$-*O,S*}$_3$]·0.75 C_6H_6 (**2**) and the unexpected pentacoordinate derivative [InCl{$Ph_2P(Se)NP(S)Ph_2$-*Se,S*}$_2$] (**3**). These compounds have been characterized by means of IR, ^{1}H- and ^{31}P-NMR spectroscopy, positive-ion FAB mass spectrometry and elemental analysis. The molecular structures have been determined by single-crystal X-ray diffraction analysis. The coordination geometry in **2** resembles that observed in the three analogous tris-chelates incorporating the corresponding symmetrical oxygen, sulfur and selenium ligands. Compound **3** exhibits a very distorted trigonal-bipyramidal geometry at indium, where both the selenium and chlorine atoms are in equatorial positions, while the sulfur atoms are in axial positions.

Introduction

Inorganic chelate rings have been the subject of increasing interest in recent years, since they constitute a bridge between traditional inorganic heterocycles (containing mainly non-metallic elements) and classical coordination compounds.[1,2] The anions of the ligands $[R_2(X)PNHP(X')R_2]$ (**1**: R = Ph, Me, *i*-Pr, and OPh, but not all permutations) are excellent chelating agents, which form stable phosphazene metallacycles. They have also found important use as metal extracting agents.[2,3] Compounds containing the symmetric ligands **1a**–**c** have been extensively studied.[4] In contrast, chelate complexes with the asymmetric ligands (**1d**–**f**) have been less well studied, with only few examples known to date.[2,5,6] This is in part due to the long absence of a simple synthetic procedure for such systems. However, more convenient synthetic methods have been reported in the last few years.[2][5]

		X	X′
	**1a**	O	O
	1b	S	S
	1c	Se	Se
	1d	O	S
	1e	O	Se
1	**1f**	S	Se

In the course of our studies on the coordination chemistry of the imidobis(diphenylphosphanechalcogenide) ligands (**1**) with heavy main group elements, we synthesized some heavier Group 13 complexes [In(III) and Ga(III)] with the symmetric anions **1a**–**c**.[4b–4d] In order to explore possible changes that might be induced by asymmetric ligands (**1d** and **1f**), we decided to synthesize indium(III) derivatives with these ligands.

We report herein on the synthesis and spectroscopic characterization of the indium(III) tris-chelate [In{$Ph_2P(O)NP(S)Ph_2$-*O,S*}$_3$] (**2**) and the unexpected pentacoordinate indium(III) complex [InCl{$Ph_2P(S)NP(Se)Ph_2$-*S,Se*}$_2$] (**3**).

Results and Discussion

The compounds were prepared from $InCl_3$ and the appropriate $K(Ph_2PSNPXPh_2)$ salt (X = O or Se) in a 1:3 molar ratio. In the reaction with the ligand **1f**, only the bis-chelate [InCl{$Ph_2P(Se)NP(S)Ph_2$-*Se,S*}$_2$] (**3**) was obtained, even on employing different molar proportions. There was no evidence for the formation of the expected tris-chelate.

Both complexes were obtained as air-stable, colourless, crystalline solids, and were found to be soluble in some organic solvents (e.g. $CHCl_3$, CH_2Cl_2, benzene, THF), but not in others (hexane, ethanol). They were characterized by partial elemental analyses (C, H, N), IR, ^{1}H- and ^{31}P-NMR spectroscopy, and positive-ion FAB mass spectrometry. The crystal and molecular structures of both compounds (**2** and **3**) were determined by means of single-crystal X-ray diffraction analysis.

Characteristic infrared bands of the new compounds were assigned by comparison with the spectra of reported compounds containing the $[Ph_2PSNPXPh_2]^-$ ligand.[2, 4–7] The FAB mass spectrum of **2** exhibits a low intensity signal for the molecular ion, but rather intense ion fragments containing ^{115}In, e.g. $[S_2O_2(PPh_2)_4N_2{}^{115}In^+]$ [*m/z* (%): 979

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(100)], [SO(PPh$_2$)$_2$N^{115}In $^+$] [*m/z* (%): 546 (45)]. In the case of compound **3**, the base peak corresponds to the expected first fragmentation, i.e. [M$^+$ − Cl] (*m/z*: 1107). All of the observed signals exhibit the expected isotopic pattern.

The ^{31}P{^{1}H}-NMR spectra each feature two signals attributable to two non-equivalent phosphorus nuclei P$_S$ and P$_X$. Upon chelation to In(III), there is a small change in δP and a reduction in ^1J(PSe) for the bonded [Ph$_2$P(S)NP(X)Ph$_2$]$^-$ ligand [**2**: δ(P) = 33.6, 23.3; **3**: δ(P) = 40.53, 28.24; ^1J(PSe) = 738 Hz] in comparison to K[Ph$_2$P(S)NP(X)Ph$_2$] [X = O: δ(P) = 35.3, 13.9; X = Se: δ(P) = 37.6, 26.7; ^1J(PSe) = 682 Hz].[5]

Structural Description

The structures of the compounds are built-up from discrete [In{Ph$_2$P(O)NP(S)Ph$_2$-*O,S*}$_3$] (**2**) and [InCl{Ph$_2$P(S)NP(Se)Ph$_2$-*S,Se*}$_2$] (**3**) molecules. Compound **2** crystallizes with benzene molecules in a 4:3 ratio. The molecular structures of **2** and **3** are shown in Figures 1 and 2, respectively.

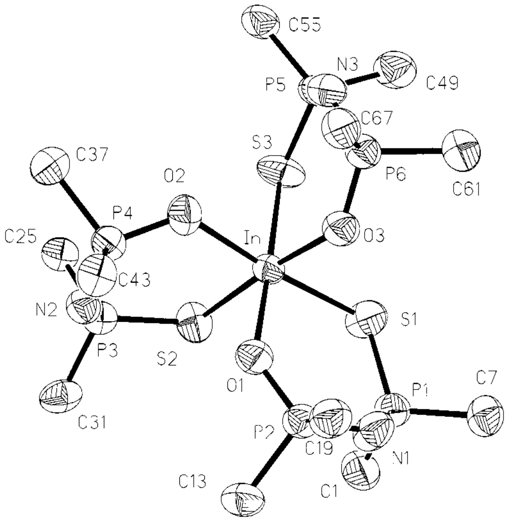

Figure 1. ORTEP view of [In{Ph$_2$P(O)NP(S)Ph$_2$-*O,S*}$_3$]·3/4 C$_6$H$_6$, **2**; phenyl groups are omitted for clarity; selected bond lengths [Å] and angles [°]: In−O(1) 2.121(4), In−O(2) 2.144(4), In−O(3) 2.125(4), In−S(1) 2.591(1), In−S(2) 2.611(1), In−S(3) 2.595(1), S(1)−P(1) 2.009(3), S(2)−P(3) 2.010(3), S(3)−P(5) 2.021(2), O(1)−P(2) 1.505(5), O(2)−P(4) 1.533(5), O(3)−P(6) 1.507(5), P(1)−N(1) 1.566(6), P(2)−N(1) 1.594(6), P(3)−N(2) 1.582(5), P(4)−N(2) 1.587(5), P(5)−N(3) 1.578(6), P(6)−N(3) 1.592(6); O(1)−In−O(2) 87.8(1), O(1)−In−O(3) 85.4(1), O(1)−In−S(1) 97.2(1), O(1)−In−S(2) 92.1(1), O(1)−In−S(3) 178.3(1), O(2)−In−S(1) 174.6(1), O(2)−In−S(2) 95.9(1), O(2)−In−S(3) 91.1(1), O(3)−In−O(2) 87.8(1), O(3)−In−S(1) 91.0(1), O(3)−In−S(2) 175.4(1), O(3)−In−S(3) 95.9(1), S(1)−In−S(3) 83.73(7), S(1)−In−S(2) 85.45(7), S(3)−In−S(2) 86.60(6), In−S(1)−P(1) 106.42(9), In−S(2)−P(3) 104.61(9), In−S(3)−P(5) 105.69(9), In−O(1)−P(2) 134.3(3), In−O(2)−P(4) 127.7(3), In−O(3)−P(6) 132.1(3), P(1)−N(1)−P(2) 133.6(4), P(3)−N(2)−P(4) 128.8(3), P(5)−N(2)−P(6) 128.8(4), N(1)−P(1)−S(1) 119.7(2), N(2)−P(3)−S(2) 118.5(2), N(3)−P(5)−S(3) 119.7(2), N(1)−P(2)−O(1) 117.9(3), N(2)−P(4)−O(2) 118.1(3), N(3)−P(6)−O(3) 118.2(3)

In **2**, the coordination geometry at indium is similar to that observed in the three analogous compounds incorporating the corresponding symmetrical ligands, [In{Ph$_2$P(X)NP(X′)Ph$_2$-*X,X′*}$_3$] [X = X′ = O (**4**), S (**5**), Se (**6**)].[4b−4d] The indium atom is bonded to three ligands through the sulfur and oxygen atoms, leading to a very distorted octahedron. This may be largely attributed to the asymmetry of the ligand. The molecule corresponds to the facial isomer. The In−X bond lengths [av. In−O 2.13(4), In−S 2.599(2) Å] agree well with the values found for the corresponding bonds in **4** [av. In−O 2.127(9) Å] and **5** [av. In−S 2.63(3) Å],[4a] as well as those found in previous structure determinations.[8−10] The O−In−S bite angles [av. 96.3(2)°] are larger than the corresponding O−In−O [**4**: av. 89.5(7)°] and S−In−S [**5**: av. 91.9(16)°] bite angles observed in the two analogous compounds. The inter-ligand angles fall in the range 83.73(7)° to 92.1(1)°.

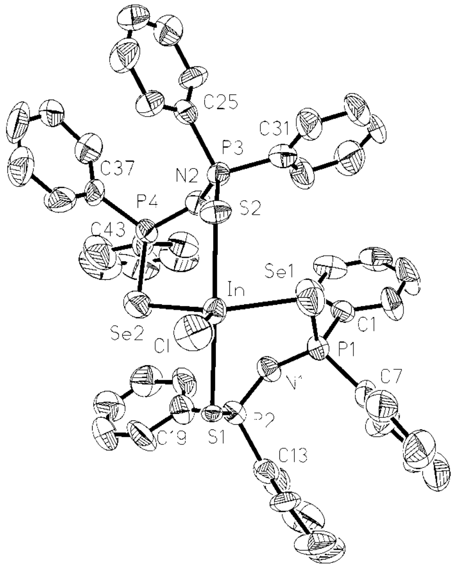

Figure 2. ORTEP view of [InCl{Ph$_2$P(Se)NP(S)Ph$_2$-*Se,S*}$_2$], **3**; selected bond lengths [Å] and angles [°]: In−Cl 2.422(3), In−Se(1) 2.570(2), In−Se(2) 2.583(2), In−S(1) 2.693(3), In−S(2) 2.642(3), Se(1)−P(1) 2.160(4), Se(2)−P(4) 2.184(4), S(1)−P(2) 2.088(4), S(2)−P(3) 2.048(4), P(1)−N(1) 1.582(10), P(2)−N(1) 1.591(10), P(3)−N(2) 1.597(9), P(4)−N(2) 1.603(10); Cl−In−Se(1) 115.5(1), Cl−In−Se(2) 114.4(1), Cl−In−S(1) 84.0(1), Cl−In−S(2) 84.6(1), Se(1)−In−Se(2) 129.98(7), S(1)−In−S(2) 168.53(8), Se(1)−In−S(2) 85.55(9), Se(2)−In−S(2) 98.37(9), Se(1)−In−S(1) 97.76(7), Se(2)−In−S(1) 87.96(7), In−Se(1)−P(1) 101.8(1), In−-Se(2)−P(4) 102.4(1), In−S(1)−P(2) 99.1(1), In−S(2)−P(3) 103.7(1), P(1)−N(1)−P(2) 130.9(6), P(3)−N(2)−P(4) 127.7(6), N(1)−P(1)−Se(1) 116.2(4), N(1)−P(2)−S(1) 115.8(4), N(2)−P(4)−Se(2) 118.0(4), N(2)−P(3)−S(2) 117.4(4)

The pentacoordinate geometry found in [InCl{Ph$_2$P(S)NP(Se)Ph$_2$-*S,Se*}$_2$] (**3**) was completely unexpected since all of the previously studied indium(III) complexes with the analogous [R$_2$(X)PNHP(X′)R$_2$]$^-$ ligands are tris-chelates.[4b−4d] This structure is also interesting in view of the fact that many of the known pentacoordinate indium structures result from intermolecular associations[9] and only a few examples correspond to discrete pentacoordinate molecules.[10] In complex **3**, only two of the ligands are attached to the indium atom through the sulfur and selenium atoms. The resulting arrangement can be described as a very distorted trigonal bipyramid (TP), where Se(1), Se(2), and a chlorine atom are equatorially positioned, while S(1) and

S(2) are axially positioned. The diaxial angle is 168.53(8)°, while the average equatorial angle is 119.9(10)°. Four of the remaining In−donor atom angles are less than 90°. The S−In−Se bite angles [98.37(9)° and 97.76(7)°] are larger than the corresponding S−In−S [**5**: av. 91.9(16)°] and Se−-In−Se [**6**: av. 96.9(9)°] bite angles in the octahedral compounds with the symmetrical ligands.[4c−e]

The axial In−S bond lengths resemble those found in the analogous sulfur tris-chelate [av. **5**: 2.63(3) Å],[4b] while the In−Se distances [In−S 2.583(2) and 2.570(2) Å] are shorter than the corresponding bonds in the analogous selenium tris-chelate [**6**: av. 2.75(3) Å].[4d] These In−Se lengths are closer to those measured for the less crowded [In{Se(2,4,6-*t*-$Bu_3C_6H_2$)}$_3$] derivative.[8b] The In−Cl bond length [2.422(3) Å] is similar to the equatorial In−Cl distance in the pentacoordinate [(*n*-C_4H_9)$_4$N]$_2$[InCl{$S_2C_2(CN)_2$}$_2$], 2.418(2) Å,[10a] and the axial In−Cl length in [Et_4N]$_2$[$InCl_5$], 2.415(2) Å.[10b] The average In−Cl equatorial bond length in the trigonal-bipyramidal adduct $InCl_3$·$2PPh_3$ is 2.383(5) ± 0.05 Å.[10d]

In both compounds **2** and **3**, the resulting $InSXP_2N$ (X = O, Se) chelate rings may be considered as having a very distorted boat conformation with the indium and nitrogen atoms at the apices. A similar arrangement was found for asymmetric $PbOSP_2N$ rings[6b] as well as for the symmetric InO_2P_2N rings in **4**, which also exhibit a boat conformation.[4c] The symmetric InS_2P_2N chelate rings adopt a twisted boat conformation (**5**).[4b] In contrast, the $InSe_2P_2N$ ring in **6** displays both conformations (boat and twisted boat), but with the selenium and phosphorus atoms at the apices.[4d] Average P−S [**2**: 2.013(4); **3**: 2.068(4) Å], P−O [**2**: 1.515(5); **3**: 2.172(4) (X = Se) Å], and P−N [**2**: 1.582(6); **3**: 1.586(10) Å] bond lengths are consistent with a delocalized π-bond structure involving the five ligand atoms of the chelate ring, as has been noted for cyclic phosphazene.[11]

The packing in the crystal structures is largely determined by van der Waal's forces. There are no particularly short intermolecular contacts.

Experimental Section

Chemicals of commercial grade were purchased from Aldrich and were used as supplied. Solvents were distilled prior to use. The asymmetric [R_2(X)PNHP(X′)R_2] ligands **1d** [12] and **1f**[5] were prepared by published methods. They were converted to the corresponding potassium salts by treatment with KO*t*Bu according to a previously described procedure.[13] The ^1H- and $^{31}P\{^1H\}$-NMR spectra were obtained at room temperature in $CDCl_3$ on a Varian Unity spectrometer operating at 299.94 MHz and 121 MHz, respectively [external references: $Si(CH_3)_4$ and 85% H_3PO_4]. FAB^+ MS (3-nitrobenzyl alcohol matrix) were measured on a Jeol JMS-SX102A instrument. The IR spectrum of **2** (KBr pellet) was recorded on a Nicolet FT-IR Magna 750 spectrometer, while that of **3** (Nujol) was recorded on a Bruker IFS28 spectrometer. Elemental analyses of **2** and **3** were performed with a Galbraith Laboratories (Knoxville, TN) analyzer and a Fison's Instruments (Italy) EA 1108 apparatus, respectively.

[In{Ph_2P(O)NP(S)Ph_2-*O,S*}$_3$] (2): A solution of $InCl_3$ (0.032 g, 0.15 mmol) in water (5 mL) was added to a solution of K[Ph_2P(S)NP(O)Ph_2] (0.207 g, 0.44 mmol) in methanol (3 mL). The white solid formed was filtered off, washed with water, and dried in vacuo. Yield: 0.13 g (61%); m.p. > 320°C. − ^{31}P NMR ($CDCl_3$): δ = 33.6 (s), 23.3 (s). − IR (KBr): 1230 cm^{-1} vs [ν(PN)]

Table 1. Crystallographic and structure solution data for **2**·3/4C_6H_6 and **3**

	2·3/4 C_6H_6	3
Formula	$C_{72}H_{60}InN_3O_3P_6S_3$·3/4 C_6H_6	$C_{48}H_{40}ClInN_2P_4S_2Se_2$
Formula mass	1470.75	1141.01
Cryst. size [mm]	0.59 × 0.34 × 0.23	0.34 × 0.24 × 0.14
Diffractometer	Siemens P4 PC	Siemens P4 PC
Radiation	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)
Temperature	293(2) K	293(2) K
Crystal system	Triclinic	Monoclinic
Space group	*P*1bar	*Cc*
a [Å]	11.62(2)	20.214(3)
b [Å]	15.47(2)	12.637(2)
c [Å]	22.341(2)	21.162(2)
α [°]	102.97(1)	90.0
β [°]	100.37(1)	115.12(1)
γ [°]	92.77(1)	90.0
V [$Å^3$]	3836.8(8)	4894.4(12)
Z	2	4
ρ_{calcd} [mg/cm^3]	1.265	1.548
F(000)	1501	1780
μ [mm^{-1}]	0.561	2.272
θ range [°]	1.36 to 25.00	1.96 to 30.00
Reflections collected	15662	13079
Independent reflections	13423 (R_{int} = 0.0502)	7321 (R_{int} = 0.00)
Parameters refined	852	539
R (F_o)	0.0642	0.0585
R_w (F_o)	0.1638	0.1282
Largest diff. peak/hole	1.205/−0.896 e$Å^{-3}$	1.331/−0.521 e$Å^{-3}$
Goodness-of-fit	1.042	0.80

+ 1176 s [ν(PN)/δ(CH)], 1125 s [ν(PO)], 740 m [γ(CH), Ph], 530 vs [γ(PNP)], 560 m [ν(PS)]. − MS (FAB$^+$) ($CHCl_3$): *m*/*z*: 1411 [M^+], 1334 [$O_3S_3P_6Ph_{11}N_3{}^{115}In^+$], 979 [$S_2O_2(PPh_2)_4N_2{}^{115}In\ ^+$], 903 [$S_2O_2P_4Ph_7N_2{}^{115}In\ ^+$], 546 [$SO(PPh_2)_2N^{115}In\ ^+$], 514 [$O(PPh_2)_2N^{115}In\ ^+$], 416 [$S(PPh_2)_2N^+$], 400 [$OP_2Ph_4N^+$]. − $C_{72}H_{60}InN_3P_6O_3S_3$ (1412.1): calcd. C 61.24, H 4.28, N 2.98; found C 61.10, H 4.14, N 2.87.

[InCl{Ph_2P(Se)NP(S)Ph_2-*Se,S*}$_2$] (3): The synthetic procedure was very similar to that used for **2**, starting from $InCl_3$ (0.044 g, 0.2 mmol) and K[Ph_2P(Se)NP(S)Ph_2] (0.32 g, 0.6 mmol). Yield: 0.17 g (77%); m.p. 198 °C. − ^{31}P NMR ($CDCl_3$): $\delta = 40.53$ [s, P(s)], 28.24 [s, ^1J(PSe) = 738 Hz, P(Se)]. − IR (Nujol): 1198 cm^{-1} vs [ν(PN)] + 1174 s [ν(PN)/δ(CH)], 744 m [γ(CH), Ph], 529 vs [γ(PNP)/ν(PSe)], 582 m [γ(PNP)/ν(PS)]. − MS (FAB$^+$) ($CHCl_3$): *m*/*z*: 1107 [{$^{80}SeS(PPh_2)_2N$}$2^{115}In\ ^+$], 611 [$^{80}SeS(PPh_2)N^{115}In\ ^+$], 496 [$^{80}SeS(PPh_2)_2N^+$], 464 [$^{80}Se(PPh_2)_2N^+$], 416 [$S(PPh_2)_2N^+$], 384 [$(PPh_2)_2N^+$]. − $C_{48}H_{40}ClInN_2P_4S_2Se_2$ (1141.01): calcd. C 50.52, H 3.53, N 2.45, S 5.62; found C 50.41, H 3.39, N 2.35, S 5.15.

X-ray Diffraction Studies: Crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into benzene (**2**) or chloroform (**3**) solutions of the corresponding compound. Details of the data collections and refinements are summarized in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares calculations using the program system SHELXL-97.[14] Non-hydrogen atoms were refined anisotropically, while H atoms were refined using a riding model ($U = 0.06$). The Flack parameter for **3** was $\eta = 0.003(19)$.[15] A semiempirical (ψ scan) absorption correction was applied for **3** (0.92957/0.62808). The crystal structure data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-113996 (**2**) and CCDC-113995 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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