Transformations of P-chalcogenide precursors with a hydrated metal salt

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Abstract

The preparation, characterisation and X-ray structures of the three Ni(II) salts $[Ni\{ArP(OH)S_2\}_2(thf)_2]$ (**1**) (Ar = 4-anisyl), $[Ni\{PhP(OH)Se_2\}_2(thf)_2]$ (**2**) and $[Ni\{P(OH)_2S_2\}_2(thf)_4]$ (**3**) are reported.
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1. Introduction

The development of synthetic routes to elaborate metal frameworks containing neutral or anionic phosphorus-chalcogenido ligands such as R_3PE, $[RPE_3]^{2-}$, $[PE_4]^{3-}$ (E = S, Se) (R = organic group) gave rise to well-defined metal chalcogenide nanoparticles, promoted coordination chemistry in that area and above all continues to produce unusual novel compounds [1–5]. The principle of weak interactions (e.g., hydrogen bonding or weak electrostatic interaction between chalcogenide atoms and heavier alkali metal atoms), however, has not been extensively exploited in the area of phosphorus-chalcogenides. Instead synthetic efforts continue to concentrate on metal complexes with ligands designed by formally replacing O atoms in phosphate ions with OR, SR, S, Se, OSe [6–9]. In previous work it was shown that reactions of metal salts MX (X = alkoxide, thiolate, carboxylate) with reagents of the type $[RP(E)(\mu\text{-}E)]_2$ (R = organic group, E = S, Se [10,11]) and binary phosphorus sulfides offer an alternative route to complexes containing P/S- or P/Se-based anionic ligands [12–14]. Built on these initial results, current investigations concentrate on the synthesis of molecular and supramolecular arrangements of P–S and P–Se anions, held together by weak interactions. In this context we describe a case study on the reactivity of phosphorus-chalcogenide precursors $[RP(E)(\mu\text{-}E)]_2$ (R = organic group, E = S, Se) and P_2S_5 with hydrated metal salts, which was carried out in order to determine to what extent hydrogen bonding can be used as ordering principle in phosphorus-chalcogenide coordination chemistry.

2. Experimental

2.1. General remarks

All operations were carried out in an atmosphere of purified dinitrogen. Solvents were dried and freshly distilled prior to use. Woollins' reagent was prepared according to a published procedure [11].

Compound **1**: A mixture of Lawesson's reagent 202 mg (0.50 mmol) and NaS^{t}Bu 112 mg (1.00 mmol) was dissolved in 8 mL THF. The colorless solution was stirred for about 5 h at room temperature, and then added to $[NiCl_2 \cdot 6H_2O]$ 119 mg (0.50 mmol). The filtrate was layered with 20 mL hexane. Storage of the solution at room temperature for 2 weeks produced purple crystals of **1**.

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Yield 0.19 g (63%). M.p. 195 °C (decomposition). Elemental Anal. Calc. for $C_{22}H_{32}NiO_6P_2S_4 \cdot 0.5(C_4H_8O)$: C, 39.68; H, 4.66. Found: C, 39.56; H 4.71%. ^{1}H NMR (25 °C, 400 MHz, DMSO-d_6): δ (ppm) = 8.21–8.31 (m, 4H, Ar–H), 7.11–6.87 (m, 4H, ArH), 3.81 (s, 2H, POH), 3.73 (s, 6H, OCH$_3$), 3.53 (m, 8H, OCH$_2$), 1.65 (m, 8H, OCH$_2$CH$_2$); ^{31}P NMR (25 °C, 161.975 MHz, DMSO-d_6, 65% H$_3$PO$_4$): δ (ppm) = 42.3, 56.9 (br); **1** was insoluble in other commonly used NMR solvents; IR (KBr), $\tilde{v}$(cm^{-1}) = 2880 w (CH$_3$O), 2293 br, 1591 m, 1497 s (P–C), 1256 s, 657 s (P=S).

Compound **2**: A mixture of Woollins' reagent 266 mg (0.50 mmol) and NaS^{t}Bu 112 mg (1.00 mmol) was dissolved in 10 mL THF. The colorless solution was stirred for about 5 h at room temperature, and then added to [NiCl$_2 \cdot 6$H$_2$O] 119 mg (0.50 mmol). The filtrate was layered with 20 mL hexane. Storage of the solution at room temperature for 2 weeks produced brown crystals of **2**. Alternative procedure: a mixture of Woollins' reagent 266 mg (0.50 mmol) and [Ni(OAc)$_2 \cdot 4$H$_2$O] 125 mg (0.50 mmol) was dissolved in 8 mL THF. The brown solution was stirred overnight at room temperature, and then the filtrate was layered with 40 mL hexane. Storage of the solution at room temperature for 2 weeks produced brown crystals of **2**. Yield 0.23 g (60%). M.p. 180 °C (decomposition). Elemental Anal. Calc. for $C_{20}H_{28}NiO_4P_2Se_4$: C, 31.24; H, 3.67. Found: C, 30.88; H, 3.49%. ^{1}H NMR (25 °C, 400 MHz, THF-d_8): δ (ppm) = 12.19 (s, 2H, POH), 8.17 (m, 4H, Ar–H), 7.54 (m, 6H, ArH), 3.65 (m, 8H, OCH$_2$), 1.80 (m, 8H, OCH$_2$CH$_2$) ^{31}P NMR (25 °C, 161.975 MHz, THFd_8, 65% H$_3$PO$_4$): δ(ppm) = 37.9 (s. + d satellites, ^1J(P,Se) = 520 Hz); IR (KBr), $\tilde{v}$(cm^{-1})

= 3129 br, 1478 m (P–C ar.), 1434 s, 1110 s, 900 br s, 685 s (P=S).

Compound **3**: A mixture of P$_2$S$_5$ 111 mg (0.50 mmol) and NaS^{t}Bu 112 mg (1.00 mmol) was dissolved in 7 mL THF. The yellow solution was stirred for about 5 h at room temperature, and then added to [NiCl$_2 \cdot 6$H$_2$O] 119 mg (0.50 mmol). The filtrate was layered with 20 mL hexane. Storage of the solution at room temperature for 2 weeks produced purple crystals of **3**. Yield 0.09 g (39% based on NaS^{t}Bu supplied). M.p. 250 °C (decomposition). Elemental Anal. Calc. for $C_8H_{20}NiO_6P_2S_4$: C, 20.84; H, 4.73. Found: C, 20.62; H, 4.17%; ^{1}H NMR (25 °C, 400 MHz, DMSO-d_6): δ (ppm) = 3.91 (s, 4H, POH), 3.59 (m, 4H, OCH$_2$), 1.75 (m, 4H, OCH$_2$CH$_2$); ^{13}C NMR (25 °C, 100.62 MHz, DMSO-d_6): δ (ppm) = 67.0, 25.1; ^{31}P NMR (25 °C, 161.975 MHz, DMSO-d_6, 65% H$_3$PO$_4$): δ (ppm) = −0.8; discrepancies between THF content in isolated crystals, crystal structure and NMR spectra result from placing several solid samples of **3** under dynamic vacuum for various periods of time prior to analysis.

2.2. X-ray crystallographic study

Data were collected on a STOE IPDS II and STADI V diffractometer equipped with CCD detector using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (all data) using the SHELXTL program package [15]. Hydrogen atoms were placed in calculated positions, non-hydrogen atoms were assigned anisotropic thermal parameters. In Table 1 details of the refinement are listed.

Table 1
Details of the X-ray data collection and refinements

Compounds	1	2	3
Formula	$C_{22}H_{32}NiO_6P_2S_2$	$C_{20}H_{28}NiO_4P_2Se_4$	$C_{16}H_{36}NiO_8P_2S_4$
Formula weight	641.37	768.91	605.34
T (K)	173(2)	150(2)	200(2)
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	8.3593(6)	9.905(2)	8.059(2)
b (Å)	9.4774(12)	22.466(3)	9.431(3)
c (Å)	10.4564(14)	11.906(4)	10.392(3)
α (°)	64.376(13)	90	71.86(4)
β (°)	75.010(9)	92.90(2)	77.80(4)
γ (°)	71.497(9)	90	65.62(4)
V (Å^3)	701.14(14)	2646.2(10)	680.5(4)
Z	1	4	1
ρ_{calc} (g cm^{-3})	1.519	1.930	1.477
μ (mm^{-1})	1.139	6.380	1.173
$F(0\,0\,0)$	334	1496	318
2θ Range (°)	7.72–62.88	3.88–53.92	4.14–51.68
Reflections collected	5271	7506	5318
Unique data	3044	5157	2430
R_{int}	0.0302	0.0577	0.0675
Parameters	161	280	145
S (Goodness-of-fit)	1.279	1.001	1.056
wR_2 (all data)	0.1653	0.1053	0.1409
R_1 [$I > 2\sigma(I)$]	0.0419	0.0486	0.0475
Peak, hole (e Å^{-3})	1.067, −1.294	1.147, −0.678	0.441, −0.727

## 3. Results and discussion

Recently it was shown that the reaction of Lawesson's reagent (L.R.) $[ArP(S)(\mu\text{-}S)]_2$ (Ar = 4-anisyl) gives rise to 1D-polymeric arrangements of $[K\{ArP(S^{t}\text{-}Bu)S_2\}]_4$-tetramers (Scheme 1) [16]. By a similar reaction of Woollins' reagent (W.R.) $[PhP(Se)(\mu\text{-}Se)]_2$ with NaS^tBu, $\frac{1}{\infty}[Na_2(PhPSe_3)(thf)_3]_\infty$ was obtained in good yield (Scheme 1) [14]. Both polymeric alkali metal complexes are potentially useful starting materials for the construction of a variety of polymeric metal architectures containing the $[ArP(S^tBu)S_2]^-$ or the $[PhPSe_3]^{2-}$ anion.

In a first attempt to build up hydrogen-bonded oligomeric structures NaS^tBu was reacted with P-chalcogenide precursors (L.R., W.R., P_2S_5) to generate in situ alkali metal complexes of P-chalcogenido anions. Metathesis reactions with hydrated Ni(II) salts were subsequently used for controlled hydrolysis of P-chalcogenido anions. The results of these efforts are summarized in Scheme 2.

In the solid state the structure of 1 consists of a $[Ni\{ArP(OH)S_2\}_2]$ structural motif which has been observed earlier [17]. In 1 THF is strongly hydrogen-bonded to hydroxy groups of the central $[Ni\{ArP(OH)S_2\}_2]$ moiety forming an overall monometallic entity (Fig. 1). In DMSO-d_6 solutions of 1, evidence for the P–OH fragment was found in the ^1H NMR spectrum at δ 3.81 indicating that H-bonds are cleaved. In the ^{31}P NMR, however, the observation of two resonances pointed towards decomposition of crystals of 1 in DMSO-d_6. In the solid state the P–O bond distance found in the $[ArP(OH)S_2]^-$ anion in 1 [P–O 1.569(2) Å] is slightly longer than P–O distances found in the related anion $[ArP(O)S_2]^{2-}$ [P–O 1.497(5)–1.505(5) Å] [13]. Compound 1 could be used in future as a building block for supramolecular assembly reactions but at this stage it serves as an example to illustrate how easy PS-precursors like L.R. can be converted when reacted with an alkali metal salt and, in a second reaction step, with a hydrated transition metal salt (here $[NiCl_2 \cdot 6H_2O]$).

The synthetic route was applied for the synthesis of the Se compound 2 which is isostructural to 1 (Fig. 2, Scheme 2). $[PhP(OH)Se_2]^-$ anions were formed during the course of the reaction. The substitution pattern at the phosphorus atom in 2 is rare and only few examples of P-based ligands are known which both contain hydroxyl groups and Se atoms [18]. Crystals of 2 were soluble in THF-d_8 and a proton resonance of the hydroxy group in the P–O–H···O(thf) fragment was observed at δ 12.19. The P–O bond distances found in the $[PhP(OH)Se_2]^-$ anions in 2 [P–O 1.561(5) and
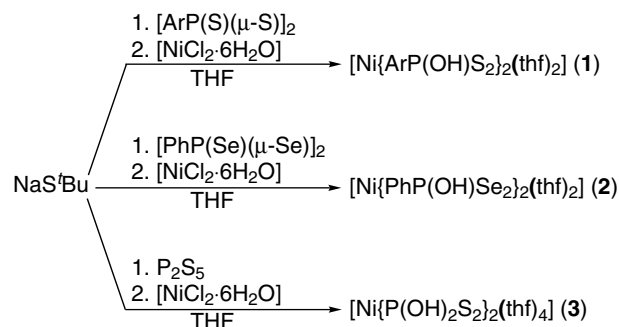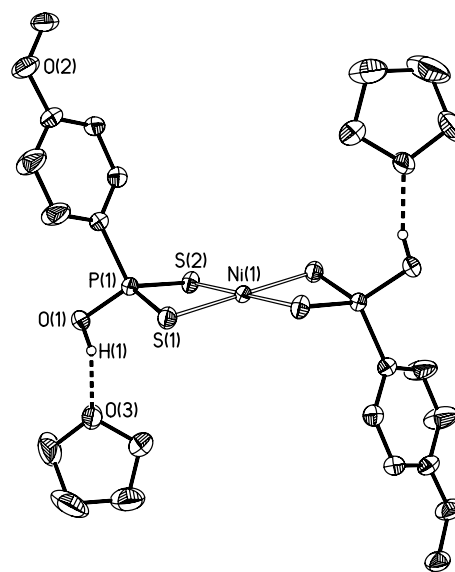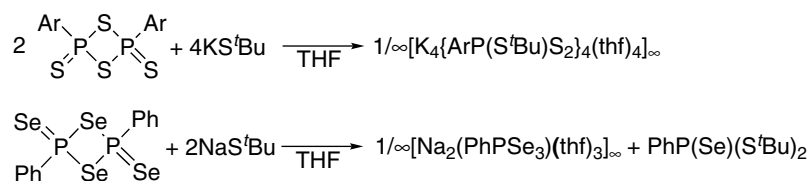
Scheme 2. Synthesis of 1–3 (Ar = 4-anisyl).

Fig. 1. Molecular structure of 1 (50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Ni(1)–S(1) 2.2301(8), Ni(1)–S(2) 2.2273(7), P(1)–O(1) 1.569(2), P(1)–C(1) 1.789(3), P(1)–S(1) 2.0099(10), P(1)–S(2) 2.0039(10), O(1)···O(3) 2.514(3), S–Ni(1)–S 87.94(3), 92.06(3), O(1)–P(1)–S(2) 116.39(10), C(1)–P(1)–S(2) 112.32(10), O(1)–P(1)–S(1) 113.07(9), C(1)–P(1)–S(1) 113.15(10), S(2)–P(1)–S(1) 100.89(4).

1.565(6) Å] are slightly longer than the P–O distance found in the related anion $[ArP(O)Se_2]^{2-}$ [P–O 1.525(5) Å] [19]. In the solid state molecules of 2 form pseudo dimeric arrangements with nonbonding Se···Se distances of ca. 3.8 Å (Fig. 3).

Similar to the P/S- and P/Se-chalcogenide precursors employed so far, an initial investigation of reactions of P_2S_5 with alkali metal thiolates was performed and a preliminary result is reported here. Compound 3 was obtained

Scheme 1. Generation of the $[ArP(S^tBu)S_2]^-$ and the $[PhPSe_3]^{2-}$ anion (Ar = 4-anisyl).
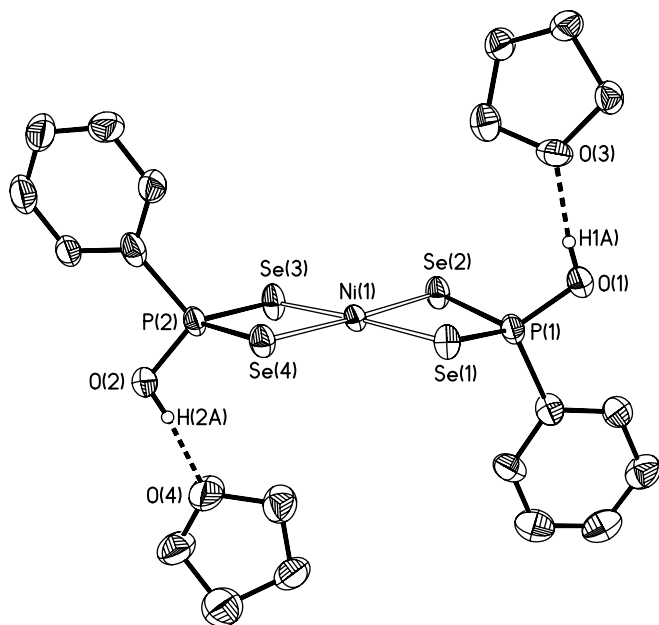
Fig. 2. Molecular structure of **2** (50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Se(1)–Ni(1) 2.3498(11), Se(2)–Ni(1) 2.3509(11), Se(3)–Ni(1) 2.3307(11), Se(4)–Ni(1) 2.3507(11), Se(1)–P(1) 2.1610(18), Se(2)–P(1) 2.1592(18), Se(3)–P(2) 2.1619(17), Se(4)–P(2) 2.1716(19), P(1)–O(1) 1.561(5), P(2)–O(2) 1.565(6), O(1)···O(3) 2.549(9), O(2)···O(4) 2.527(9), Se(1)–Ni(1)–Se(2) 90.32(4), Se(1)–Ni(1)–Se(4) 91.02(4), Se(3)–Ni(1)–Se(1) 177.04(6), Se(3)–Ni(1)–Se(4) 89.60(4), Se(3)–Ni(1)–Se(2) 89.16(4), Se(4)–Ni(1)–Se(2) 177.58(5), Se(2)–P(1)–Se(1) 100.98(7), Se(3)–P(2)–Se(4) 99.15(7), P–Se–Ni 83.78(5)–85.27(5), O–P–Se 114.6(2)–115.7(2), C–P–Se 111.0(2)–113.7(2).
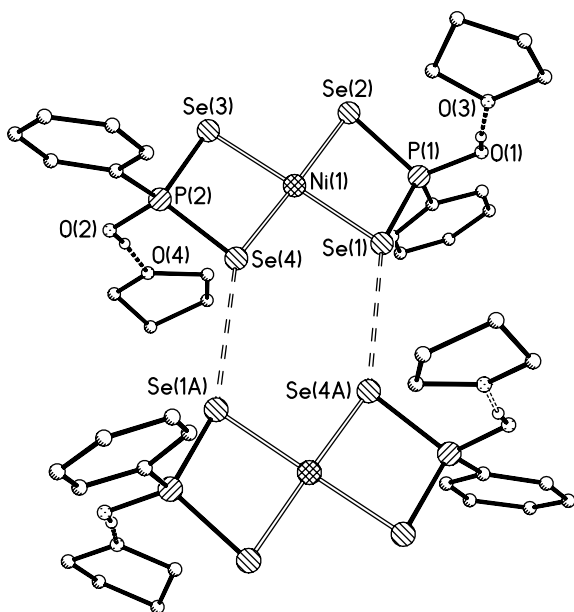

Fig. 3. Pseudodimeric arrangement of two molecules of **3** in the solid state [Se(1)···Se(4A) *ca.* 3.8 Å]. Final label A denotes symmetry operation −x, −y + 1, −z.

in moderate yield. In the solid state **3** consists of two [P(OH)$_2$S$_2$]$^-$ anions coordinating Ni(1) via the soft S donor centres whilst hydroxy groups are involved in hydrogen-bonding (Fig. 4).
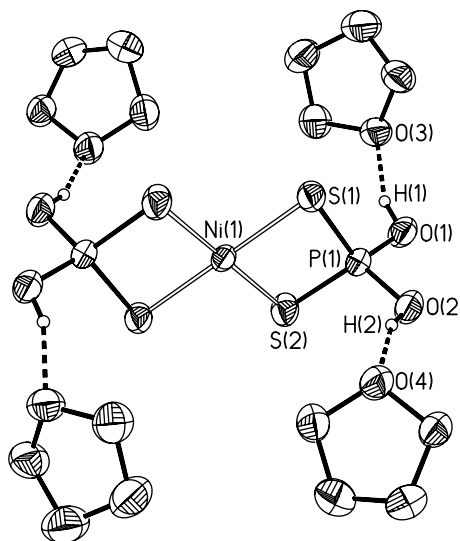

Fig. 4. Molecular structure of **3** (50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Ni(1)–S(1) 2.2187(11), Ni(1)–S(2) 2.2368(16), P(1)–S(1) 2.0140(16), P(1)–S(2) 2.0002(14), P(1)–O(1) 1.549(3), P(1)–O(2) 1.555(2), S–Ni–S 87.98(6), 92.02(6), 179.999(2), O(1)···O(3) 2.507(4), O(2)···O(4) 2.527(4), O(1)–P(1)–O(2) 99.41(14), O(1)–P(1)–S(1) 114.69(11), O(1)–P(1)–S(2) 115.34(11), O(2)–P(1)–S(1) 114.25(11), O(2)–P(1)–S(2) 112.99(12), S(2)–P(1)–S(1) 100.87(6).

So far the closest related compound to **3** represents sodium dithiophosphate Na$_3$PO$_2$S$_2$ by Jansen et al., which was synthesized to investigate its ionic conducting properties [20–22]. Although mechanistic investigations of the fragmentation of P/S-cage molecules were in the present case hindered by the poor solubility of byproducts current and future work focuses on this aspect.

4. Conclusion

The preparation and structural characterisation of three Ni(II) salts containing [ArP(OH)S$_2$]$^-$ (Ar = 4-anisyl), [PhP(OH)Se$_2$]$^-$ and [P(OH)$_2$S$_2$]$^-$ anions are reported. The syntheses were performed by nucleophilic fragmentation reactions of neutral P-chalcogenides with alkali metal salts and subsequent metatheses with [NiCl$_2$ · 6H$_2$O].

5. Supplementary material

CCDC 614760, 614761 and 614762 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via htpp://www.ccdc.cam. ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit @ccdc.cam.ac.uk.

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