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New Salts of the Waterstable $P_2Se_6^{4-}$ Anion

Christiane Rotter, Michael Schuster, Sebastian Gebler, Thomas M. Klapötke, and Konstantin Karaghiosoff*

Department für Chemie, Ludwig Maximilians Universität München, Butenandtstr. 5-13, 81377 München, Germany

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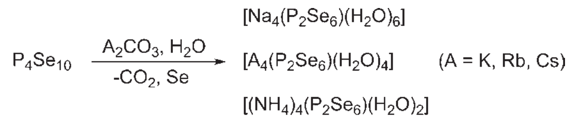
The structures of two new salts of the $P_2Se_6^{4-}$ anion, $[(py_2Li)]_4[P_2Se_6]\cdot 2py$ and $[pyH]_4[P_2Se_6]\cdot H_2O$, prepared using a new synthetic route in solution starting from easily available educts, are presented. The salts are characterized also in solution by means of multinuclear (^{31}P, ^{77}Se, ^{7}Li) NMR spectroscopy. The ^{31}P and ^{77}Se NMR spectrum of the waterstable $P_2Se_6^{4-}$ anion are discussed in detail for the first time. The chemical shift of the $P_2Se_6^{4-}$ anion in the Li^+ salts depends strongly on the solvent used. Remarkably, the newly synthesized salts are stable in water.

Introduction

Chalcogenophosphate anions $P_nCh_m^{x-}$ containing the heavier chalcogens sulfur, selenium, and tellurium are, in contrast to the well-known and well investigated oxophosphate anions, still a challenge in the field of preparative inorganic chemistry. Considering only the selenophosphate anions $P_nSe_m^{x-}$ contributions to this intriguing family of anions originates from the groups of Kanatzidis and Dorhout.[1,2] Most representatives are synthesized by methods from the field of solid state chemistry.[1,2] In our work group, a new and alternative method to synthesize chalcogenophosphate anions has been developed starting from easily available educts in solution under mild conditions.[3]

One of the few well-known selenophosphate anions is the hexaselenohypodiphosphate anion $P_2Se_6^{4-}$. Main group and transition metal salts of this anion (e.g., $K_2MgP_2Se_6$[4] or $Cd_2P_2Se_6$[5] salts) have been the subject of investigations due to their interesting physical properties like photoconductivity or ferroelectricity. Most of the contributions to the chemistry of the hexaselenohypodiphosphate anion originate from solid state chemistry.[6] Typical syntheses of metal hexaselenohypodiphosphates involve reaction of the elements (the metal, red phosphorus, and elemental selenium) at high temperatures, resulting in the formation of thermodynamically favored modifications of the corresponding salts. Alkali metal hexaselenohypodiphosphates and, in particular, the lithium salt are of current interest due to possible ion conductivity. In the case of the lithium salt, it might be of interest as a material for lithium ion batteries.[6]

Scheme 1. Syntheses of $M_4P_2Se_6$ (M = Na, K, Rb, Cs, NH_4) according to literature.[7]



No syntheses of metal hexaselenohypodiphosphates in solution have been described in the literature so far. The only exception is the recently reported reaction of P_4Se_{10} glass with metal carbonates in water, resulting in the formation of $[Na_4(P_2Se_6)(H_2O)_6]$, $[M_4(P_2Se_6)(H_2O)_4]$ (M = K, Rb, Cs), and $[(NH_4)_4(P_2Se_6(H_2O)_2]$ reported by Kanatzidis et al. (Scheme 1).[7]

The use of water as a reaction medium in the case of P and Se compounds often causes the formation of toxic H_2Se. Therefore, the development of a general synthesis of metal hexaselenohypodiphosphates in solution, avoiding protic solvents, would be highly desirable. Here, we present the

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*To whom correspondence should be addressed. E-mail: klk@cup.uni-muenchen.de.

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synthesis of two new salts of the $P_2Se_6^{4-}$ anion prepared in solution under mild conditions.

Experimental Section

General Procedure. All reactions were carried out under an inert gas atmosphere using Schlenk techniques. Argon (Messer Griesheim, purity 4.6 in 50 L steel cylinder) was used as the inert gas. All glass vessels were stored in a 130 °C drying oven and were flame-dried in vacuum at 10^{-3} mbar before use.

White phosphorus (ThermPhos) was peeled under water, washed with dry THF, and dried under a vacuum. P_4Se_3 and the alkali metal diselenides were prepared according to a literature procedure and stored in a drybox under a nitrogen atmosphere.[8,9] Elemental gray selenium (Aldrich) was used as received.

The melting point was determined in a capillary using a Büchi B540 instrument and is uncorrected.

The solvents used were dried by commonly known methods and freshly distilled before use.

NMR Spectroscopy. NMR spectra were recorded with a Jeol EX 400 Eclipse instrument operating at 161.997 MHz (^{31}P), 76.321 MHz (^{77}Se), and 155.526 MHz (^{7}Li). Chemical shifts are referred to 85% H_3PO_4 (^{31}P), $(CH_3)_2Se$ (^{77}Se), and a 0.1 M solution of LiCl in D_2O (^{7}Li). All spectra were measured at 25 °C. For the simulation of the ^{31}P NMR spectra, the PERCH program package was used.[10]

X-Ray Diffraction. The molecular structures in the crystalline state were determined using an Oxford Xcalibur3 diffraction instrument equipped with a Spellman generator (voltage 50 kV, current 40 mA) and a Kappa CCD detector with X-ray radiation wavelength of 0.71073 Å (Mo Kα). The data collection was performed with the CrysAlis CCD software and the data reduction with the CrysAlis RED software.[11,12] The structures were solved with SIR-92 and SHELXS-97 and refined with SHELXL-97 and finally checked using PLATON.[13−17] The absorptions were corrected using a SCALE3 ABSPACK multi-scan method.[18] All relevant data and parameters of the X-ray measurements and refinements are given in Table 1. Further information on the crystal structure determinations has been deposited with the Cambridge Crystallographic Data Centre[19] as supplementary publication No. 764249 (**1**) and 763988 (**2**).

Table 1. Crystallographic Data

	$[py_2Li]_4$-$[P_2Se_6]\cdot 2py$ (**1**)	$[pyH]_4[P_2Se_6]\cdot H_2O$ (**2**)
empirical formula	$C_{25}H_{25}Li_2N_5PSe_3$	$C_5H_8NOPSe_3$
formula mass	677.23	365.97
temp (K)	100	200
cryst size (mm)	0.2 × 0.2 × 0.2	0.2 × 0.15 × 0.1
cryst description	orange block	yellow block
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	10.9618(5)	9.4755(2)
b (Å)	17.9666(9)	13.0642(3)
c (Å)	14.4622(7)	8.4883(2)
β (deg)	92.110(4)	92.009(2)
V (Å^3)	2846.3(2)	1050.12(4)
Z	4	4
ρ_{calcd} (g cm^{-1})	1.580	2.315
μ (mm^{-1})	3.955	10.610
$F(000)$	1332	680
θ range (deg)	3.6779−32.6745	3.7850−33.3985
index ranges	$-13 \le h \le 13$ $-22 \le k \le 22$ $-17 \le l \le 17$	$-8 \le h \le 11$ $-16 \le k \le 16$ $-10 \le l \le 9$
reflns collected	27582 ($R_{int} = 0.0618$)	5237 ($R_{int} = 0.0192$)
reflns observed	3548	1759
reflns unique	5573	2046
R1, wR2 (all data)	0.0713, 0.0628	0.0277, 0.0516
R1, wR2 (2σ data)	0.0295, 0.0506	0.0201, 0.0469
max/min transm	1.0/0.84917	0.346/0.161
data/restr/params	5573/0/315	2046/2/112
GOF on F^2	0.951	1.051
larg. diff peak/hole (e/Å^3)	0.583/-0.517	0.600/-0,464

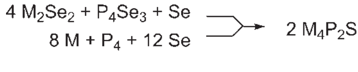
$[py_2Li]_4[P_2Se_6]\cdot 2py$ (1). Li_2Se_2 (1.508 g, 8.77 mmol), P_4Se_3 (792 mg, 2.19 mmol), and gray selenium (173 mg, 2.19 mmol) were suspended in 30 mL of pyridine. Alternatively, elemental lithium (382 mg, 55.04 mmol), P_4 (853 mg, 6.88 mmol), and gray selenium (6.523 g, 82.61 mmol) were suspended in 60 mL of pyridine. An exothermic reaction was observed. The reaction mixture became green. Afterward, the suspension was refluxed for 2 h (130 °C oil bath temperature). Yellow crystals of **1** were obtained on cooling the reaction mixture to room temperature overnight. The crystals were separated using a G3 frit and washed twice with 5 mL of cold pyridine and twice with 5 mL of diethylether. The yellow crystals of **1** are very sensitive toward light and air. Yield: 2.4 g (40.4%, 1.7 mmol). m.p.: decomposition > 50 °C. Elemental analysis: $C_{25}H_{25}Li_2N_5PSe_3$, theor.: C, 44.34; H, 3.72; N, 10.34. Observed: C, 43.14; H, 3.52; N, 9.84.

$[pyH]_4[P_2Se_6]\cdot H_2O$ (2). A total of 0.2 mmol (135 mg) of $[py_2Li]_4[P_2Se_6]\cdot 2py$ are dissolved in 2 mL of water. On keeping the solution for 2 days in a closed glass vessel at +4 °C, a few crystals of $[pyH]_4[P_2Se_6]\cdot H_2O$ were obtained.

Results and Discussion

Synthesis. Alkali metal salts of the $P_2Se_6^{4-}$ anion can be prepared in solution under mild conditions (20−130 °C) starting from the corresponding alkali metal diselenide M_2Se_2 (M = Li, Na), P_4Se_3, and elemental selenium or alternatively from the elements in the required stoichiometric ratio (the alkali metal, white phosphorus, and gray selenium) as educts. A polar and preferably basic solvent like *N*-methyl imidazole, pyridine, DMPU (dimethylpropylenurea), or THF is required (Scheme 2).

Scheme 2. Syntheses of Salts Containing the $P_2Se_6^{4-}$ Anion (M = Li, Na)



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(12) *CrysAlis RED*, version 1.171.32.5 (release 08−05−2007 CrysAlis171 . NET); Oxford Diffraction Ltd.: Oxfordshire, U.K., **2007** (compiled May 8 2007, 13:10:02).

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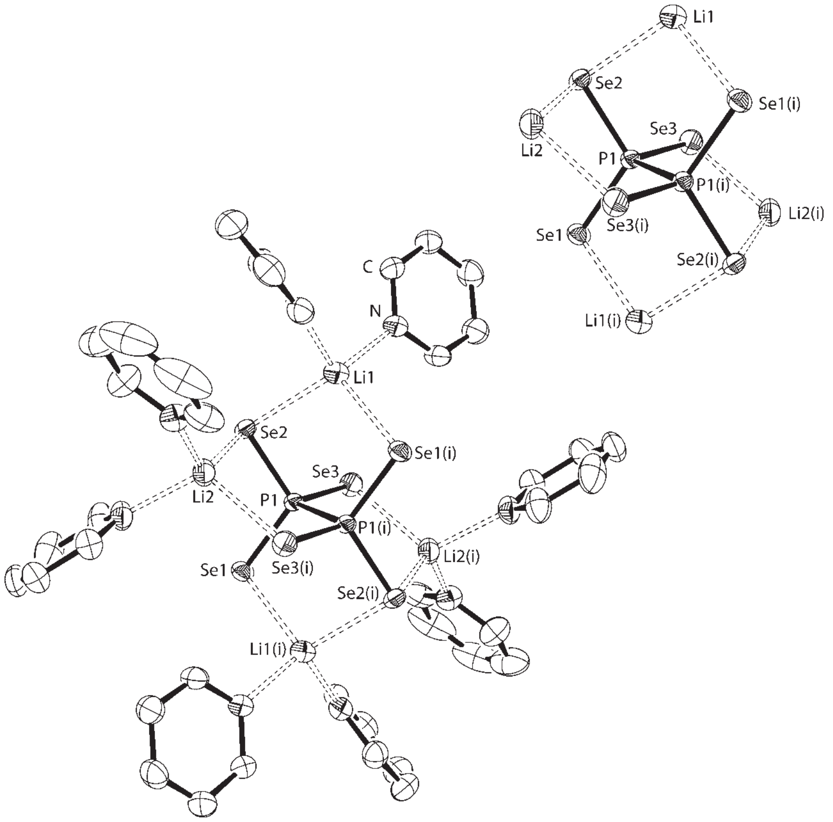
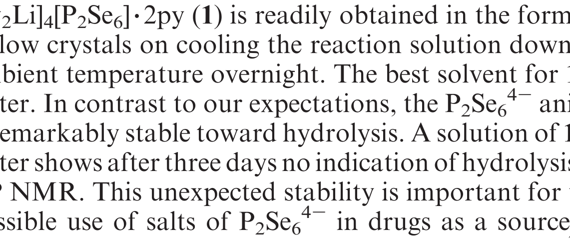


Figure 1. Molecular structure of **1** in the crystal. Ellipsoids are drawn at the 50% probability level. In the upper right corner, the molecular structure is shown without the pyridine molecules. Hydrogen atoms are omitted for clarity. $i = -x, -y, -z$.

Scheme 3. Syntheses of **1** and **2**



If pyridine is used as a solvent, the lithium salt $[py_2Li]_4[P_2Se_6]\cdot 2py$ (**1**) is readily obtained in the form of yellow crystals on cooling the reaction solution down to ambient temperature overnight. The best solvent for **1** is water. In contrast to our expectations, the $P_2Se_6^{4-}$ anion is remarkably stable toward hydrolysis. A solution of **1** in water shows after three days no indication of hydrolysis in ^{31}P NMR. This unexpected stability is important for the possible use of salts of $P_2Se_6^{4-}$ in drugs as a source of selenium. It also enabled us to determine the complete ^{31}P and ^{77}Se NMR spectroscopical data of the $P_2Se_6^{4-}$ anion, which are reported here in detail (see below).

From the water solution of **1**, single crystals of the hitherto unknown pyridinium salt $[pyH]_4[P_2Se_6]\cdot H_2O$ (**2**) were obtained. The structure of the salt was determined by single crystal X-ray diffraction (Scheme 3). Compound **2** resulted, remarkably stable in water at +4 °C, and showed no sign of decomposition even after several months.

$[py_2Li]_4[P_2Se_6]\cdot 2py$ (1). $[py_2Li]_4[P_2Se_6]\cdot 2py$ (**1**) could be obtained in high yield using Li_2Se_2, P_4Se_3, and elemental selenium as educts in pyridine. After refluxing the reaction solution, **1** crystallizes as yellow crystals which are light- and air-sensitive. Interestingly, salt **1** is poorly soluble in pyridine (after crystallization), THF, acetonitrile, benzonitrile, TMEDA (tetramethylethylenediamine), and triethylamine. It dissolves only in highly polar solvents like DMPU, HMPA (hexamethylphosphoramide), *N*-methyl imidazole, DMF (dimethylformamide), EtOH, MeOH, and H_2O. Salt **1** crystallizes in the monoclinic space group $P2_1/c$ with four formula units in the unit cell.

The crystal structure consists of $P_2Se_6^{4-}$ anions. Each anion is coordinated to four lithium cations. Each $P_2Se_6^{4-}$ anion adopts an ethane like structure with a staggered conformation around the P—P bond and is coordinated to four lithium cations. The Li^+ cations are coordinated to two selenium atoms located at different phosphorus atoms (P1 and P1(*i*)) of the same anion. Four of the selenium atoms (Se2, Se3, Se2(*i*), Se3(*i*)) of the $P_2Se_6^{4-}$ anion are coordinated each to one Li atom, whereas the last two selenium atoms (Se1 and Se1(*i*)) are each coordinated to two lithium atoms. The coordination sphere of the Li^+ cations is completed by coordination of two pyridine molecules, resulting in a slightly distorted tetrahedral surrounding. This coordination of the lithium atoms to the $P_2Se_6^{4-}$ anion results in the formation of $(py_2Li)_4(P_2Se_6)$ structural units, which are packed to yield the crystal. The additional pyridine molecules are located between these units and complete the packing of the crystal (Figure 1).

Conformation as well as P—P bond distance (226.9(1) pm) and P—Se bond distances with an average value of 217 pm found for $P_2Se_6^{4-}$ in **1** do not significantly differ from those already described in literature for isolated

Table 2. Selected Distances [pm] and Angles [deg] of **1** and **2**

$[py_2Li]_4[P_2Se_6]\cdot 2py$ (**1**)		$[pyH]_4[P_2Se_6]\cdot H_2O$ (**2**)	
	distances [pm]		
P1−P1(*i*)	226.9(1)	P1−P1(*i*)	227.3(1)
P1−Se1	219.2(1)	P1−Se1	218.4(1)
P1−Se2	216.5(1)	P1−Se2	218.5(1)
P1−Se3	217.2(1)	P1−Se3	217.9(1)
Se1−Li2	261(1)		
Se1−Li1	261(1)		
Se2−Li2(*i*)	256(1)		
Se3−Li1(*i*)	254(1)		
	angles [deg]		
Se1−P1−Se2	111.9(1)	Se1−P1−Se2	113.8(1)
Se1−P1−Se3	110.6(1)	Se1−P1−Se3	112.2(1)
Se2−P1−Se3	114.2(1)	Se2−P1−Se3	110.2(1)
Se1−P1−P1(*i*)	104.1(1)	Se1−P1−P1(*i*)	104.9(1)
Se2−P1−P1(*i*)	107.0(1)	Se2−P1−P1(*i*)	108.1(4)
Se3−P1−P1(*i*)	108.4(1)	Se3−P1−P1(*i*)	107.4(1)
P1−Se1−Li1	91.8(1)		
P1−Se1−Li2	91.9(1)		
Li1−Se1−Li2	105.2(2)		
P1−Se2−Li2(*i*)	99.0(1)		
P1−Se3−Li1(*i*)	96.6(1)		

Table 3. Se−Li Distances in **1** Compared to Observed Distances in Lithium Selenolates

compound	*d*(Se−Li) [pm]
1	255; 261
$[py_2Li][PhSe]_2py_2Yb(SePh)_2$[22]	257; 269
$[bipyLi][PhSe]$[23]	255; 259

[a] Average value.

hexaselenohypodiphosphate anions like in $Na_4P_2Se_6$ or $K_4P_2Se_6$ described by Dorhout et al. (Table 2).[20,21]

Although a solvent-free $Li_4P_2Se_6$ has been prepared, to the best of our knowledge, its structure in the solid state has not been determined yet by single crystal X-ray diffraction. Of particular interest are therefore the Se−Li distances. They range between 254 and 261 pm, which is in good agreement with the found Se−Li distances in lithium selenolates, where the lithium atoms have a comparable coordination sphere (Table 3).[22,23]

In **1**, the coordination sphere of the lithium cation is completed by solvent molecules and not by selenium atoms of other anions. This explains the solubility of **1** in polar solvents, which is described below. In contrast, solvent free hexaselenohypodiphosphate salts are almost insoluble in polar solvents.

$[pyH]_4[P_2Se_6]\cdot H_2O$ (2). Yellow single crystals of $[pyH]_4[P_2Se_6]\cdot H_2O$ (**2**) were obtained from a water solution of **1** after 2 days standing at room temperature. Compound **2** crystallizes in the monoclinic space group *P*2₁/*c* with four formula units in the unit cell (Figure 2).

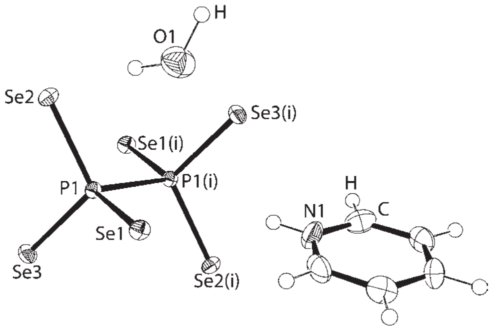


Figure 2. Molecular structure of **2** in the crystal. Ellipsoids are drawn at the 50% probability level. $i = 1 - x, 1 - y, 1 - z$.

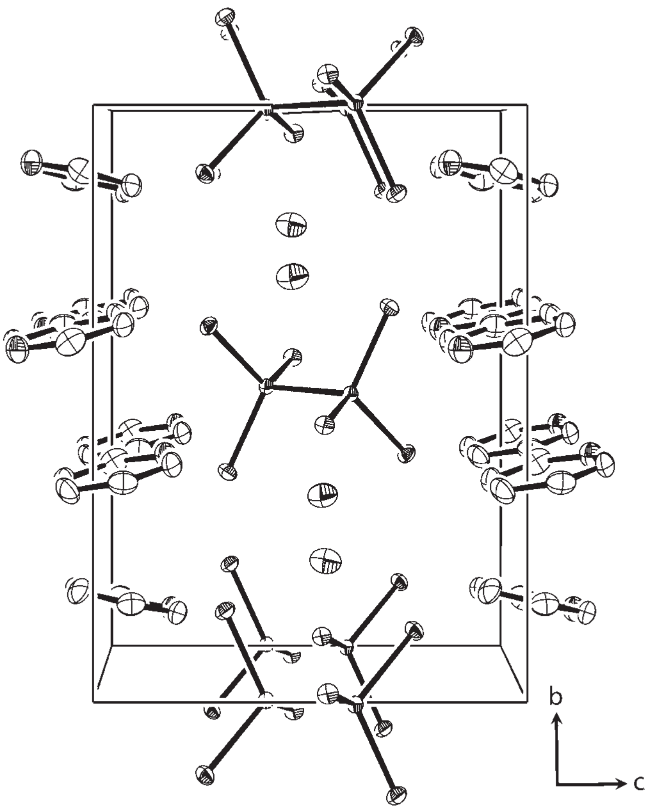


Figure 3. Unit cell of **2**. View along the *a* axis. Hydrogen atoms are omitted for clarity.

The crystal structure consists of isolated $P_2Se_6^{4-}$ anions and pyH^+ cations (Figure 2). The $P_2Se_6^{4-}$ anion adopts an ethane like conformation. Its structural parameters do not deviate much from those of other salts reported in the literature (Table 2).[6] Despite the presence of water molecules and pyH^+ cations in the crystal, no hydrogen bonds were found between the $P_2Se_6^{4-}$ anions and the water molecules or the pyH^+ cations or between H_2O molecules and the cations.

In the crystal, cations and anions form stacks along the *b* axis. The solvent molecules H_2O are located between the anions. Only electrostatic interactions between the pyH^+ cations and the $P_2Se_6^{4-}$ anions can be observed within the unit cell (Figure 3).

Multinuclear NMR Spectroscopy. The hexaselenohypodiphosphate anion $P_2Se_6^{4-}$ was characterized in solution (D_2O) by ^{31}P and ^{77}Se NMR spectroscopy (Figure 4). The isotopomer without ^{77}Se nuclei contains two isochronous phosphorus atoms and displays a singlet at 40.3 ppm in D_2O.

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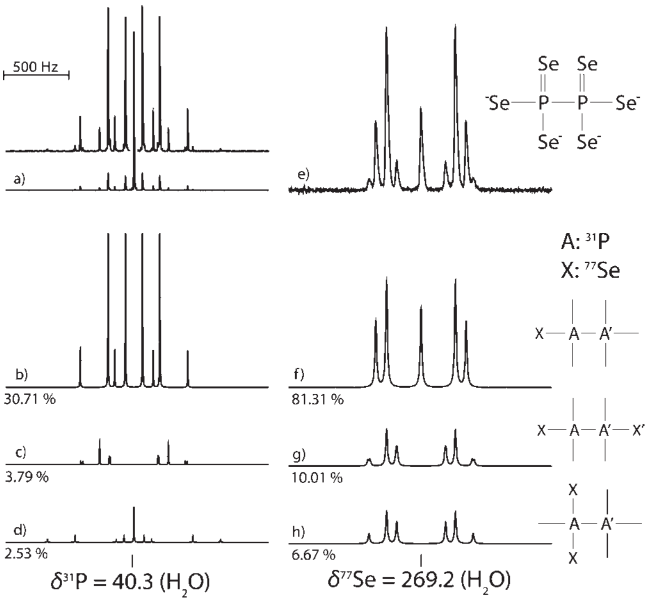

Figure 4. $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra of $P_2Se_6^{4-}$: (a) observed ^{31}P NMR spectrum in D_2O (0.3 M, 1655 scans, 40 min measuring time); (b) calculated ^{31}P NMR spectrum for the isotopomer with one ^{77}Se nucleus; (c and d) calculated ^{31}P NMR spectra for the isotopomers with two ^{77}Se nuclei; (e) observed ^{77}Se NMR spectrum in D_2O (0.3 M, 60 000 scans, 18 h measuring time); (f) calculated ^{77}Se NMR spectrum for the isotopomer with one ^{77}Se nucleus; (g and h) calculated ^{77}Se NMR spectra for the isotopomers with two ^{77}Se nuclei.

In the isotopomer with one ^{77}Se nucleus, the two phosphorus nuclei are magnetically inequivalent and form together with one ^{77}Se nucleus an AA′X spin system, which is of higher order. As expected, the ^{77}Se satellites in the ^{31}P NMR spectrum display the eight line pattern for the A part.[24] From this, the $^1J_{PP}$ coupling constant is directly evaluated and agrees well with the −210 Hz found in tetraselenohypodiphosphonate anions.[25] The $^1J_{SeP}$ coupling constant (−532 Hz) is in between the values found for two coordinated selenium atoms (P−Se−) and the values observed in phosphorus selenides ($R_3P{=}Se$).[26] The $^2J_{SeP}$ coupling constant is 9 Hz. In addition to the isotopomer with one ^{77}Se nucleus, the isotopomers with two ^{77}Se nuclei could also be observed in the ^{31}P NMR spectrum. The isotopomer where both ^{77}Se nuclei are bonded to different phosphorus atoms represent an AA′XX′ spin system. The isotopomer where both ^{77}Se nuclei are bonded to the same phosphorus atom could also be observed in the ^{31}P NMR spectrum but with less intensity, however (AA′X_2 spin system).

The ^{77}Se NMR spectrum shows the expected five line pattern for the X part of AA′X, and in addition, it shows also the signals for the isotopomer with two ^{77}Se nuclei bonded to different phosphorus atoms (X part of AA′XX′; ^{77}Se satellites in the ^{77}Se NMR spectrum). From this, the remarkably large coupling constant $^3J_{SeSe}$ of 12 Hz is determined.

The ^{31}P NMR chemical shift of the $P_2Se_6^{4-}$ anion in solutions of compound **1** depends strongly on the solvent used. The phosphorus NMR signal is shifted to lower field in the series of solvents H_2O, MeOH, HMPA, DMPU, pyridine, *N*-methyl imidazole, 2-methyl pyridine, and DMF (Table 4).

Table 4. ^{31}P and ^{7}Li NMR Chemical Shifts of $P_2Se_6^{4-}$ and ^{7}Li NMR Chemical Shifts of LiCl in Different Solvents

solvent	$\delta^{31}P$	δ^7Li	δ^7Li (LiCl)	$\Delta\delta^7Li$
water	40.3	−1.02	−0.09	−0.93
HMPA	50.3	−0.53	−0.22	−0.31
DMPU	52.1	−1.30	−0.03	−1.27
pyridine	52.3	2.82	3.06	−0.24
N-methyl imidazole	52.6	2.67	2.89	−0.22
DMF	55.3	0.79	1.07	−0.28

One reason for this rather large change in the ^{31}P NMR chemical shift ($\Delta\delta = 15$) might be the coordination of the lithium cations by the solvent used, which would destroy the $Li_4P_2Se_6$ clusters found for the solid state. Therefore, ^{7}Li NMR spectra of solutions of compound **1** in different solvents as well as the ^{7}Li NMR spectra of LiCl in the same solvents for comparison were measured.

In all cases, $\delta\ ^7Li$ of the salt $[py_2Li]_4[P_2Se_6]\cdot 2py$ is at higher field compared to δ^7Li of LiCl in the same solvent. The difference $\Delta\delta^7Li$ is largest in the case of DMPU and water and smallest in the case of *N*-methyl imidazole and pyridine.

Eckert et al have investigated the $Li_4P_2Se_6$ using ^{31}P solid state NMR spectroscopy. [27] The reported $^1J_{PP}$ coupling constant is 210 ± 5 Hz, which corresponds very well to the $^1J_{PP}$ observed in solution. The reported isotropic ^{31}P NMR chemical shifts in the solid state are 55.1 and 46.5 ppm. The average value (50.8 ppm) is in good agreement with the ^{31}P NMR chemical shifts observed in solution by us and Kanatzidis as well.[7]

Conclusions

Here, we presented the two new salts $[py_2Li]_4[P_2Se_6]\cdot 2py$ (**1**) and $[pyH]_4[P_2Se_6]\cdot H_2O$ (**2**) containing the $P_2Se_6^{4-}$ anion. Both compounds could be characterized in the solid state using single crystal X-ray diffraction. Compound **1** is a rare example of a $P_2Se_6^{4-}$ salt where the coordination sphere of the lithium cations is completed by solvent molecules and not by the $P_2Se_6^{4-}$ anions, resulting in isolated neutral clusters. Compound **2** is a rare example of a salt of the $P_2Se_6^{4-}$ anion with a non-metal cation yielding isolated anions in the solid state.

Due to the solubility of the new compounds **1** and **2** in polar solvents, the $P_2Se_6^{4-}$ anion was also investigated by ^{31}P and ^{77}Se solution NMR spectroscopy, yielding the full set of chemical shifts and coupling constants. The ^{31}P NMR chemical shift of the $P_2Se_6^{4-}$ anion in solution as well as the $^1J_{PP}$ correspond very well to those reported for this anion in the solid state.

The most surprising result is the stability of the new salts **1** and **2** in water, which makes them interesting for possible applications as educts for further reactions.

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