The Facile Synthesis of Bis(dichalcogenophosphinate)s and a Remarkable $[Li_8(OH)_6]^{2+}$ Polyhedron

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Abstract

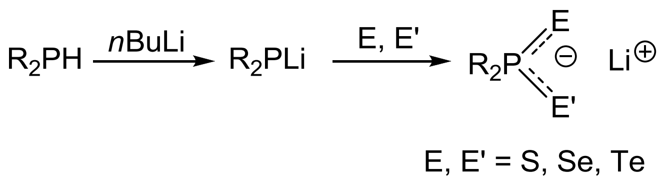
The synthesis and characterization of three lithium complexes of novel bis(dichalcogenophosphinate) ligands are reported: $(PhP(S)_2CH_2CH_2P(S)_2Ph)Li_2(THF)_4$ (**2**), $(PhP(Se)_2CH_2CH_2P(Se)_2Ph)Li_2(THF)_4.(PhP(Se)_2CH_2CH_2P(Se)_2Ph)Li_2(THF)_6$ (**3**) and $[PhP(Te)_2CH_2CH_2P(Te)_2Ph][Li_8(OH)_6(THF)_8]$ (**4**). The synthetic route to these complexes proceeds via the insertion reaction of elemental chalcogens into the phosphorus-lithium bonds of 1,2-dilithio-1,2-di(phenylphosphine)ethylene (**1**). X-ray analysis of **2** revealed anisobidentate coordination of the lithiums by the dithiophosphinate groups. In contrast, the diselenophosphinate groups in **3** coordinate the lithium centers in both isobidentate and mono-dentate modes, and the ditellurophosphinate groups in **4** form non-coordinate separate ion pairs. The counter-cation in **4** is shown to be a unique $[Li_8(OH)_6]^{2+}$ rhombic dodecahedral polyhedron, putatively formed from the capping of a hexameric $[Li(OH)]_6$ aggregate with lithium cations on its open faces.

Introduction

One of the most studied classes of chalcogeno-phosphorus compounds are the dithio-phosphorus acids – namely dithiophosphinic, dithiophosphonic and dithiophosphoric acid [R_2PS_2H, $R(RO)PS_2H$ and $(RO)_2PS_2H$ respectively] - and their conjugate bases.[1] This is due to their ease of preparation (and in some cases commercial availability), as well as their many applications including as pesticides, lubricant and plastic additives, reagents for organic synthesis, extraction agents, analytical reagents and vulcanization accelerators.[1] In addition, the coordination chemistry of dithiophosph(in)ates with transition metals, main-group metals and lanthanides and actinides has been extensively studied over the past fifty years and they have been shown to be very versatile ligands with a wide range of coordination chemistries.[2-7]

Diselenophosph(in)ates exhibit increased thermal and hydrolytic instability when compared to their lighter dithiophosph(in)ate homologs. Despite this potential drawback, diselenophosph(in)ates have been studied in some depth both for their diverse coordination chemistry, in particularly with soft metal centers such as copper(I),[8] and for their potential applications such as precursors to metal selenide semi-conducting materials.[9-13] In contrast, the heavier ditellurophosp(in)ate homologs are virtually unreported – the only structurally characterized example being the solvent separate ion pair complex [Ph_2PTe_2][$Li(THF)_{3.5}(TMEDA)_{0.25}$] (TMEDA = tetramethyl-ethylenediamine).[14]

We have recently reported upon a clean and high-yielding route to dichalcogenophosphinates based upon the treatment of metallated secondary phosphines with two equivalents of elemental chalcogen (Scheme 1).[14,15] Using this preparative route we were able to synthesize and structurally characterize for the first time ditellurophosphinate and mixed chalcogen selenotellurophoshinate compounds.[14] In addition, an extension of the synthetic route to primary dimetallated phosphines has been shown to yield trithiophosphonate[16,17] and triselenophosphonate[15] complexes. We now report upon a further adaptation of this preparative route for the synthesis of bis(dichalcogenophosphinate) species with sulfur, selenium and tellurium.



Scheme 1

Although oxygen containing bisphosph(in)ates comprising two diorganophosph(in)ate groups within the same molecule are extremely well known and have been extensively studied (not least for their medical applications),[18] their analogous heavier chalcogen bis(dichalcogenophosph(in)ate)s remain virtually unreported. This is particularly surprising in the case of the sulfur homologs given the large body of work on mono-dithiophosph(in)ates (*vide supra*). The most likely rationale for their rarity in the literature is the current absence of a simple and clean preparative route to these compounds. As far as we are aware, the only crystallographically characterized example of a bis(dichalcogenophosph(in)ate is that of the methylene bridged bis(diselenophosphinate) $[K_2(PhPSe_2)_2CH_2]$ reported by Woollins and co-workers, which was prepared from the reduction of the five-membered heterocycle $PhP(Se)CH_2PhP(Se)SePPh$ with potassium metal.[19] In addition, although no crystallographic characterizations are available Kuchen *et al* reported in the 1970s on the synthesis of a series of bis(dithiophosphinic acids) bridged by butyl or longer alkyl chains $RP(S)(SH)(CH_2)_n$ $RP(S)(SH)$ (R= CH_3, C_6H_5, p-C_6H_4OMe; n = 4-10).[20] These were prepared via the reaction of di-Grignard reagents with perthiophosphonic anhydrides $(RPS_2)_2$. We now present a new and much more facile route to bis(dichalcogenophosphinate)s starting from commercially available bis(diphenylphosphino)ethane (dppe).

Experimental Section

General Procedures. All reactions and manipulations were carried out under an inert atmosphere of dry nitrogen or argon using standard double manifold and glove-box techniques. Purification and drying of the solvents were done using standard methods. All chemicals used were purchased from Sigma-Aldrich. 1,2-dilithio-1,2-di(phenylphosphine)ethylene (**1**) was prepared from 1,2-bis(diphenylphosphino)ethane and lithium metal using standard literature procedures.[21] NMR spectra were recorded on a Joel EX270 Delta Upgrade spectrometer. External standards used were TMS (^{1}H, ^{13}C), 85% H_3PO_4 (^{31}P) or Me_2Se (^{77}Se). Melting points were measured in sealed capillaries under nitrogen. Microanalytical data were obtained from the Science Technical Support Unit, London Metropolitan University.

Preparation of $(PhP(S)_2CH_2CH_2P(S)_2Ph)Li_2(THF)_4$ (2)

A solution of **1** (150 mg, 0.28 mmol) in 10 mL THF was treated with powdered elemental S_8 (36 mg, 0.14 mmol) at -78ºC. The mixture was warmed to room temperature and stirred for 1 h to give a clear yellow solution. Colorless crystals of **2** were obtained from the solution on standing for 1 day at 5 ºC. Yield 174 mg, 92%. Mp > 250ºC. ^{1}H NMR (270 MHz, d_6-DMSO): δ = 1.72 (m, 16 H, THF), 1.78-2.22 (br m, 4 H, CH_2CH_2), 3.58 (16 H, THF), 7.25-7.27 (m, 6 H, *m/p*-C_6H_5), 7.93 (m, 4 H, *o*-C_6H_5). ^{13}C NMR(67 MHz, d_6-DMSO): δ = 25.11 (THF), 40.4 ($^{1}J_{CP}$ = 47 Hz, -PCH_2-), 66.99 (THF), 126.56, 128.01, 130.32 (*o/m/p*-C_6H_5). ^{31}P NMR (109

MHz, d_6-DMSO): δ = 64.1. IR: υ (cm^{-1}) = 1404 s, 1377 s, 1306 m, 1177 w, 1155 m, 1104 s, 1043 m, 890 m, 755 w, 725 m, 648 m, 540 m, 486 m. Elemental analysis for $C_{30}H_{46}O_4Li_2P_2S_4$ calcd(%) C 53.40, H 6.87; found C 53.42, H 6.89.

Preparation of $(PhP(Se)_2CH_2CH_2P(Se)_2Ph)Li_2(THF)_4.(PhP(Se)_2CH_2CH_2P(Se)_2Ph)Li_2(THF)_6$ (3)

A solution of **1** (150 mg, 0.28 mmol) in 10 mL THF was treated with powdered elemental grey Se (88 mg, 1.12 mmol) in 2 mL THF at -78ºC. The mixture was stirred at room temperature for 1 h to give a colorless solution. Colorless crystals of **3** were obtained from the solution on standing for 1 day at -30 ºC. Yield 205 mg, 73%. Mp > 250ºC. ^{1}H NMR (270 MHz, d_6-DMSO): note that two molecules of coordinated THF were lost in the isolation procedure δ = 1.72 (m, 32 H, THF), 1.80-2.20 (br m, 8 H, CH_2CH_2), 3.58 (m, 32 H, THF), 7.25-7.27 (m, 12 H, *m,p*- C_6H_5), 7.93 (m, 8 H, *o*- C_6H_5). ^{13}C NMR(67 MHz, d_6-DMSO): δ = 25.10 (THF), 40.4 ($^1J_{CP}$ = 44 Hz, -PCH_2-), 66.99 (THF), 126.48, 128.32, 130.70 (*o/m/p*-C_6H_5). ^{31}P NMR (109 MHz, d_6-DMSO): δ = 24.18 (m, $^1J_{PSe}$ = -686, $^3J_{pp}$ = 67, $^4J_{PSe}$ = 5 Hz). ^{77}Se NMR (51.5 MHz, d_6-DMSO): δ = -6.5 (d, $^1J_{PSe}$ = -684 Hz). IR: υ (cm^{-1}) = 1377 s, 1303 m, 1151 m, 1094 m, 1040 m, 890 m, 750 w, 721 m, 692 m, 518 m, 500 m, 465 w. Elemental analysis for $C_{60}H_{92}O_8Li_4P_4Se_8$ calcd(%) C 41.78, H 5.38; found C 41.12, H 5.29.

Preparation of $[PhP(Te)_2CH_2CH_2P(Te)_2Ph][Li_8(OH)_6(THF)_8]$ (4)

A solution of **1** (150 mg, 0.28 mmol) in 10 mL THF was treated with powdered elemental Te (143 mg, 1.12 mmol) in 2 mL THF at -78ºC. The mixture was warmed to 0 ºC and stirred for 1 h to give an orange solution which was filtered over celite. A small batch of yellow needles of **4** were obtained from the solution on standing for 7 days at -30 ºC. The extreme air and moisture sensitivity of **4** hampered further spectroscopic studies, however analysis of the reaction mixture with ^{31}P NMR spectroscopy revealed an almost quantitative yield of the bis(ditellurophosphinate): ^{31}P NMR (109 MHz, THF/C_6D_6), -131.1 (d satellites, $^1J_{PTe}$ = 1361 Hz).

X-ray Structure Determinations of 2, 3, and 4. The crystals were all taken directly from the mother liquor, covered with a perfluorinated ether and mounted on the top of a glass capillary under a flow of cold gaseous nitrogen. The data were collected using Nonius Kappa CCD (**2**) and Bruker P4 (**3** and **4**) diffractometers using Mo-Kα (**2** and **3**) and Cu-Kα (**4**) radiation; the latter was a rotating anode source. All three diffractometers were fitted with Oxford Cryostream low-temperature devices. Crystal data and other information on the structure determination procedures are given in Table 1.

The crystals of **3** were found to be relatively weak scatterers of X-rays, and so the data collection was trimmed to a maximum 2θ of 45°, resulting in a data set with a mean I/σ of ca. 10.3. The crystals of **4** were found to be very weak scatterers of X-rays, despite the use of a rotating anode copper source in an effort to generate as much intensity as possible. Even with the data collection trimmed to a maximum 2θ of 115°, the mean I/σ of the data set is still only ca. 2.5. It is thus unsurprising that the structure is poorly resolved. Despite this, however, the basic structural framework is clear.

The structures were solved by direct methods,[22] and refined using full-matrix least-squares based on F^2.[23] Full occupancy non-hydrogen atoms were refined with anisotropic displacement parameters, and isotropic hydrogen atoms were constrained with a riding model. Both THF molecules in the structure of **2** were found to be disordered. Two orientations were found for the methylene groups in the O(1) based THF molecule with occupancies of 50:50, whilst three orientations were found for the methylene groups in the O(2) based molecule with occupancies of 34:33:33. The O(1) and O(5) based THF molecules in the structure of **3** were also found to be disordered. In each case two orientations were found for the two methylene atoms not linked to the oxygen, with occupancies of ca. 87:13 and 58:42% respectively. The geometries of the partial occupancy orientations were optimised, and the non-hydrogen atoms of the major occupancy orientations were refined anisotropically, whilst those of the minor occupancy orientations were refined isotropically. The oxygen atoms of the Li_8O_6 cube in the structure of **4** were assumed to be protonated for charge balance reasons. These hydrogen atoms could not be located, and so the atom list for the asymmetric unit is low by H_3, and the UNIT low by H_{12}. The geometries of all four of the tetrahydrofuran molecules in **4** were optimised.

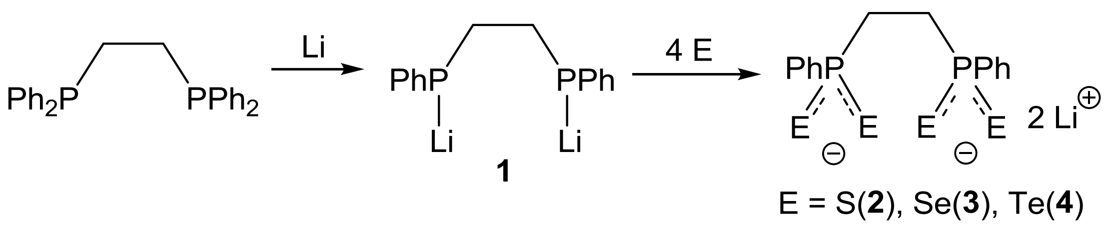
Table 1. Crystallographic data for compounds **2**, **3** and **4**.

data	**2**	**3**	**4**
chemical formula	$C_{30}H_{46}O_4S_4P_2Li_2$	$C_{38}H_{62}O_6Se_4P_2Li_2$. $C_{30}H_{46}O_4Se_4P_2Li_2$	$C_{46}H_{84}O_{14}Te_4P_2Li_8$
fw	674.73	1868.86	1488.99
T (K)	180(2)	183(2)	183(2)
Crystal system	Trigonal	Monoclinic	Monoclinic
space group	R-3 (no. 148)	$P2_1$/n (no. 14)	P2(1)/n (no. 14)
a (Å)	28.5600(7)	16.969(5)	12.8696(13)
b (Å)	-	13.379(3)	15.3157(16)
c (Å)	12.2070(4)	18.139(7)	16.1711(14)
β (deg)	-	91.38(3)	91.215(7)
V ($Å^3$)	8622.9(4)	4117(2)	3186.7(5)
Z	9	2	2
ρ_{calcd} (g cm^{-3})	1.169	1.508	1.552
μ (mm^{-1})	0.361	3.678	15.204
Reflections Collected	26981	5544	4571

Reflections Independent (R_{int})	3880(0.0972)	5334 (0.0393)	4350 (0.0723)
GOF on *F*2	1.059	0.954	0.966
R_1 (I>2σ(I))	0.0778	0.0440	0.1255
wR_2(I>2σ(I))	0.2023	0.0850	0.3078

Results and Discussion

The bis(dichalcogenophosphinate) complexes **2-4** were all prepared via a common route starting from dppe (Scheme 2). Treatment of dppe with elemental lithium gave 1,2-dilithio-1,2-di(phenylphosphine)ethylene (**1**) in high yield in accordance with literature procedures.[21,24] Subsequent reaction with powdered elemental chalcogen (either S_8, Se or Te) gave the desired bis(dichalcogenophosphinate). Each complex was fully characterized by multinuclear NMR spectroscopy as well as X-ray crystallography.



Scheme 2

The sulfur derivative $(PhP(S)_2CH_2CH_2P(S)_2Ph)Li_2(THF)_4$ **2** was prepared as colorless crystals in a clean and high yielding (92%) process. Single crystal X-ray diffraction studies reveal **2** to crystallize in the centrosymmetric trigonal space group R-3. The structure of **2** contains two symmetry related dithiophosphinate groups bridged by an ethylene group (Figure 1); selected bond lengths and angles are listed in Table 2.

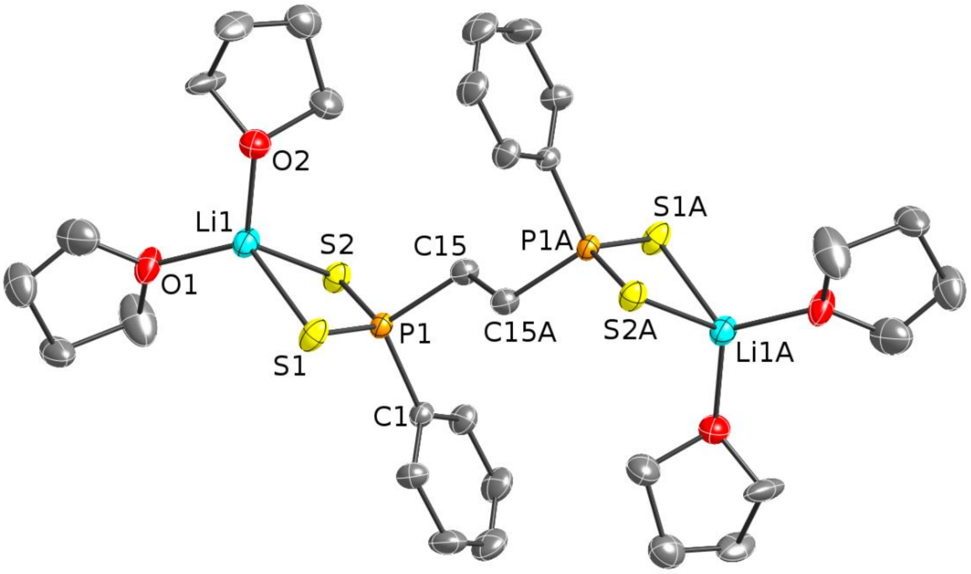


Figure 1. Solid-state structure of $(PhP(S)_2CH_2CH_2P(S)_2Ph)Li_2(THF)_4$ **2**. Hydrogen atoms and disorder in the THF molecules are omitted for clarity. Thermal ellipsoids are displayed at 30% probability level. Symmetry transformations used to generate equivalent atoms: 2/3-x,1/3-y,1/3-z

Table 2. Selected bond lengths (Å) and angles (deg) for complex **2**.

P(1)–S(1)	1.9749(17)	S(1)-Li(1)	2.494(9)
P(1)-S(2)	2.0028(16)	S(2)–Li(1)	2.491(9)
P(1)-C(1)	1.827(4)	Li(1)-O(1)	1.908 (9)
P(1)-C(15)	1.842(5)	Li(1)-O(2)	1.915(10)
P(1)-S(1)-Li(1)	79.3(2)	S(1)-Li(1)-S(2)	84.2(3)
P(1)-S(2)-Li(1)	78.9(2)	S(1)-P(1)-S(2)	114.34(7)
C(1)-P(1)-S(1)	111.37(16)	C(15)-P(1)-S(1)	112.27(17)
C(1)-P(1)-S(2)	110.39(15)	C(15)-P(1)-S(2)	106.15(16)
C(1)-P(1)-C(15)	101.5(2)		

Dichalcogenophosph(in)ates have been shown to display a range of coordination patterns.[1] Monodentate coordination through just one chalcogen atom (**A**; Figure 2) is uncommon, with bidentate chelating (**B**, **C**) or bridging (**D**-**G**) more frequently observed.[1] In the chelating mode the ligand can coordinate to the metal from the two chalcogen atoms in either an isobidentate symmetrical mode (**B**) or an anisobidentate asymmetrical mode (**C**). Similar symmetrical and asymmetrical modes have been observed for these ligands when they bridge two or more metal atoms (**D**-**G**). In complex **2** the dithiophosphinate groups coordinate the lithium cation in an anisobidentate fashion (type **C**) with unequal phosphorus-sulfur bond lengths (P(1)-S(1) 1.975(2); P(1)-S(2) 2.003(2) Å) indicative of incomplete delocalization of the negative charge throughout the PS_2 fragment. Sulfur-lithium bond lengths are approximately equal (S(1)-Li(1) 2.494(9); S(2)-Li(1) 2.491(9) Å). The resultant four membered S(1)-P(1)-S(2)-Li(1) chelate ring is close to planar (sum of internal angles = 356.81˚) with a S(1)-Li(1)-S(2) bite angle of 84.2(3)˚ and a S(1)-P(1)-S(2) angle of 114.34(7)˚. Two other lithium dithiophosph(in)ates have been previously crystallographically characterized – $(Cp^*{}_2PS_2Li.DME)_2$ in which the ligand adopts an isobidentate type **B** coordination mode,[25] and $[(Cy_2PS_2)_4Li_5(OH)]_2$ in which the ligands bridge up to four metal centers in four different bonding modes.[26]

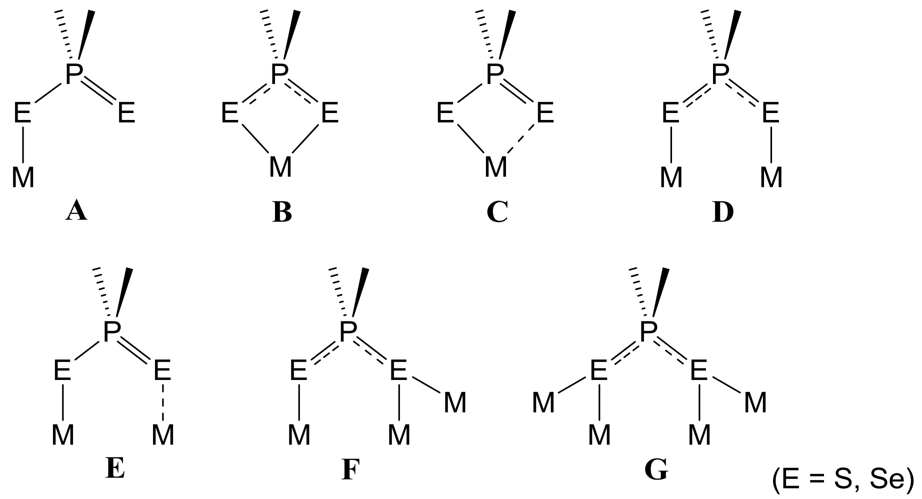


Figure 2 Coordination patterns for dichalcogenophosph(in)ates

The homologous tetra-selenium ligand (**3**) was prepared in an analogous fashion to **2** with an overall 73% yield of crystalline product. Single crystal X-ray diffraction studies show **3** to crystallize in the centrosymmetic space group P2(1)/n and contain two chemically distinct species within the lattice; $(PhP(Se)_2CH_2CH_2P(Se)_2Ph)Li_2(THF)_4$ and $(PhP(Se)_2CH_2CH_2P(Se)_2Ph)Li_2(THF)_6$ (Figure 3). These species differ in the coordination mode of the diselenophosphinate units and also the degree of THF solvation of the lithium cations.

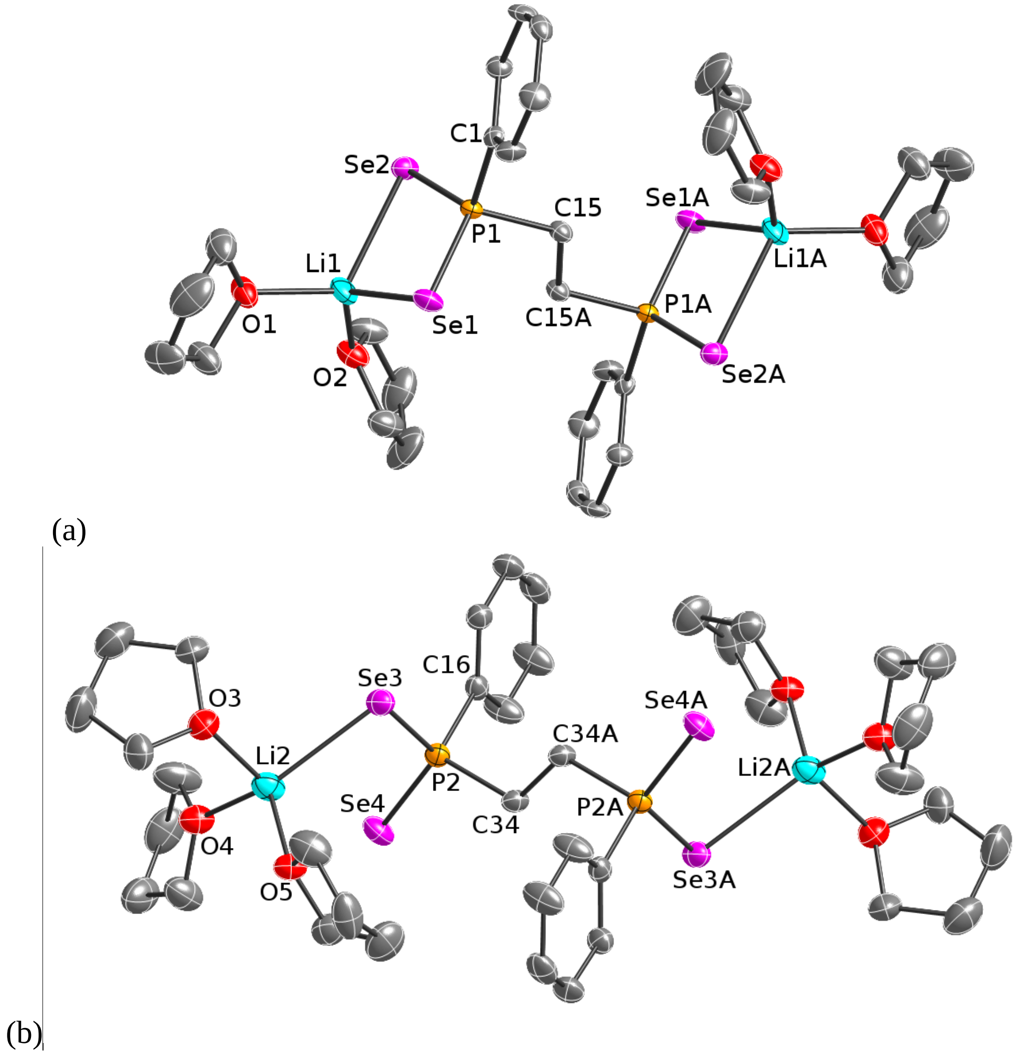


Figure 3. Solid-state structures of a) $(PhP(Se)_2CH_2CH_2P(Se)_2Ph)Li_2(THF)_4$ and b) $(PhP(Se)_2CH_2CH_2P(Se)_2Ph)Li_2(THF)_6$ which co-crystallize in **3**. Hydrogen atoms and disorder in the THF molecules are omitted for clarity. Thermal ellipsoids are displayed at

30% probability level. Symmetry transformations used to generate equivalent atoms: 2+x,1+y,1+z

Table 3. Selected bond lengths (Å) and angles (deg) for **3**.

P(1)-Se(1)	2.1514(18)	P(1)-C(1)	1.822(6)
P(1)-Se(2)	2.1508(19)	P(1)-C(15)	1.840(7)
Se(1)-Li(1)	2.630(14)	Li(1)-O(1)	1.926(14)
Se(2)-Li(1)	2.603(13)	Li(1)-O(2)	1.905(13)
P(3)-Se(3)	2.155(2)	P(3)-C(34)	1.838(6)
P(3)-Se(4)	2.1409(19)	Li(2)-O(3)	2.012(14)
Se(3)-Li(4)	2.634(13)	Li(2)-O(4)	1.930(13)
P(3)-C(16)	1.847(6)	Li(2)-O(5)	1.944(12)
P(1)-Se(1)-Li(1)	77.7(3)	Se(1)-Li(1)-Se(2)	87.5(3)
P(1)-Se(2)-Li(1)	78.3(3)	Se(1)-P(1)-Se(2)	114.58(8)
C(1)-P(1)-Se(1)	111.6(2)	C(15)-P(1)-Se(1)	109.2(2)
C(1)-P(1)-Se(2)	109.9(2)	C(15)-P(1)-Se(2)	109.7(2)
C(1)-P(1)-C(15)	100.9(3)	Se(3)-P(3)-Se(4)	116.54(8)
P(3)-Se(3)-Li(2)	96.5(3)	C(16)-P(2)-Se(3)	109.0(2)
C(34)-P(2)-Se(3)	108.9(2)	C(16)-P(2)-Se(4)	110.0(2)
C(34)-P(2)-Se(4)	108.1(2)	C(16)-P(2)-C(34)	104.6(3)

In the first of the the bis(diselenophosphinate) molecules $(PhP(Se)_2CH_2CH_2P(Se)_2Ph)Li_2(THF)_4$ (Figure 3a) the lithium cations are each solvated by two THF molecules (Li(2)-O(2) = 1.905(13); Li(2)-O(1) =1.926(14) Å) and are also coordinate to two selenium atoms from a diselenophosphinate group (Se(1)-Li(2)=2.630(14); Se(2)-Li(2)=2.604(13) Å). The diselenophosphinate group therefore adopts a type **B** (Figure 2) isobidentate coordination mode with equivalent phosphorus – selenium distances (Se(1)-

P(1)=2.1514(18), Se(2)-P(1)=2.1508(19) Å). This is indicative of delocalisation of the negative charge in the PSe_2 unit and a phosphorus-selenium bond order of 1.5. The four-member Se-P-Se-Li chelate is approximately planar (sum of internal angles = 358.1˚) with a Se(1)-Li(2)-Se(2) bite angle of 87.5(3)˚ and a Se(2)-P(1)-Se(1) angle of 114.58(8) ˚.

In the other co-crystalline molecule $(PhP(Se)_2CH_2CH_2P(Se)_2Ph)Li_2(THF)_6$ (Figure 3b) each lithium cation is coordinated by three THF molecules (mean Li-O = 1.962 Å) with just one lithium- selenium bonding interaction (Se(3)-Li(4) = 2.634(13) Å). The other selenium atom Se(4) is non-coordinated to the lithium centre (Li(4)...Se(4) distance = 3.516(13) Å) and in contrast to $(PhP(Se)_2CH_2CH_2P(Se)_2Ph)Li_2(THF)_4$ the diselenophosphinate unit therefore adopts a rare monodentate coordination mode (**A**, Figure 2). Phosphorus-selenium bond distances in $(PhP(Se)_2CH_2CH_2P(Se)_2Ph)Li_2(THF)_6$, Se(3)-P(3) 2.155(2) and Se(4)-P(3) 2.1409(19) Å, are slightly asymmetric (with more double bond character in the non-coordinating P(3)-Se(4) unit) but are still indicative of P-Se bond orders in-between 1 and 2 with some delocalization of the negative charge. The Se(4)-P(3)-Se(3) angle of 116.54(8)˚ is slightly widened compared to that in $(PhP(Se)_2CH_2CH_2P(Se)_2Ph)Li_2(THF)_4$. The disparity displayed in coordination modes between the diselenophosphinate groups in the two co-crystalline molecules can be accounted for by the steric requirements of fitting three THF molecules around Li(3), itself a consequence of the weaker Li-Se bonding in **3** when compared to the S-Li bonding in **2**.

^{31}P NMR spectroscopic studies on **3** in D_6-DMSO confirm the formation of the bis(diselenophosphinate) ligand (Figure 4). The $^{1}J_{PSe}$ coupling constant of -686 Hz lies in between common single bond $^{1}J_{P\text{-}Se}$ and double bond $^{1}J_{P=Se}$ values,[27] and is comparable in magnitude to that reported for other diselenophosphinates.[15] In addition, $^{3}J_{PP}$ and $^{4}J_{PSe}$ coupling constants of 67 and 5 Hz respectively are observed. ^{77}Se NMR studies reveal one doublet resonance at δ = -6.5 ($^{1}J_{PSe}$ = -684 Hz). NMR studies therefore indicate the presence of just one species in solution, at variance with the two different coordination modes observed in the solid-state structure. This is most likely accounted for by the formation of solvent-separated ion pairs in solution, comprising of the dianionic $[PhP(Se)_2CH_2CH_2P(Se)_2Ph]^{2-}$ ligand and DMSO/THF solvated lithium cations.

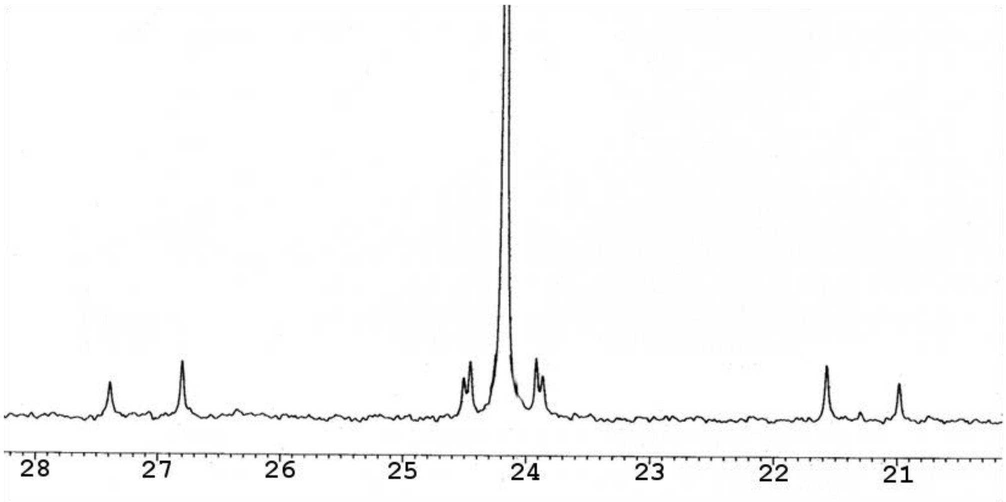
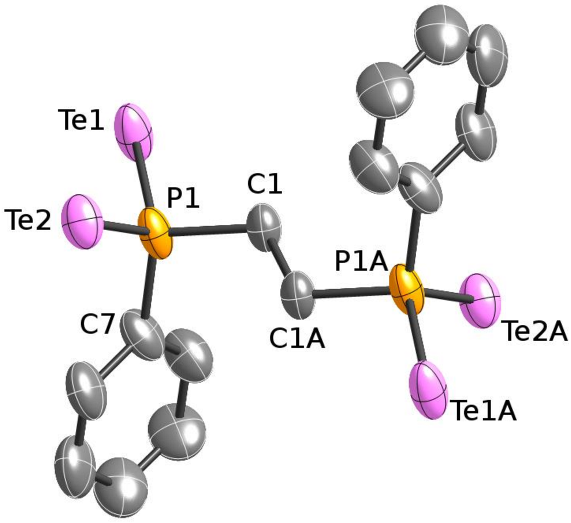


Figure 4. ^{31}P NMR spectrum (109 MHz) of **3** in D_6-DMSO. The main peak at 24.2 ppm has been truncated for ease of viewing.

The tellurium derivate **4** was prepared analogously to **2** and **3**. ^{31}P NMR studies on the reaction mixture indicate near quantitative conversion of the dilithiated bisphosphine **1** into the bis(ditellurophosphinate) **4**; one main NMR resonance was observed at -131.1 ppm with ^{127}Te doublet satellites ($^1J_{PTe}$ = 1361 Hz). Due to the broad nature of the NMR resonances it was not possible to resolve any further $^3J_{PP}$ or $^4J_{PTe}$ couplings. The $^1J_{PTe}$ coupling constant is comparable to that reported for the ditellurophosphinate $[Ph_2PTe_2][Li(THF)_{3.5}(TMEDA)_{0.25}]$ (1530 Hz)[14], but lower in magnitude than $^1J_{PTe}$ values for typical triorganophosphane tellurides (1548-1743 Hz)[27], thus indicative of a slight elongation of a PTe double bond.

Initial attempts to crystallize **4** were unsuccessful, however on storage for several weeks a small batch of yellow needles were obtained. Although the crystallographic data for **4** is of poor quality, the composition and overall structural features are salient: namely a bis(ditellurophosphinate) dianion and a $[Li_8(OH)_6]^{2+}$ polyhedral cluster cation solvated by eight THF molecules (Figure 5).

(a)



(b)

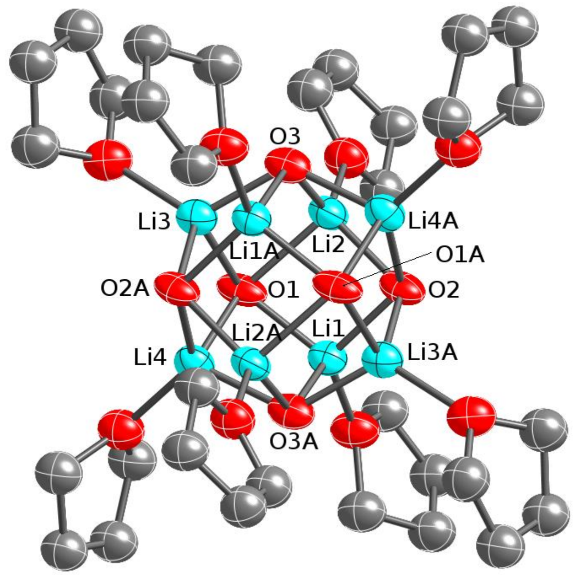


Figure 5. Solid-state structures of a) the $[PhP(Te)_2CH_2CH_2P(Te)_2Ph]^{2-}$ dianion and b) the $[Li_8(OH)_6(THF)_8]^{2+}$dication present in **4**. Hydrogen atoms are omitted for clarity. Thermal

ellipsoids are displayed at 20% probability level. Symmetry transformations used to generate equivalent atoms: x,1+y,1+z; 1+x, y,1+z

The bis(ditellurophosphinate) $[PhP(Te)_2CH_2CH_2P(Te)_2Ph]^{2-}$ anion in **4** (Figure 5a) lies on a center of symmetry. The phosphorus - tellurium bond lengths, P(1)-Te(1) 2.397(8) and P(1)-Te(2) 2.377(7) Å, are equivalent and indicative of negative charge delocalization throughout the PTe_2 unit. The Te(1)-P(1)-Te(2) bond angle is 119.5(4)˚. Structural parameters for **4** are therefore directly comparable to the only other crystallographically characterized ditellurophosph(in)ate, $[Ph_2PTe_2][Li(THF)_{3.5}(TMEDA)_{0.25}]$; mean P-Te 2.390 Å, Te-P-Te 118.56(15)˚.[14] The absence of any Te-Li bonding interactions in **4**, leading to the formation of the separated ion pair structure, can be accounted for by the known weakness of Te-Li bonding.[14]

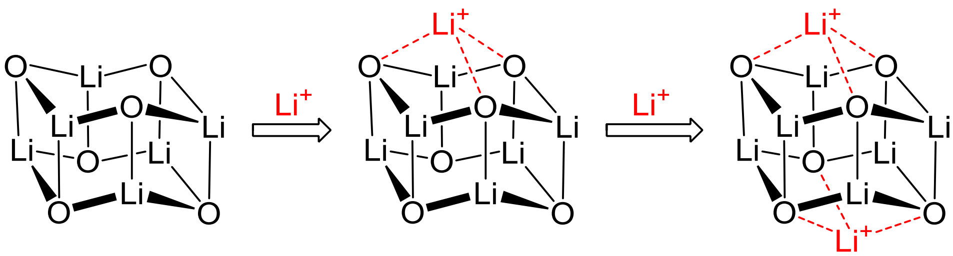


Figure 6. Putative formation of the $[Li_8(OH)_6]^{2+}$polyhedral dication in **4**. Hydrogen atoms are omitted for clarity.

The polyhedral cation in **4**, $[Li_8(OH)_6(THF)_8]^{2+}$ (Figure 5b), is unique in the field of lithium coordination chemistry. We believe it to be formed from the reaction of lithium cations in the reaction mixture with small amounts of moisture which had slowly impregnated the reaction vessel on prolonged storage. It is a rare example of a molecule containing LiOH units, and is, as far as we are aware, the first homoleptic LiOH cluster. The cluster is perhaps best considered as a hexameric $(LiOH)_6$ aggregate, capped above and below by additional lithium cations (Figure 6), with each lithium solvated by one THF molecule. Hexameric $[LiOR]_6$ clusters comprising of two stacked six-membered Li_3O_3 rings (of chair conformation) are well known in the literature:[28] These include lithium alkoxides such as [LiO*t*Bu]$_6$[29] and $[LiOCMePh]_6$[30], lithium aryloxides such as $[LiOPh.THF]_6$ [31] and lithium silanolates such as $[t\text{BuMe}_2\text{SiOLi}]_6$[32]. Moreover, there are two published examples of aggregates in which an additional lithium cation caps one side of such a hexamer to give a hepta-metallic $Li_7(OR)_6$ type cluster (see Figure 6). These are $[Li_7(Ot\text{Bu})_6][Cu_2(Si(SiMe_3)_3)_2]$[33] which contains a cationic $[Li_7(OR)_6]^+$ cluster and the neutral complex $[(ROLi)_6.LiCH_2Ph]$ (ROH = 1-methyl-(S)-2-(hydroxymethyl)pyrrolidine) in which the unshielded “top side” of the aminoalkoxide cluster is capped by the lithium center of benzyllithium via three Li−O interactions.[34] However, the structure of the lithium hydroxide polyhedron in **4** is, to our knowledge, the first example where a $[LiOR]_6$ hexamer can formally be considered to be capped both on top and beneath the hexamer (see Figure 6), thus giving a rhombic dodecahedral cluster with 14 vertices, 12 faces and 24 edges (Figure 7). The unique formation of an octa-metallic $[Li_8(OR)_6]^{2+}$ cluster in **4** is presumably facilitated by the low steric requirements of the OH groups in this case.

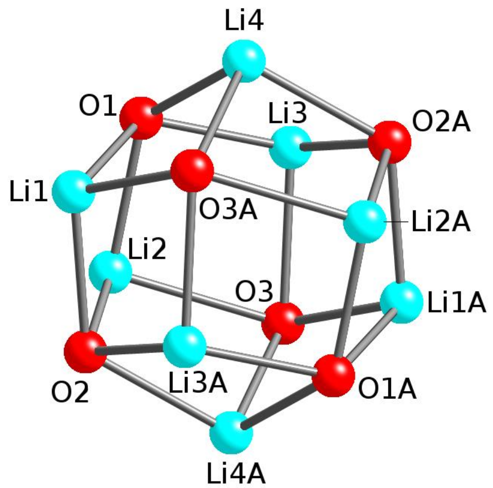


Figure 7. Picture of the Li_8O_6 core of the $[Li_8(OH)_6(THF)_8]^{2+}$ polyhedron in **4**.

Within the $[Li_8(OH)_6(THF)_8]^{2+}$ polyhedron all the lithium cations and all the hydroxyl groups sit in approximately equivalent coordination environments: Each lithium cation binds to three OH groups and a THF oxygen giving a distorted tetrahedral environment, whilst each OH group caps four lithium cations giving a square based pyramid geometry at oxygen (Figure 7). The poor quality of the crystallographic data prohibits a detailed analysis of the bond lengths within the polyhedron. Li-OH bond distances within the cluster lie in the range 1.84(4) to 2.10(4) Å (mean 1.94 Å), whilst Li-O(THF) bonds lie in the range 1.96(3) to 1.99(3) Å (mean 1.98 Å).

Concluding Remarks

The first clean and high yielding route to bis(dichalcogenophosphinate)s has been achieved for sulfur, selenium and tellurium homologs, using elemental chalcogen insertion reactions into the phosphorus-lithium bonds of 1,2-dilithio-1,2-di(phenylphosphine)ethylene. The tellurium homolog **4** is of particular interest, not only as a rare example of a ditellurophosphinate containing ligand, but also due to the observation of a unique $[Li_8(THF)_8(OH)_6]^{2+}$ polyhedral counter cation. This polyhedral cluster most likely arises from the reaction of Li^+ cations in solution with H_2O contaminant. It can be considered to be formally formed from the capping of a $Li_6(OH)_6$ hexamer both above and below the hexameric rings with Li^+ cations, thus giving the first reported rhombic dodecahedral Li_6O_8 polyhedron. This is presumably facilitated by the low steric demands of the OH group.

It should be noted that unlike mono(dichalcogenophosphinate)s, which have been extensively reported in the literature and have found many industrial applications,[1] bis(dichalcogenophosphinate)s remain virtually unstudied. However, the enhanced bridging / chelating ability of these ligands make them suitable targets for further study both for their coordination chemistry,[1,3] as well as for their performance in a range of industrially important processes (for example, metal extraction technologies[35]). Research in this area is ongoing.

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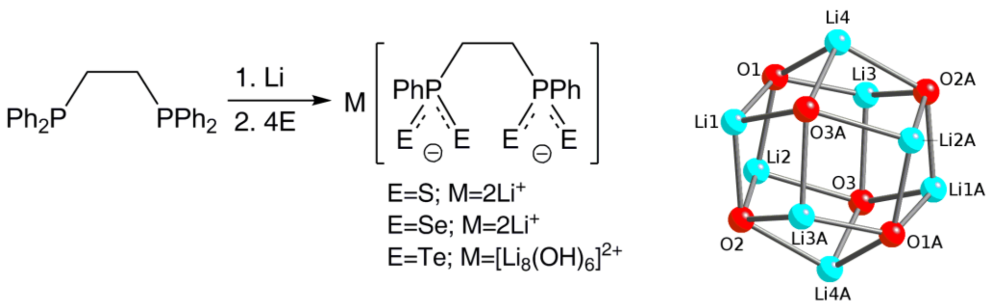

The facile and high yielding synthesis of novel bis(dichalcogenophosphinate) ligands is reported for the sulfur, selenium and tellurium homologs, utilizing the insertion reaction of elemental chalcogen into phosphorus-lithium bonds. The bis(tellurophosphinate) complex is of particular interest due to the unique $[Li_8(OH)_6]^{2+}$ counter cation - a rhombic dodecahedral polyhedron putatively formed from the capping of a hexameric aggregate with lithium cations on its open faces.

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