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Coordination Chemistry of Diselenophosphinate Complexes: The X-ray Single-Crystal Structures of $[K(Se_2PPh_2)(THF)_2]_2$ and $[In(Se_2PPh_2)_3]\cdot L$ (L = THF, PhMe)

Robert P. Davies,* Claire V. Francis, Andrew P. S. Jurd, M. Giovanna Martinelli, Andrew J. P. White, and David J. Williams

Department of Chemistry, Imperial College London, South Kensington, London SW7 2AZ, U.K.

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Reaction of potassium diphenylphosphide with elemental selenium is shown to give $[K(Se_2PPh_2)(THF)_2]_2$ **1**, which further reacts with $InCl_3$ to yield $[In(Se_2PPh_2)_3]$ **2**. Crystallization of **2** from either THF or PhMe gave **2**·THF or **2**·PhMe, respectively, both of which form loosely linked dimers in the solid state via Se···Se intermolecular van der Waals interactions. Decomposition of **2** has been studied by TGA.

The chemistry of metal selenolates is of topical interest, due in part to their potential use as single-source precursors to binary and ternary metal chalcogenides.[1] Within this area, we have recently been interested in the synthesis and coordination chemistry of chalcogeno−phosphorus ligand systems, and have published of late on the synthesis of lithium selenophosphinite, diselenophosphinate, and triselenophosphonate complexes.[2] These seleno−phosphorus ligands were shown to be more stable, easier to handle, and far less pungent than alkyl and aryl selenolates.[2,3] This has now led us to look at the synthesis and characterization of other main group metal complexes of these ligands.

The indium(III) complexes of seleno−phosphorus ligands are of particular interest to us due to their potential application as single-source precursors to indium selenide thin films and quantum dots. Precedent to these applications lies in the reported use of dithiophosphinate and phosphinochalcogenoic amidate complexes such as $[Cd(S_2PR_2)_2]$ (R = CH_3,[4] C_2H_5[5]) and $[M\{tBu_2P(Se)NR\}_2]$ (M = Zn, Cd, Cr, Mn, Fe, Co; R = *i*Pr, c-C_6H_{11})[6] for the growth of semiconducting metal chalcogenide thin films using chemical vapor deposition (CVD) processes, and in the recently reported effectiveness of imino−bis(diisopropylphosphine selenide) complexes, e.g., $Cd[N(SeP\mathit{i}Pr_2)_2]_2$, as reagents for the one-step synthesis of metal selenide quantum dots.[7] In addition, although dithiophosphinate complexes of main group metals are well-known,[8] there are very few structurally characterized main group metal complexes of the homologous diselenophosphinates or diselenophosphates, the only examples being the alkali metal complexes $[Ph_2PSe_2Li\cdot THF\cdot TMEDA]$[2] [TMEDA = $\{(CH_3)_2NCH_2\}_2$], $[Na_2(Se_2PPh_2)_2\cdot THF\cdot 5H_2O]$,[9] and $[K_2(PhPSe_2)_2CH_2]$[10]

Potassium diselenophosphinate $[K(Se_2PPh_2)(THF)_2]_2$ **1** was obtained in 79% yield from the reaction of potassium diphenylphosphide with 2 equiv of gray selenium powder in THF/toluene (Scheme 1).

Scheme 1

$$Ph_2PK \xrightarrow[THF]{2Se} [K(Se_2PPh_2)(THF)_2]_2 \xrightarrow[-KCl]{InCl_3} In(Se_2PPh_2)_3$$

X-ray diffraction studies[11] show **1** to crystallize as discrete centrosymmetric dimers with a central $K_2P_2Se_4$ cage bounded by phenyl and THF units (Figure 1). The P−Se bond lengths of 2.132(2) Å [Se(1)] and 2.150(2) Å [Se(2)] are intermediate between those expected for P−Se single (2.26 Å)[2] and double (2.09 Å)[12] bonds, indicative of delocalization of the negative charge across the PSe_2 unit and a P−Se bond order of 1.5.

* To whom correspondence should be addressed. E-mail: r.davies@imperial.ac.uk.

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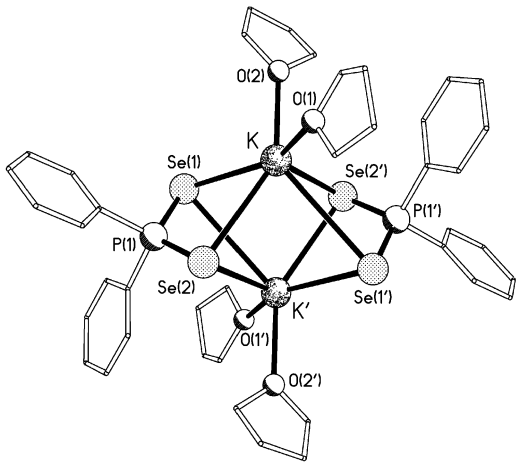

Figure 1. Molecular structure of $[K(Se_2PPh_2)(THF)_2]_2$ **1**.

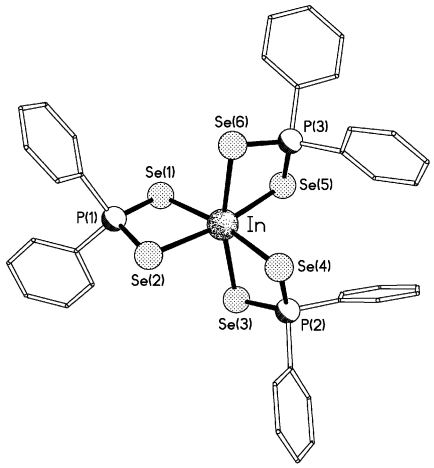

Figure 2. Molecular structure of the $[In(Se_2PPh_2)_3]$ complex in **2**·THF. Though a molecule with a Δ configuration is shown, the crystals of both **2**·THF and **2**·PhMe are racemic and there are equal numbers of Δ and Λ forms present.

This delocalization can also be observed in solution using ^{31}P NMR spectroscopy from the $^1J_{PSe}$ coupling constant (−642 Hz) which is midway between expected values for single (−200 to −600 Hz) and double (−800 to −1200 Hz) P−Se bonds.[13] The infrared spectrum of a Nujol mull of **1** shows strong absorptions at 561 and 490 cm^{-1} which can be ascribed to the asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of the PSe_2 groups. The solid-state structure reveals the diselenophosphinate ligands in **1** to bridge the two potassium centers in a μ_2-η^2,η^2 mode with each Ph_2PSe_2 ligand coordinating in an isobidentate (symmetric) fashion to one potassium center and anisobidentately (asymmetrically) to the other. This results in a distorted K_2Se_4 octahedral core, with three short K−Se contact distances [K−Se(1) 3.402(2) Å, K−Se(2) 3.431(2) Å, K−Se(2′) 3.378(3) Å] and one long one [K−Se(1′) 3.913(3) Å]. There are no significant interdimer interactions.

Metathesis reactions of **1** with $InCl_3$ gave the tris(diselenophosphinato)indium complex $[In(Se_2PPh_2)_3]$ **2**, which was crystallized from toluene/THF to yield yellow prisms of **2**·THF (46% yield), and from toluene in the absence of THF to give yellow needles of **2**·PhMe (40% yield). Unlike the crystals of **1**, those of **2**·THF were observed to be air and moisture stable, showing no discernible decomposition (using ^1H and ^{31}P NMR spectroscopy) over a period of six weeks when left open to the atmosphere. Single-crystal X-ray analysis[11] of both **2**·THF and **2**·PhMe revealed (Figure 2) a pair of structures with isostructural $[In(Se_2PPh_2)_3]$ units (rms deviation 0.13 Å for the P_3Se_6In core) and an included solvent molecule. In each case the diselenophosphinate ligands coordinate in an approximate isobidentate fashion, forming four-membered Se−P−Se−In chelate rings with In−Se distances in the range 2.6992(12)−2.7782(13) Å for **2**·THF [2.7181(12)−2.7986(12) Å for **2**·PhMe] and P−Se distances in the range 2.168(3)−2.180(3) Å [2.163(3)−2.187(3) Å]. Though slightly longer than seen in **1**, these P−Se distances are again indicative of a bond order of ca. 1.5. This is also reflected in the $^1J_{PSe}$ (^{31}P NMR) coupling constant of −649 Hz, and in the infrared asymmetric and symmetric bond stretches at 534 and 445 cm^{-1}. The geometry at the indium center is trigonally distorted octahedral as a consequence of the restricted bite, 80.05(4)−80.18(3)° [79.58(3)−80.90(3)°], of the chelating diseleneophosphinate ligand with the trans Se−In−Se bond angles in the range 164.83(4)−170.40(4)° [161.74(4)−171.33(4)°]. The structures of the $[In(Se_2PPh_2)_3]$ unit in **2**·THF and **2**·PhMe are therefore similar to that reported for the sulfur homologue $[In(S_2PPh_2)_3]$,[14] although the more restricted bite of the dithiophosphinate ligand (av 77.9° cf. av 80.2° for the seleno species) leads to a greater trigonal distortion of the geometry at the metal center. However, in contrast to $[In(S_2PPh_2)_3]$, **2**·THF and **2**·PhMe both show a packing motif with dimerization between centrosymmetrically related $[In(Se_2PPh_2)_3]$ units occurring via noncovalent Se···Se interactions (Figure 3). Though the basic motif is the same, the Se···Se contact distances for the two solvates of **2** differ markedly. In **2**·THF only one of the Se···Se separations [3.8145(14) Å] is noticeably less than the sum of the van der Waals radii (4.0 Å), and thus falls within the range of previously reported intermolecular nonbonding Se···Se distances (3.3−3.9 Å),[15]

(11) Crystal data for **1**: $C_{40}H_{52}K_2O_4P_2Se_4$, $M = 1052.80$, $P2_1/n$ (No. 14), $a = 10.2778(8)$ Å, $b = 17.8297(13)$ Å, $c = 12.8935(16)$ Å, $\beta = 93.158(8)°$, $V = 2359.1(4)$ Å^3, $Z = 2$ (C_i symmetry), $\rho_{calcd} = 1.482$ g cm^{-3}, μ(Mo Kα) = 3.390 mm^{-1}, $T = 233$ K, colorless prisms; 4137 independent measured reflections, $R_1 = 0.062$, $wR_2 = 0.129$, 1985 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 50°$], 265 parameters. For **2**·THF: $C_{36}H_{30}P_3Se_6In$·C_4H_8O, $M = 1216.19$, $P2_1/n$ (No. 14), $a = 13.1962(10)$ Å, $b = 15.2780(15)$ Å, $c = 21.780(3)$ Å, $\beta = 94.606(8)°$, $V = 4376.9(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.846$ g cm^{-3}, μ(Mo Kα) = 5.669 mm^{-1}, $T = 293$ K, yellow prisms; 7666 independent measured reflections, $R_1 = 0.055$, $wR_2 = 0.099$, 4539 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 50°$], 408 parameters. For **2**·PhMe: $C_{36}H_{30}P_3Se_6In$·C_7H_8, $M = 1236.22$, $P2_1/n$ (No. 14), $a = 12.8500(15)$ Å, $b = 15.427(2)$ Å, $c = 22.395(2)$ Å, $\beta = 98.512(9)°$, $V = 4390.6(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.870$ g cm^{-3}, μ(Mo Kα) = 5.652 mm^{-1}, $T = 183$ K, yellow needles; 5738 independent measured reflections, $R_1 = 0.047$, $wR_2 = 0.079$, 3907 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 45°$], 396 parameters.

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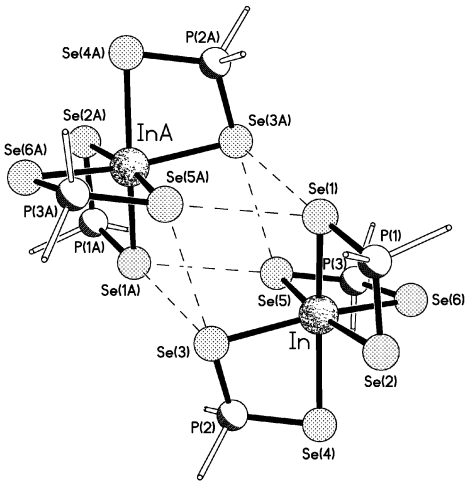

Figure 3. Dimerization via intermolecular nonbonding Se···Se interactions in **2**·PhMe (the phenyl rings have been omitted for clarity).

Table 1. Intermolecular Distances (Å) and Angles (deg) for **2**·THF and **2**·PhMe

	2·THF	**2**·PhMe
Se(1)···Se(3A)	3.8145(14)	3.5340(14)
Se(3)···Se(5A)	4.334(2)	3.7958(14)
Se(1)···Se(5A)	4.007(2)	3.7234(14)
P(1)−Se(1)···Se(3A)	160.96(8)	173.79(7)
P(1)−Se(1)···Se(5A)	108.96(9)	113.78(8)
P(2)−Se(3)···Se(1A)	113.03(7)	106.24(7)
P(2)−Se(3)···Se(5A)	169.59(8)	173.45(7)
P(3)−Se(5)···Se(1A)	177.37(8)	173.36(8)
P(3)−Se(5)···Se(3A)	123.09(8)	118.29(8)

whereas in **2**·PhMe the Se···Se contacts range between 3.5340(14) and 3.7958(14) Å (Table 1). Such nonbonding Se···Se interactions are well-known and have found utility in crystal engineering, for example in the formation of tubular structures from the columnar stacking of chalcogen containing macrocyclics.[15] In contrast to **2**·THF and **2**·PhMe, the closest intermolecular S···S separation in the structure of $[In(S_2PPh_2)_3]$ is 4.40 Å.[14]

Previous quantum chemical model calculations have shown the so-called nonbonding chalcogen−chalcogen intermolecular interactions in chalcogenoethers (R_2X; X = S, Se, Te) to arise due to interaction of the occupied *n*p orbital on the chalcogen of a R_2X molecule with the empty σ^* orbital of the R−X bond of an adjacent R_2X molecule (Figure 4a).[15,16] This results ideally in a linear RX···X interaction ($\theta_1 = 180°$) perpendicular to one of the chalcogenoether groups ($\theta_2 = 90°$). Inspection of the intermolecular interactions in **2**·THF and **2**·PhMe reveals that similar interactions may well be occurring between the Se 4p or π orbital on one diselenophosphinate ligand and the P−Se σ^* orbital of an adjacent diselenophosphinate (Figure 4b), with θ_1 values observed in the range 160.96(8)−173.79(7)° and θ_2 values in the range 106.24(7)−118.29(8)° (Table 1). In **2**·THF one selenium [Se(3)] on each complex would therefore be acting as a donor and one [Se(1)] as an acceptor; however, in **2**·PhMe each complex contains three seleniums [Se(1), Se(3), and Se(5)] which act as both donors and acceptors (similar dual donor and acceptor behavior has been reported for chalcogenoethers[15]).

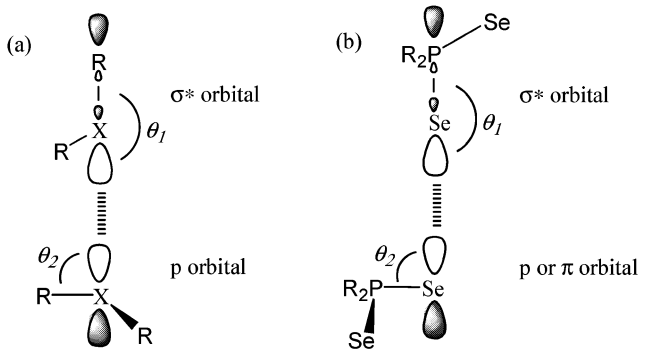

Figure 4. Interaction of the occupied p orbitals with the empty σ^* orbitals in (a) chalcogenoethers and (b) **2**·THF and **2**·PhMe.

In order to study the decomposition pathway of **2** and to evaluate its potential use as a single-source precursor for In_2Se_3, TGA (10 °C min^{-1}, 20−500 °C, under N_2) was carried out on **2**·THF. A small weight loss was observed for **2**·THF in the range 85−125 °C, attributable to the loss of lattice THF, and a more significant weight loss of 75.2% from 375 to 450 °C, attributable to decomposition of **2** to In_2Se_3 (calculated weight loss of 79.6% for In_2Se_3 formation from **2**). Elemental analysis on the decomposition product is consistent with its assignment as In_2Se_3, showing no major contamination by carbon, hydrogen, or phosphorus (C, H, P found <0.5%). The air and moisture stability of **2**, its facile synthesis, and its lack of a pungent odor give it several advantages in terms of ease of use over existing indium selenide single-source precursors such as air-sensitive and noxious alkylindium selenolates [e.g., $In(SePh)_3$ and $Me_2In(SePh)$][17] and indium selenocarbamates $In(Se_2CNR^1R^2)_3$ which, although excellent air-stable precursors, need to be prepared from toxic and noxious carbon diselenide.[18] More detailed studies on the utility of **2** as a single-source precursor toward thin films and nanoclusters are currently being undertaken.

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Supporting Information Available: Three X-ray crystallographic files in CIF format, full experimental details for all compounds, and the TGA plot for **2**·THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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