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Alkali Metal Tetraselenohypodiphosphonates: Synthesis, NMR Spectroscopy and Crystal Structures

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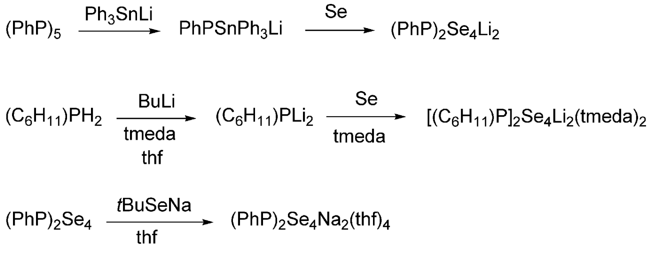
The one-pot reaction of alkyl or aryl dichlorophosphanes $RPCl_2$ with alkali metal selenides M_2Se and M_2Se_2 in a 2:2:1 molar ratio provides a simple and general route to alkali metal tetraselenohypodiphosphonates $(RP)_2Se_4M_2$ (M = Li, Na; R = alkyl, aryl). The new compounds were characterized by multinuclear (^{31}P, ^{77}Se, ^{1}H, ^{13}C) NMR spectroscopy and in two cases by single-crystal X-ray diffraction. The crystal structure of the first solvent-free alkali metal tetraselenohypodiphosphonate salt is presented. The structures reveal a great coordination flexibility of the $(RP)_2Se_4^{2-}$ anions.

Introduction

Phosphorus sulfur anions containing a $>PS_2^-$ function are well known in the literature and are an important class of anions. In particular, the chemistry of dithiophosphinate and dithiophosphate anions has been extensively investigated.[1,2] They have found applications, for example, as lubricant oil additives[3] or as extraction agents.[4] The pioneering work of Kuchen revealed a rich and intriguing complex chemistry for dithiophosphinate anions.[5]

Organophosphorus anions with the heavier group 16 homologues selenium and tellurium are expected to display more interesting coordination chemistry. However, organophosphorus anions with selenium and tellurium are less well documented. Only a few anions including $RPSe_3^{2-}$,[6–8] $R_2PSe_2^-$,[5,7] $R_2PTe_2^-$,[9,10] R_2PSe^-,[7] R_2PTe^-,[10] R_2PSeTe^-[10] and $(RP)_2Se_6^{2-}$[11] have been reported in the literature.

In the course of systematic studies on selenophosphate[12] and selenophosphonate anions in our laboratory, our attention was attracted by the tetraselenohypodiphosphonate anion $(RP)_2Se_4^{2-}$. It contains four selenium atoms available for coordination and is a potentially interesting soft multidentate chelating ligand. There are only three reports in the literature describing the synthesis of $(RP)_2Se_4^{2-}$ anions. The first tetraselenohypodiphosphonate anion, $(PhP)_2Se_4^{2-}$, was reported in 1988 by Schmidpeter et al. and results from the oxidation of $PhP(SnMe_3)^-$ by elemental selenium.[13] A similar route was followed by Davies et al., who obtained the corresponding cyclohexyl-substituted derivative as the lithium salt by oxidation of $(C_6H_{11})PLi_2$ with elemental selenium (Scheme 1).[10]



Scheme 1. Synthetic routes to anions $(RP)_2Se_4^{2-}$ described in the literature.

A different strategy was followed by Rothenberger et al. They started from $(PhP)_2Se_4$ (Woollins' Reagent), which on reduction with *t*BuSeNa yielded the phenyl derivative $(PhP)_2Se_4^{2-}$.[11]

Here we describe a general and straightforward synthesis of lithium and sodium salts of alkyl and aryl tetraselenohypodiphosphonate anions by starting from easily available materials. The new salts were characterized by multinuclear (^{31}P, ^{77}Se, ^{1}H, ^{13}C) NMR spectroscopy. In addition, to illustrate the coordination behaviour of the hypodiphosphonate anions, the molecular and crystal structures of $(PhP)_2Se_4[Li(thf)_2]_2$ (**2e**) and $[(2\text{-}C_4H_3S)P]_2Se_4Na_2$ (**1g**) are presented and discussed. Compound **1g** represents the first structurally characterized solvent-free tetraselenohypodiphosphonate salt.

Results and Discussion

Sodium tetraselenohypodiphosphonates **1a**–**g** were readily prepared by one-pot reaction of the corresponding dichlorophosphane $RPCl_2$ with Na_2Se and Na_2Se_2 in a molar ratio of 2:2:1. When Li_2Se and Li_2Se_2 were used in place of the sodium selenides, corresponding lithium tetraselenohypodiphosphonates **2c**,**e** were obtained (Scheme 2).

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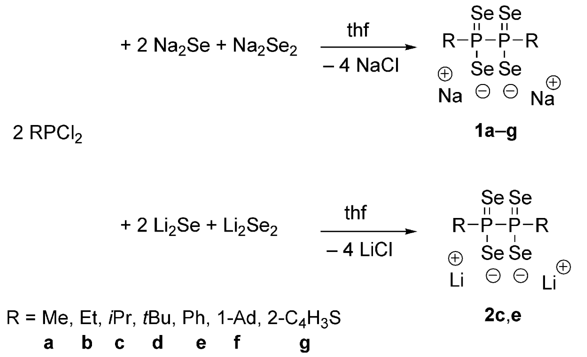

Scheme 2. General synthesis of alkali metal tetraselenohypodiphosphonate salts.

By keeping the exact stoichiometry, the $(RP)_2Se_4{}^{2-}$ anions were formed as the only products detectable by ^{31}P NMR spectroscopy. If the sodium selenide used was contaminated by small amounts of Na_2Se_2, the triselenophosphonate anions $RPSe_3{}^{2-}$ were observed as byproducts.[14]

Tetraselenohypodiphosphonates **1** and **2** were isolated as colourless crystalline solids. The isolated yields ranged from 25% for **1d** to 96% for thiophene-substituted derivative **1g**. The salts are stable at ambient temperature under an inert gas atmosphere. Exposed to air, however, they are rapidly oxidized and adopt a red colour. Hypodiphosphonates **1** and **2** are practically insoluble in pentane and toluene and readily soluble in polar organic solvents like thf and acetonitrile.

Identity and structure of the $(RP)_2Se_4{}^{2-}$ anions in salts **1** and **2** result unambiguously from their ^{31}P and ^{77}Se NMR spectra. The ^{31}P NMR spectra display, in addition to the singlet for the isotopomer without magnetically active selenium, the characteristic eight-line pattern for the A part of an AA′X spectrum,[15] which results from the isotopomer with one ^{77}Se nucleus (Figure 1). From this spectrum, the "hidden" coupling constant between the practically isochronous, but magnetically inequivalent, phosphorus nuclei can be directly extracted.[13] In addition, the signals of the isotopomer with two ^{77}Se nuclei each bonded at a different phosphorus atom are visible (A part of AA′XX′). The small $^3J_{SeSe}$ coupling constant causes the expected ten-line pattern to collapse to a six-line pattern, four lines of which fall under the lines of the isotopomer with one ^{77}Se nucleus. This is confirmed by the ^{77}Se NMR spectrum (Figure 2), which shows in addition to the expected five lines for the isotopomer with one ^{77}Se nucleus (X part of AA′X)[15] the X part of the AA′XX′ for the isotopomer with two ^{77}Se nuclei. Four of the six lines are clearly visible here.

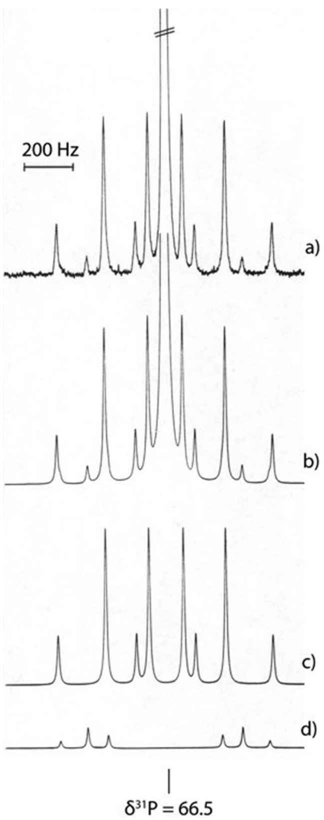

Figure 1. $^{31}P\{^1H\}$ NMR spectrum of **1c** (0.1 M in thf): (a) observed spectrum showing the ^{77}Se satellite pattern; (b) calculated total spectrum (98.9% of the total ^{31}P intensity) resulting from the addition of the signal for the isotopomer without ^{77}Se (73.0%); (c) the spectrum of the isotopomer with one ^{77}Se nucleus (A part of AA′X, 23.9%); (d) the spectrum of the isotopomer with two ^{77}Se nuclei bonded to different phosphorus atoms (A part of AA′XX′, 2.0%).

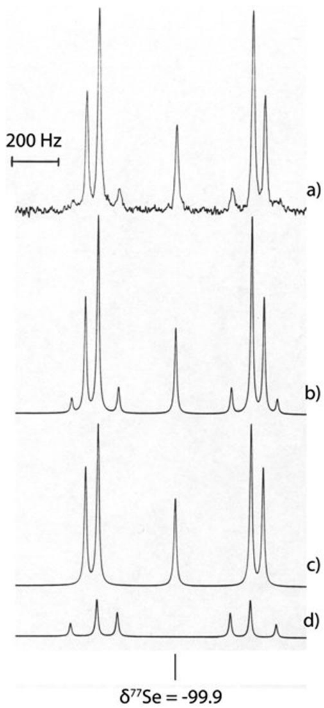

Figure 2. $^{77}Se\{^1H\}$ NMR spectrum of **1c** (0.1 M in thf): (a) observed spectrum; (b) calculated total spectrum (91.9% of the total ^{77}Se intensity) resulting from the addition of (c) the spectrum of the isotopomer with one ^{77}Se nucleus (X part of AA′X, 78.9%) and of (d) the spectrum of the isotopomer with two ^{77}Se nuclei bonded to different phosphorus atoms (X part of AA′XX′, 13.0%).

The ^{31}P and ^{77}Se NMR spectroscopic data of the hypodiphosphonate anions in **1** and **2** are presented in Table 1. The ^{31}P chemical shifts of **1a**–**g** range from 32 to 102 ppm; the shifts at lowest field are observed for the *t*Bu (**1d**) and 1-Ad (**1f**) derivatives. The ^{77}Se NMR signal appears between –123 and +68 ppm at the low-field end of the range typical for phosphane selenides (+149 to –497 ppm).[16] The $^{1}J_{PP}$ coupling constant is large with values between 51 and 183 Hz and most probably negative.[13] The values for $^{1}J_{SeP}$ (–591 to –684 Hz) are typical for one-coordinate selenium bonded to phosphorus and compare well to those observed for phosphane selenides.[16] The ^{31}P and ^{77}Se NMR spectroscopic data of lithium hypodiphosphonates **2** differ only slightly from those observed for the corresponding sodium salts. The data in Table 1 are also in agreement with those reported for cyclohexyl derivative **1** (R = C_6H_{11}).

Table 1. ^{31}P and ^{77}Se NMR spectroscopic data of alkali metal tetraselenohypodiphosphonates **1** and **2** (in thf).[a]

	$\delta^{31}P$ [ppm]	$\delta^{77}Se$ [ppm]	$^{1}J_{PP}$ [Hz]	$^{1}J_{SeP}$ [Hz]	$^{2}J_{SeP}$ [Hz]
1a	32.6	–72.6	(–)137.0	–593.0	–4.4
1b	53.7	–122.8	(–)148.0	–591.9	–4.7
1c	66.4	–99.9	(–)182.8	–596.3	–3.3
1d	101.7	68.3	(–)51.9	–683.5	+0.5
1e[b]	54.5	–85.3	(–)142.7	–618.8	+0.8
1f	100.6	35.5	(–)56.9	–680.7	+0.4
1g	35.0	–34.8	(–)126.2	–619.8	<0.2
2c	64.1	–110.5	(–)178.9	–602.7	–7.4
2e	54.5	–70.2	(–)145.3	–636.4	+4.3

[a] The relative signs for $^{1}J_{SeP}$ and $^{2}J_{SeP}$ result from the iterative spectral fitting by assuming a negative value[17] for $^{1}J_{SeP}$. [b] The data for **1e** differ slightly from those reported.[11]

The tetraselenohypodiphosphonate anions can act as chelating ligands coordinating through two selenium atoms bonded either to the same phosphorus atom (**A**) or to different phosphorus atoms (**B**) (Figure 3). In addition, a combination of the two coordination modes is also possible.

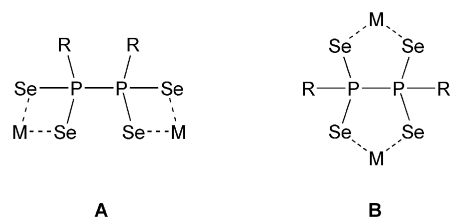

Figure 3. Coordination modes of the tetraselenohypodiphosphonate anions $(RP)_2Se_4^{2-}$.

The two structures of tetraselenohypodiphosphonate salts reported so far in the literature fit well in this scheme. In the case of $[(C_6H_{11})P]_2Se_4[Li(tmeda)]_2$, exclusive coordination of the hypodiphosphonate anion through the selenium atoms at different phosphorus atoms (mode **B**) is observed.[10] For $(PhP)_2Se_4Na_2(thf)_3$, however, Rothenberg et al. observed that both coordination modes (**A** and **B**) are simultaneously present in the crystal structure. In order to learn more on the coordination ability of the tetraselenohypodiphosphonate anions, the molecular and crystal structures of the lithium salt $(PhP)_2Se_4[Li(thf)_2]_2$ (**2e**·4thf) and the sodium salt $[(2\text{-}C_4H_3S)P]_2Se_4Na_2$ (**1g**) were determined by single-crystal X-ray diffraction.

$(PhP)_2Se_4[Li(thf)_2]_2$ (**2e**·4thf) crystallizes in the monoclinic space group $P2_1/n$ with two formula units in the unit cell. A view of the molecular structure is shown in Figure 4.

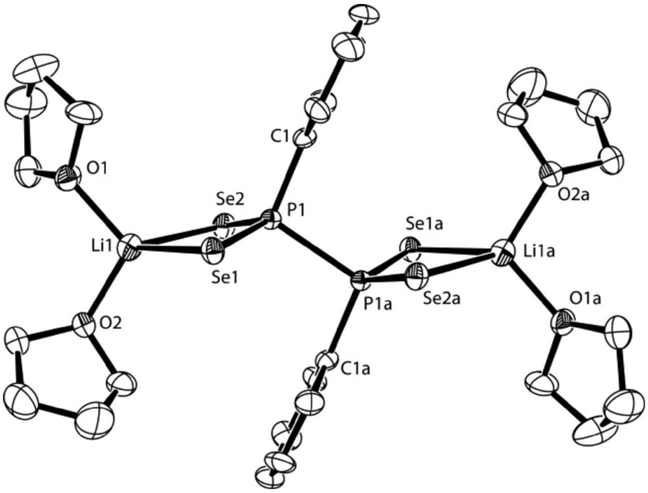

Figure 4. ORTEP view of the molecular structure of $(PhP)_2Se_4[Li(thf)_2]_2$ (**2e**·4thf) in the crystal (ellipsoids at 50 %). Label letter 'a' denotes the symmetry operation 1 – *x*, –*y*, –*z*.

The tetraselenohypodiphosphonate anion adopts a *trans* conformation around the P–P bond with the two phenyl groups in *anti* orientation to one another. Each half of the anion coordinates through both selenium atoms to one lithium ion acting as a bidentate chelating ligand (mode **A**). The slightly distorted tetrahedral coordination sphere around the lithium ions is completed by two thf molecules. This arrangement results in the formation of the units shown in Figure 4, which are packed to build the crystal.

Selected distances and angles for $(PhP)_2Se_4[Li(thf)_2]_2$ (**2e**·4thf) are contained in Table 2. The P–P distance of 2.251(1) Å is typical for a P–P single bond (2.2 Å). The P–Se distances of 2.146(1) and 2.147(1) Å are practically identical and are in between the distances characteristic for a P–Se single and a P–Se double bond. The coordination around the phosphorus atoms is slightly distorted tetrahedral. Both Se–Li distances [2.571(7) and 2,601(7) Å] compare well with those in the cyclohexyl derivative $[(C_6H_{11})P]_2Se_4[Li(tmeda)]_2$[10] and similar[7] compounds.

Table 2. Selected distances [Å] and angles [°] for $(PhP)_2Se_4[Li(thf)_2]_2$ (**2e**·4thf).

Se1–P3	2.146(1)	Se2–Li1	2.601(7)
Se2–P3	2.147(1)	P3–C1	1.818(3)
P3–P3a	2.251(1)	O1–Li1	1.908(7)
Se1–Li1	2.571(7)	O2–Li1	1.894(7)
Se1–P3–Se2	115.6(1)	P3–Se2–Li1	76.6(1)
Se1–P3–C1	110.8(1)	Se2–Li1–O2	115.8(3)
Se1–P3–P3a	108.3(1)	O1–Li1–O2	107.8(4)
Se2–P3–C1	111.2(1)	Se2–Li1–O1	111.8(3)
Se2–P3–P3a	108.1(1)	Se1–Li1–Se2	89.2(2)
P3a–P3–C1	101.8(1)	Se1–Li1–O1	116.5(3)
P3–Se1–Li1	77.3(1)	Se1–Li1–O2	115.1(3)

A comparison of the molecular structures of $(PhP)_2Se_4[Li(thf)_2]_2$ (**2e**·4thf) and $[(C_6H_{11})P]_2Se_4[Li(tmeda)]_2$[10] impressively shows the flexibility of the tetraselenohypodiphosphonate anion acting as a ligand. In both cases, individual units are observed to form the crystal and in both cases the anion acts as a bidentate chelating ligand towards lithium. The slight variation of the substituent (phenyl for cyclohexyl) and of the additional ligands (thf for tmeda) results in a change in the coordination mode from **B** in $[(C_6H_{11})P]_2Se_4[Li(tmeda)]_2$ to **A** in $(PhP)_2Se_4[Li(thf)_2]_2$ (**2e**·4thf). A second difference is observed in the P–Se distances, which are practically equal in $(PhP)_2Se_4[Li(thf)_2]_2$ (**2e**·4thf), but which differ considerably in $[(C_6H_{11})P]_2Se_4[Li(tmeda)]_2$ [2.229(2) and 2.072(2) Å].[10]

Even more fascinating is the structure of the sodium tetraselenohypodiphosphonate $[(2\text{-}C_4H_3S)P]_2Se_4Na_2$ (**1g**). This is the first structurally characterized solvent-free tetraselenohypodiphosphonate salt. It crystallizes in the orthorhombic space group *Pbcn* with four formula units in the unit cell. Figure 5 shows the structure of the hypodiphosphonate anion and its coordination to the sodium cations.

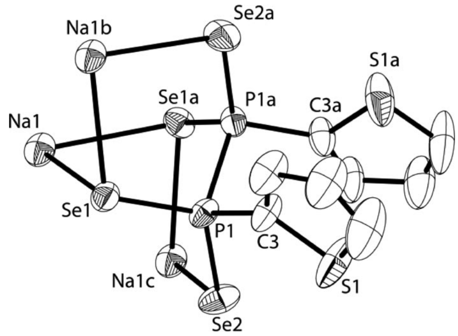

Figure 5. ORTEP view of the molecular structure of $[(2\text{-}C_4H_3S)P]_2Se_4Na_2$ (**1g**) in the crystal (ellipsoids at 50%), showing the hypodiphosphonate anion and its coordination to the sodium cations. Label letters denote the symmetry operations: a: –*x*, *y*, 0.5 – *z*; b: –*x*, 1 – *y*, –*z*; c: –*x*, 1 – *y*, 1 – *z*.

As in the case of the phenyl derivative $(PhP)_2Se_4[Li(thf)_2]_2$ (**2e**·4thf), the anion adopts a *trans* conformation around the P–P bond. In contrast, however, the two thiophene substituents are *cis* oriented to one another. Most probably the absence of additional solvent ligands and the tendency to achieve a maximum of chelating coordination around the sodium ions drives the anion in the observed conformation. In the crystal, every hypodiphosphonate anion coordinates to three sodium atoms, acting three times as a bidentate ligand. Coordination to the sodium atoms proceeds exclusively through the selenium atoms bonded to different phosphorus atoms (mode **B**). As a consequence, two of the selenium atoms coordinate simultaneously to two different sodium atoms, whereas the other two selenium atoms display only one Na–Se contact (Figure 5). Each sodium cation is coordinated by six selenium atoms from three different hypodiphosphonate anions to form a slightly distorted octahedral surrounding. This arrangement results in the formation of chains along the *c* axis (Figure 6), which pack to form the crystal.

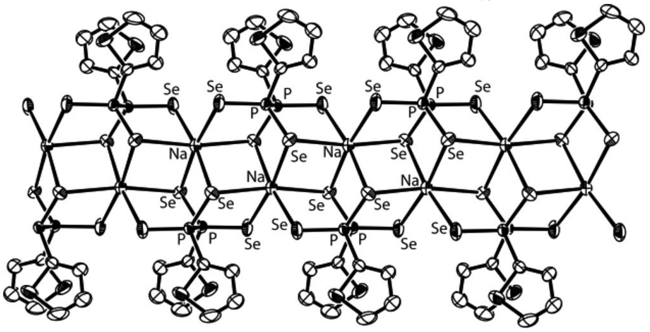

Figure 6. ORTEP view of a chain along the *c* axis in the crystal structure of $[(2\text{-}C_4H_3S)P]_2Se_4Na_2$ (**1g**) (ellipsoids at 50%).

Selected distances and angles of $[(2\text{-}C_4H_3S)P]_2Se_4Na_2$ (**1g**) are shown in Table 3. In the tetraselenohypodiphosphonate anion the coordination around the phosphorus atoms is slightly distorted tetrahedral. The P–P distance [2.252(2) Å] and the Se–P distances [2.147(1) and 2.140(1) Å] compare well to those found for $(PhP)_2Se_4[Li(thf)_2]_2$ (**2e**·4thf). The Se–Na distance of 3.067(2) Å falls within the typical range (2.921–3.148 Å) and compares well to those found in $(PhP)_2Se_4Na_2(thf)_3$ [3.022(1)–3.284(2) Å].[11]

Table 3. Selected distances [Å] and angles [°] for $[(2\text{-}C_4H_3S)P]_2Se_4Na_2$ (**1g**).

Se1–P1	2.147(1)	P1–C3	1.818(6)
Se2–P1	2.140(1)	Se1–Na1	3.067(2)
P1–P1a	2.252(2)		
Se1–P1–Se2	117.2(1)	Se2–P1–P1a	109.5(1)
Se1–P1–C3	112.2(2)	Se1–P1–P1a	107.3(1)
Se2–P1–C3	108.6(2)	P1a–P1–C3	100.8(2)
Na1–Se1–P1–Se2	–74.3(1)	Na1–Se1–P1–C3	159.1(2)
Se2–P1–P1a–Se2a	–177.8(1)	Se1–P1–P1a–Se1a	–74.2(1)

It is interesting to compare the structures of the two sodium salts $[(2\text{-}C_4H_3S)P]_2Se_4Na_2$ (**1g**) and $(PhP)_2Se_4Na_2(thf)_3$.[11] The salts are quite similar, both have an aromatic substituent bonded to phosphorus. In both cases the tetraselenohypodiphosphonate anions are coordinated to sodium ions to form chains throughout the crystal. A main difference is the presence of solvent molecules in the case of $(PhP)_2Se_4Na_2(thf)_3$, which compete with the hypodiphosphonate anions for the coordination to sodium. In this case, coordination modes **A** and **B** are observed in the same structure. In the absence of solvent molecules in the structure of $[(2\text{-}C_4H_3S)P]_2Se_4Na_2$ (**1g**), the anion adapts to the situation and only one coordination mode (**B**) is found.

Conclusions

The reaction of dichlorophosphanes $RPCl_2$ with alkali metal selenides M_2Se and M_2Se_2 (M = Li, Na) in a 2:2:1 molar ratio provides a general and convenient synthesis to alkali metal salts of the tetraselenohypodiphosphonate anions $(RP)_2Se_4^{2-}$ (R = alkyl, aryl). The easy access of tetraselenohypodiphosphonate anions by this route, starting from easily available materials, opens the door to a systematic study of the coordination behaviour of these new anions, which is under current investigation in our laboratory. Studies on the crystal structures of $(PhP)_2Se_4[Li(thf)_2]_2$ (**2e**·4thf) and $[(2\text{-}C_4H_3S)P]_2Se_4Na_2$ (**1g**) reveal a remarkable flexibility in the coordination behaviour of $(RP)_2Se_4^{2-}$ anions. Towards alkali metal ions they behave as chelating ligands that coordinate according to modes **A** and **B**. It can be expected that these properties may be finetuned by variation of the solvent and by choosing the proper substituent at phosphorus. The synthesis of the solvent-free salt $[(2\text{-}C_4H_3S)P]_2Se_4Na_2$ (**1g**) makes the tetraselenohypodiphosphonate anions $(RP)_2Se_4^{2-}$ interesting building blocks for new metal/selenium/phosphorus frameworks.

Experimental Section

General Methods: All operations were carried out under an atmosphere of dry argon (Messer Griesheim, purity 4.6 in 50 L steel cylinder) by using Schlenk techniques. All glass apparatus were stored in a drying oven (130 °C) and flame dried in vacuo (10^{-3} mbar) before use. Sodium selenide and sodium diselenide were prepared as described in the literature[18] and stored in a dry box under a nitrogen atmosphere. Lithium selenide and lithium diselenide were prepared analogously. All dichlorophosphanes were either purchased from commercial suppliers or prepared according to literature procedures[19–22] and stored in glass vessels under an argon atmosphere. The thf solvent was dried with sodium/benzophenone and freshly distilled prior to use. Melting points were determined with a Büchi B450 instrument and are uncorrected. Elemental analyses (C/H) were performed by the analytical service of the Department of Chemistry and Biochemistry. The NMR spectra were recorded with a Jeol Eclipse 400 spectrometer operating at 400.2 (^{1}H), 100.6 (^{13}C), 162.0 (^{31}P) and 76.3 MHz (^{77}Se). Chemical shifts are reported with respect to TMS (^{1}H, ^{13}C), 85% H_3PO_4 (^{31}P) and Me_2Se (^{77}Se) as external standards. Thf (^{31}P, ^{77}Se) and [D$_6$]acetone as well as [D$_6$]acetonitrile (^{1}H, ^{13}C) were used as solvents. For iterative fitting and simulation of the ^{31}P and ^{77}Se NMR spectra, the programs PERCH[23] and DAVINX[24] were used.

X-ray Crystallography: Single crystals of $(PhP)_2Se_4[Li(thf)_2]_2$ (**2e**·4thf) and $[(2\text{-}C_4H_3S)P]_2Se_4Na_2$ (**1g**) suitable for X-ray diffraction were obtained by slow evaporation of thf solutions of the corresponding salts. The crystals were introduced in perfluorinated oil and a suitable single crystal was carefully mounted on the top of a thin glass wire. Data collection for **2e**·4thf was performed with an Oxford Xcalibur3 diffractometer equipped with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector, operating with Mo-K_α radiation (λ = 0.71071 Å). Data collection was performed with the Crysalis CCD software;[25] Crysalis RED software[26] was used for data reduction. Absorption correction by using the SCALE3 ABSPACK multiscan method[27] was applied. Data collection for **1g** was performed with a Nonius Kappa CCD diffractometer. The structures were solved with SIR-92,[28] SIR-97[29] and SHELXS-97,[30] refined with SHELXL-97[31] and finally checked by using PLATON.[32] Details for data collection and structure refinement are summarized in Table 4. CCDC-698063 (for **2e**·4thf) and -698064 (for **1g**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 4. Details for X-ray data collection and structure refinement for $(PhP)_2Se_4[Li(thf)_2]_2$ (**2e**·4thf) and $[(2\text{-}C_4H_3S)P]_2Se_4Na_2$ (**1g**).

	2e·4thf	**1g**
Empirical formula	$C_{28}H_{42}Li_2O_4P_2Se_4$	$C_8H_6Na_2P_2S_2Se_4$
Formula mass	834.28	567.02
T [K]	100(2)	200(2)
Crystal size [mm]	0.35 × 0.25 × 0.1	0.13 × 0.07 × 0.03
Crystal description	colourless block	colourless platelet
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$Pbcn$
a [Å]	10.8380(3)	11.739(2)
b [Å]	11.6034(4)	29.450(6)
c [Å]	13.5115(4)	7.2019(14)
α [°]	90	90
β [°]	92.123(2)	90
γ [°]	90	90
V [Å^3]	1698.01(9)	2489.9(8)
Z	2	4
$\rho_{calcd.}$ [g cm^{-3}]	1.632	1.513
μ [mm^{-1}]	4.446	6.191
F(000)	828	1052
θ range [°]	3.76–26.00	3.15–26.00
Index ranges	$-13 \leq h \leq 13$ $-14 \leq k \leq 13$ $-16 \leq l \leq 16$	$-14 \leq h \leq 14$ $-36 \leq k \leq 35$ $-8 \leq l \leq 8$
Reflns. collected	9530	13526
Reflns. obsd.	2294	1682
Reflns. unique	3340 (R_{int} = 0.0315)	2445 (R_{int} = 0.0711)
R_1, wR_2 (2σ data)	0.0318, 0.0710	0.0446, 0.1309
R_1, wR_2 (all data)	0.0535, 0.0785	0.0744, 0.1410
GOOF on F^2	0.961	1.060
Peak/hole [e Å^{-3}]	0.793/–0.653	0.587/–0.715

General Procedure for the Synthesis of Sodium Tetraselenophosphonates 1 and Lithium Tetraselenophosphonates 2: To a suspension of Na_2Se (or Li_2Se; 2 equiv.) and Na_2Se_2 (or Li_2Se_2; 1 equiv.) in thf (100 mL) was added dropwise with stirring at –20 °C a solution of the respective dichlorophosphane $RPCl_2$ (2 equiv.) in thf (60 mL) over a period of 30 min. The reaction mixture was warmed up to ambient temperature and stirring was continued for 24 h. The resulting reaction mixture was centrifuged for 30 min, the clear thf phase was separated and the remaining solid NaCl washed with thf (2 × 30 mL). The combined thf phase was concentrated to one tenth of its volume. Upon careful addition of toluene, salts **1** and **2** precipitated as colourless crystalline solids, which were separated by filtration and dried in vacuo.

1a: From Na_2Se (5.52 g, 44.1 mmol), Na_2Se_2 (4.50 g, 22.1 mmol) and $MePCl_2$ (5.16 g, 44.1 mmol). Yield: 14.7 g (72%); colourless crystalline solid; m.p. >200 °C. ^{1}H NMR ([D$_6$]acetone): δ = 2.4 (m, CH_3) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 54.6 (m, CH_3) ppm. For ^{31}P and ^{77}Se NMR data, see Table 1. $C_2H_6Na_2P_2Se_4 \cdot 1/8C_4H_8O$ (462.8): calcd. C 6.49, H 1.52; found C 6.67, H 1.55.

1b: From Na_2Se (5.49 g, 44.0 mmol), Na_2Se_2 (4.49 g, 22.0 mmol) and $EtPCl_2$ (5.76 g, 44.0 mmol). Yield: 12.5 g (57%); colourless crystalline solid; m.p. >200 °C. ^{1}H NMR ([D$_6$]acetone): δ = 2.5 (m, 2 H, CH_2), 1.3 (m, 3 H, CH_3) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 32.0 (m, CH_2), 9.9 (m, CH_3) ppm. For ^{31}P and ^{77}Se NMR data, see Table 1. $C_4H_{10}Na_2P_2Se_4 \cdot 1/4C_4H_8O$ (499.9): calcd. C 12.01, H 2.42; found C 11.80, H 2.62.

1c: From Na_2Se (4.98 g, 39.9 mmol), Na_2Se_2 (4.06 g, 19.9 mmol) and *i*$PrPCl_2$ (5.78 g, 39.9 mmol). Yield: 3.7 g (31%); colourless crystalline solid; m.p. >200 °C. ^{1}H NMR ([D$_6$]acetone): δ = 3.1 (m 1 H, CH), 1.3 (m, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 36.5 (m, CH), 20.7 (m, CH_3) ppm. For ^{31}P and ^{77}Se NMR data, see Table 1. $C_6H_{14}Na_2P_2Se_4$·2/3C_4H_8O (558.0): calcd. C 18.65, H 3.49; found C 18.31, H 3.79.

1d: From Na_2Se (2.90 g, 23.2 mmol), Na_2Se_2 (2.36 g, 11.6 mmol) and *t*BuPCl_2 (3.69 g, 23.2 mmol). Yield: 3.5 g (25%); colourless crystalline solid; m.p. >200 °C. ^{1}H NMR ([D$_6$]acetone): δ = 1.3 (m, CH_3) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 42.3 (m, C), 25.5 (m, CH_3) ppm. For ^{31}P and ^{77}Se NMR data, see Table 1. $C_8H_{18}Na_2P_2Se_4$·C_4H_8O (610.1): calcd. C 23.62, H 4.30; found C 23.23, H 4.30.

1e: From Na_2Se (2.69 g, 21.5 mmol), Na_2Se_2 (2.08 g, 10.2 mmol) and PhPCl_2 (3.85 g, 21.5 mmol). Yield: 10.9 g (78%); colourless crystalline solid; m.p. >200 °C. ^{1}H NMR ([D$_6$]acetone): δ = 7.7 (m, 4 H, arom-H), 6.6 (m, 6 H, arom-H) ppm. ^{13}C{^{1}H} NMR ([D$_6$]-acetone): δ = 136.8 (m, C-*i*), 135.0 (m, C-*o*), 125.2 (m, C-*m*), 128.9 (m, C-*p*) ppm. For ^{31}P and ^{77}Se NMR data, see Table 1. $C_{12}H_{10}Na_2P_2Se_4$·C_4H_8O (650.1): calcd. C 29.56, H 2.79; found C 29.87, H 3.10.

1f: From Na_2Se (499 mg, 4 mmol), Na_2Se_2 (408 mg, 2 mmol) and 1-AdPCl_2 (948 mg, 4 mmol). Yield: 430 mg (31%); colourless crystalline solid. For ^{31}P and ^{77}Se NMR data, see Table 1. $C_{20}H_{30}Na_2P_2Se_4$·C_4H_8O (766.3): calcd. C 37.62, H 5.00; found C 37.74, H 5.25.

1g: From Na_2Se (750 mg, 6 mmol), Na_2Se_2 (612 mg, 3 mmol) and (2-C_4H_3S)PCl_2 (1.11 g, 6 mmol). Yield: 1.1 g (96%); colourless crystalline solid. ^{1}H NMR (CD_3CN): δ = 7.5 (m, 2 H), 7.4 (m, 2 H), 7.0 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (CD_3CN): δ = 141.9 (t, N = 56.3 Hz, C-1), 136.4 (t, N = 9.1 Hz, CH), 131.6 (t, N = 4.3 Hz, CH), 126.4 (t, N = 11.5 Hz, CH) ppm. For ^{31}P and ^{77}Se NMR data, see Table 1. $C_8H_6Na_2P_2S_2Se_4$ (590.0): calcd. C 16.28, H 1.02; found C 16.24, H 1.30.

2c: From Li_2Se (1.02 g, 11.0 mmol), Li_2Se_2 (0.94 g, 5.5 mmol) and *i*PrPCl_2 (1.59 g, 11.0 mmol). Yield: 874 mg (52%); colourless crystalline solid. For ^{31}P and ^{77}Se NMR data, see Table 1. $C_6H_{14}Li_2P_2Se_4$·2C_4H_8O (622.1): calcd. C 27.03, H 4.86; found C 7.21, H 4.95.

2e: From Li_2Se (1.02 g, 11.0 mmol), Li_2Se_2 (0.94 g, 5.5 mmol) and PhPCl_2 (1.97 g, 11.0 mmol). Yield: 1.8 g (60%); colourless crystalline solid. For ^{31}P and ^{77}Se NMR data, see Table 1. $C_{28}H_{42}Li_2O_4P_2Se_4$ (834.3): calcd. C 40.31, H 5.07; found C 40.27, H 5.19.

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