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Polymeric Organometallic Architectures of Novel P–Se Anions

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In memory of Dr. Alexander Hopkins

Abstract: The characterisation of a series of compounds obtained from Woollins' reagent (W.R.) offers a novel approach to organometallic coordination polymers. The syntheses were achieved by nucleophilic ring-opening reactions of W.R. with metal salts and crystallisation using solvent-diffusion techniques. One-dimensional coordination polymers are formed as a result, and we demonstrate that the dimensionality of the polymers can be influenced by using hydrated metal salts or by the construction of heterometallic arrangements.

Keywords: alkali metals · phosphorus · polymers · selenium · supramolecular chemistry

Introduction

In phosphorus–chalcogenide chemistry, there are several reports on the synthesis of larger molecular aggregates that describe, for example, the synthesis of polymeric coordination compounds, materials and [P/S]-functionalised DNA.[1–4] A great deal of work has also been reported on phosphorus- and sulfur- or selenium-containing compounds, such as R_3PE, $[RP(E)(ESiMe_3)_2]$, $[\{RP(E)(\mu\text{-}E)\}_2]$ (E = S, Se) (R = organic group), which are useful starting materials for metal chalcogenide nanoparticles, molecular complexes with P-chalcogenide ligands and chalcogen-transfer reactions.[5–11] However, in our view, the principle that weak interactions between atoms can be used for the formation of highly ordered structures has not been extensively exploited in the area of phosphorus–chalcogenides.[12–14] A possible reason for this is that coordination chemistry in this field is still being developed. Current synthetic efforts in the field concentrate on metal complexes with ligands designed by formally replacing O atoms in phosphate ions with OR, SR, S, Se, OSe and combinations thereof, and ultimately on the construction of larger molecular aggregates.[15–20] In previous work, it was shown that reactions of metal salts MX (X = alkoxide, thiolate, carboxylate) with Lawesson's reagent (L.R.) $[\{RP(S)(\mu\text{-}S)\}_2]$ (R = 4-anisyl)[21] or the analogous Se compound Woollins' reagent (W.R.) $[\{PhP(Se)(\mu\text{-}Se)\}_2]$[8,22] offer an alternative route to complexes containing P/S- or P/Se-based anionic ligands.[11,23–25] As far as W.R. is concerned, it was shown that nucleophilic ring-opening with alkali-metal thiolates results in polymeric arrangements of $[PhPSe_3]^{2-}$ and $[PhPSe_2Se{-}SeSe_2PPh]^{2-}$ dianions, depending on the size of the alkali metal.[25] These initial results prompted us to investigate further the synthesis of molecular and supramolecular arrangements of novel P–Se anions. Some of the results fundamental for the further development in this area are described here.

Results and Discussion

For the synthesis of selenophosphonate anions, one of the few stable and isolable starting materials is W.R., which can be prepared in high yield.[8] Here, the reactions of W.R. with the nucleophiles KO*t*Bu, NaSe*t*Bu, KOAc, $NaOAc{\cdot}3H_2O$ and CuOAc are described (Scheme 1), and an attempt is made to relate the outcome of crystallographic investigations to the type of metal salt used.

By reacting KO*t*Bu with W.R. in tetrahydrofuran, single crystals of potassium phosphonodiselenolate $^{1}_{\infty}[K_2\{PhP(OtBu)Se_2\}_2(thf)]_\infty$ (**1**) were obtained by diffusion of hexane into the reaction mixture (Scheme 1).

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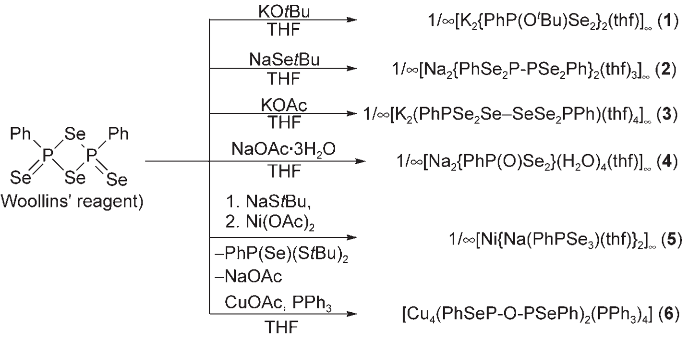

Scheme 1. Synthesis of **1**–**6**.

In the solid state, **1** consists of a polymeric arrangement, for which the asymmetric unit contains two independent $[PhP(O\textit{t}Bu)Se_2]^{2-}$ anions held together by two K^+ ions. A closer look at the structure of **1** reveals that $[PhP(O\textit{t}Bu)Se_2]^{2-}$ anions bridge the K^+ cations in different modes (Figure 1).

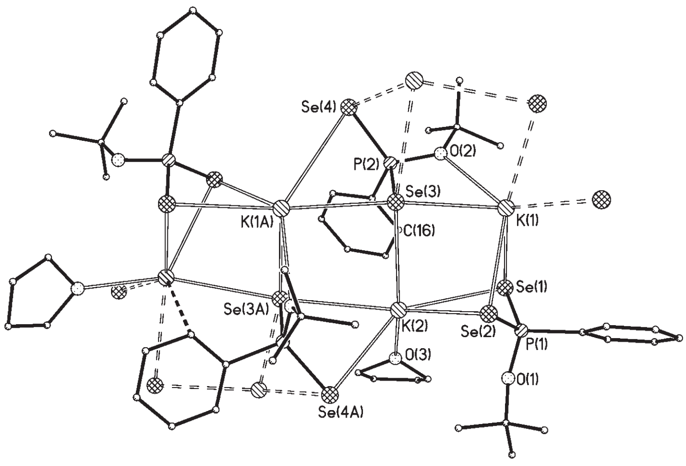

Figure 1. Section of polymeric **1** in the solid state. Label letter A denotes the symmetry operation $-x+1/2$, $y+1/2$, $-z+3/2$. Selected bond lengths [Å] and angles [°]: Se–P 2.1240(18)–2.1565(16), K–Se 3.2847(19)–3.8982(18), P(1)–O(1) 1.601(4), P(2)–O(2) 1.616(4), K(1)–O(2) 3.074(5), K(2)–O(3) 2.764(7), K(2)···C(16) 3.235(7); K(1)-Se(3)-K(1A) 167.48(4), Se(2)-K(2)-Se(3A) 147.47(5).

A $[PhP(O\textit{t}Bu)(\mu_2\text{-}Se)_2]^{2-}$ anion (containing P(1)) bridges K(1) and K(2) through Se-donor centres. The O*t*Bu group of this anion is not involved in metal coordination. In contrast, in the $[PhP(\mu\text{-}O\textit{t}Bu)(\mu_4\text{-}Se)(\mu_2\text{-}Se)]^{2-}$ anion (containing P(2)), both O- and Se-donor centres are involved in metal coordination. K–Se distances in **1** span a broad range of 3.2847(19)–3.8982(18) Å and indicate that the highly ordered arrangement in **1** is held together by electrostatic interactions of various strengths. Similar coordination has not yet been observed for $[PhP(OR)Se_2]^-$ ligands (R = Et, *i*Pr), which commonly are bidentate and chelate metal atoms through chalcogen atoms, while the introduced alkoxide group is not involved in metal coordination.[7] In **1**, K(1) and K(2) are six-coordinated by five Se atoms and an oxygen atom belonging to a $[PhP(O\textit{t}Bu)Se_2]^{2-}$ anion [K(1)] or the auxiliary ligand THF [K(2)]. Another difference in the coordination environments of the potassium ions in **1** is the close contact between K(2) and C(16) (Figure 1); similar contacts are not observed for K(1).

Follow-up investigations to this and recent results of reactions between W.R. and alkali-metal thiolates involved reactivity studies of W.R. with alkali-metal selenolates.[25] In the case of NaSe*t*Bu, this resulted in the formation of ${}^{1}_{\infty}[Na_2\{PhSe_2P{-}PSe_2Ph\}(thf)_3]_\infty$ (**2**), which was obtained as single crystals by solvent-diffusion methods (Scheme 1). Although the reaction mechanism leading to the formation of **2** has not been investigated in detail, it seems likely that mixtures of W.R. and NaSe*t*Bu initially form Na complexes containing a $[PhP(Se\textit{t}Bu)Se_2]^-$ anion that decomposes into $(\textit{t}BuSe)_2$ and the $[PhSe_2P{-}PSe_2Ph]^{2-}$ anion observed in **2**. A decomposition reaction with a similar outcome was observed in the reaction of $PhPS(SSiMe_3)_2$ with $Ag(CF_3CO_2)$, in which ${}^{1}_{\infty}[Ag_2(PhS_2P{-}PS_2Ph)(dppe)_2]_\infty$ was formed (DPPE = 1,2-bis(diphenylphosphino)ethane).[26] Compound **2** is soluble in THF or dimethylsulfoxide (DMSO) and the anion remains intact, allowing characterisation by NMR. Figure 2 (top) shows the ${}^{31}P\{{}^{1}H\}$ NMR spectrum of **2** in which a singlet resonance is observed at $\delta = 46.8$ ppm. Upon prolonged recording times centred around this singlet, eight satellite lines become visible, indicating the presence of an ABX three-spin system, which is in good agreement with an optimised simulated ${}^{31}P\{{}^{1}H\}$ NMR spectrum of **2** (Figure 2, bottom) $(Ph({}^{77}Se)SeP{-}PSe_2Ph$; ${}^{1}J(P,P) = -146$ Hz, ${}^{1}J(P,Se) = -659$ Hz, ${}^{2}J(P,Se) = 9$ Hz; ${}^{1}J(P,Se)$ and ${}^{2}J(P,Se)$ coupling constants have opposite signs).[27,28] Other isotopomeric compounds present in solution cannot be detected.

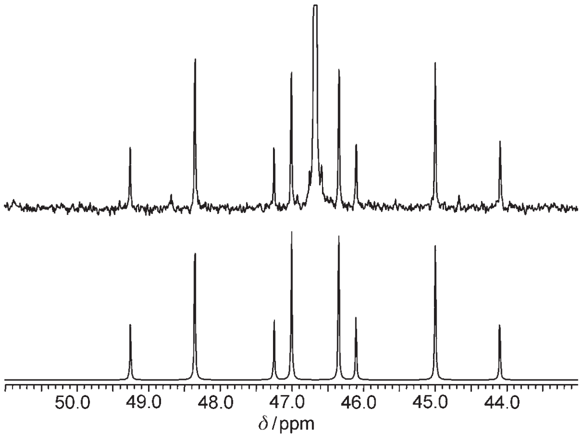

Figure 2. ${}^{77}Se$ satellites in the ${}^{31}P\{{}^{1}H\}$ NMR spectrum of **2** (top) and simulation (bottom).

In the solid state, **2** consists of a one-dimensional polymeric arrangement of $[PhSe_2P{-}PSe_2Ph]^{2-}$ anions held together by penta- [Na(2)] and hexacoordinated [Na(1)] alkali-metal ions (Figure 3). The P–P backbone of dianions is located in an alternating fashion above and below a band of two corrugated one-dimensional Na–Se(2) and Na–Se(3)

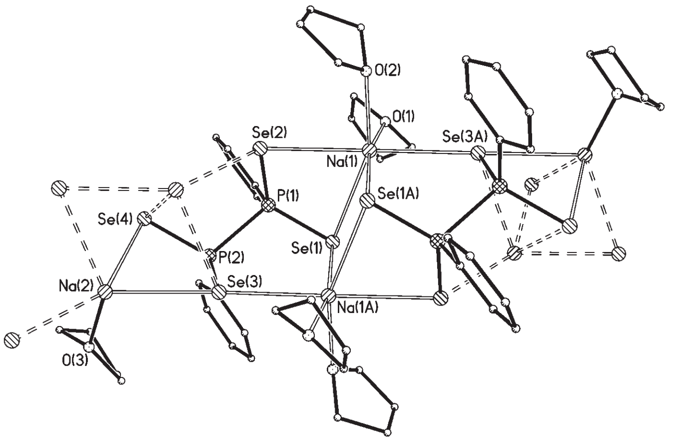

Figure 3. Section of polymeric **2** in the solid state. Label letter A denotes the symmetry operation $-x+1$, $-y$, $-z+2$. Selected bond lengths [Å] and angles [°]: Se(1)–P(1) 2.1461(13), Se–Na 3.0221(19)–3.284(2), Se(2)–P(1) 2.1500(12), Se(3)–P(2) 2.1544(12), Se(4)–P(2) 2.1459(13), P(1)–P(2) 2.2625(16), O(1)–Na(1) 2.378(4), O(2)–Na(1) 2.395(4), O(3)–Na(2) 2.291(4); Se(1)-P(1)-Se(2) 117.01(6), Se(1)-P(1)-P(2) 109.21(6), Se(2)-P(1)-P(2) 106.90(6), Se(4)-P(2)-Se(3) 113.61(5), Se(4)-P(2)-P(1) 108.89(6), Se(3)-P(2)-P(1) 107.43(6).

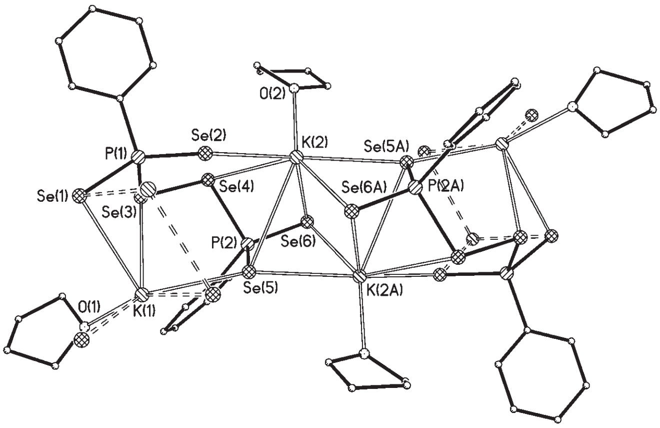

Figure 4. Section of polymeric **3** in the solid state. Label letter A denotes the symmetry operation $-x+2$, $-y$, $-z+1$. Selected bond lengths [Å] and angles [°]: Se–P 2.1296(8)–2.2996(8), Se(4)–Se(3) 2.3369(4), K–Se 3.2282(8)–3.6150(7), K(1)–O(1) 2.698(3), K(2)–O(2) 2.661(3); P(2)-Se(4)-Se(3) 102.56(2), P(1)-Se(3)-Se(4) 107.23(2), Se(5)-P(2)-Se(6) 117.69(3), Se(5)-P(2)-Se(4) 111.49(3), Se(6)-P(2)-Se(4) 99.28(3), Se(2)-P(1)-Se(1) 118.54(4), Se(2)-P(1)-Se(3) 114.61(3), Se(1)-P(1)-Se(3) 97.56(3).

strands, with Se(1) and Se(4) bridging the Na ions. The *gauche* conformation of phenyl groups in $[PhSe_2P{-}PSe_2Ph]^{2-}$ anions apparently favours this arrangement and the NMR study indicates that rotation of the P–P bond in solutions of **2** at room temperature is hindered.

Having shown that reactions of W.R. and alkali-metal alkoxides, thiolates and selenolates produce a range of novel complexes containing the anions $[PhP(OtBu)Se_2]^{2-}$, $[PhPSe_3]^{2-}$, $[PhPSe_2Se{-}SeSe_2PPh]^{2-}$ and $[PhSe_2P{-}PSe_2Ph]^{2-}$, our next efforts were directed towards exploration of reactions between the P–Se precursor W.R. and metal carboxylates. Similar to reported results of reactions between L.R. and metal carboxylates, which were thermodynamically driven by the formation of P–O and metal–S bonds in products, the formation of metal–Se bonds in a variety of conditions was now investigated.[11] Initial attempts in refluxing toluene often produced amorphous precipitates of metal selenides. Optimised reaction conditions finally yielded crystals of $^1_\infty[K_2(PhPSe_2Se{-}SeSe_2PPh)(thf)_4]_\infty$ (**3**) from a reaction mixture of W.R. and KOAc in THF (Scheme 1). In the solid state, **3** exists as a one-dimensional polymeric ladder of two dimerised [KSe] strands isostructural to a compound obtained from reactions of W.R. and KS*t*Bu (Figure 4).[25]

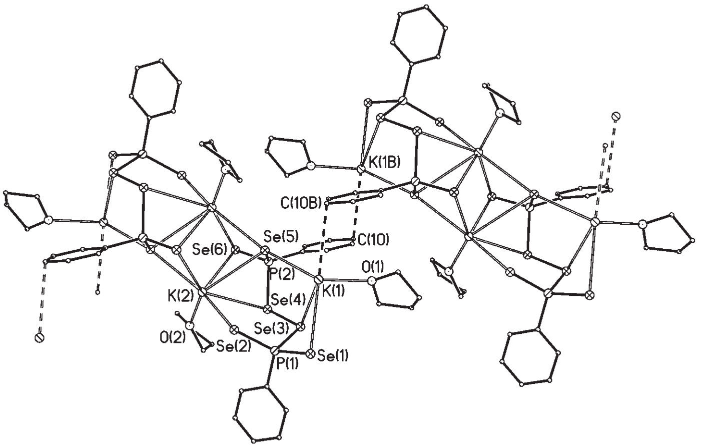

Figure 5. Arrangements of one-dimensional coordination polymeric strands of **3** in the solid state. Label B denotes the symmetry operation $-x+1$, $-y$, $-z$ (K(1)···C(10B) 3.463(3) Å).

The one-dimensional polymeric strands in **3** exhibit an orientation relative to each other in which close contacts between phenyl carbon atoms and potassium centres result in densely packed polymers (Figure 5).[25] The mechanism likely to be involved in the formation of **3** was investigated for similar reactions of L.R. by conducting GC/MS and ^{31}P NMR spectroscopy.[24,25] To investigate potentially broader applications of nucleophilic ring-opening reactions of W.R. in organometallic-polymer synthesis, hydrated metal salts were employed for combined nucleophilic ring-opening/hydrolysis of W.R. In the case of $NaOAc\cdot 3H_2O$, crystals of $^1_\infty[Na_2(PhPSe_2O)(H_2O)_4(thf)]_\infty$ (**4**) were obtained (Scheme 1). Once isolated, **4** was then insoluble in [D$_8$]THF and D_2O, preventing characterisation by NMR. The solid-state structure of a building block in **4** (Figure 6) consists of two crystallographically independent Na atoms and symmetry-equivalent Na atoms held together by an elaborate arrangement of $[PhP(O)Se_2]^{2-}$ anions and hydrogen-bonded water. Na(1) is coordinated by Se-donor centres and O atoms of THF and water.

As part of a one-dimensional polymeric strand, Na(1) is in an environment similar to that of the alkali-metal atoms in compounds **1**–**3**. Perpendicular to this arrangement Na(2), Na(2A) and symmetry-equivalent atoms are arranged by bridging μ-H_2O ligands into another one-dimensional polymeric motif observed in **4**. Altogether, this results in a self-assembled layer-sandwich structure of lipophilic surface

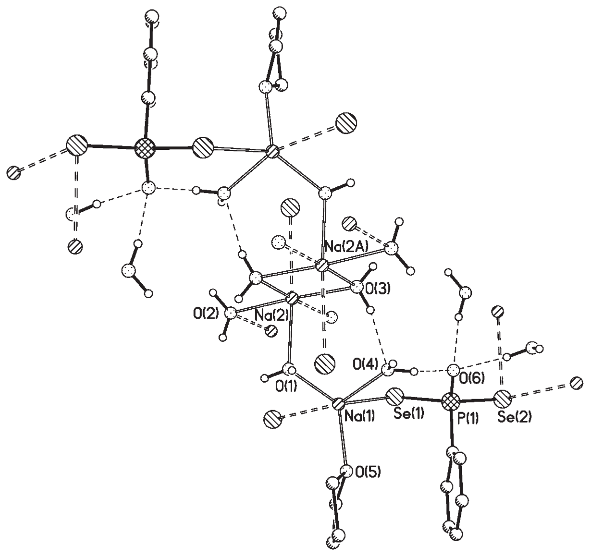

Figure 6. Structure of a building block of **4** in the solid state. Label A denotes the symmetry operation $-x+3$, $-y+2$, $-z+1$. Selected bond lengths [Å] and angles [°]: Na–O(H_2O) 2.27(2)–2.443(6), Na(1)–O(5) 2.29(3), Na–Se 3.023(3)–3.057(3), P(1)–O(6) 1.525(5), P(1)–Se(2) 2.1592(18), P(1)–Se(1) 2.1651(18); Na(2A)-O(3)-Na(2) 92.1(2), O(6)-P(1)-Se(2) 111.5(2), C(1)-P(1)-Se(2) 105.0(2), O(6)-P(1)-Se(1) 111.5(2), C(1)-P(1)-Se(1) 107.3(3), Se(2)-P(1)-Se(1) 113.59(8).

groups (topologically similar, but electronically inverse $[Na(thf)]^+$ and $[PhP(O)Se_2]^{2-}$ ions) held together by an inner polar arrangement of Na^+ and H_2O (Figure 7).

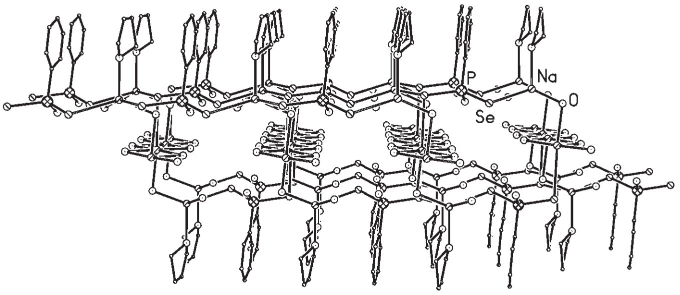

Figure 7. Packing diagram of **4** (without H atoms; only one position of disordered THF is displayed).

A challenge resulting from these findings was to try to connect polymeric assemblies by incorporating metal ions with fixed coordination geometries and to thereby apply a "building-block' approach to polymers of different dimensionality. The synthetic strategy was to carry out metathesis reactions of $[Na_2(PhPSe_3)(thf)_3]$ with substoichiometric amounts of metal salts. The first result from this strategy is the polymeric $^1_\infty[\mathrm{Ni\{Na(PhPSe_3)(thf)\}_2}]_\infty$ (**5**) that was isolated together with previously reported $[\mathrm{Ni\{Na(PhPSe_3)(thf)_3\}_2}]$ (Scheme 1).[25] Although crystals of **5** were generally of poor quality, the solid-state structure could be established (Figure 8).

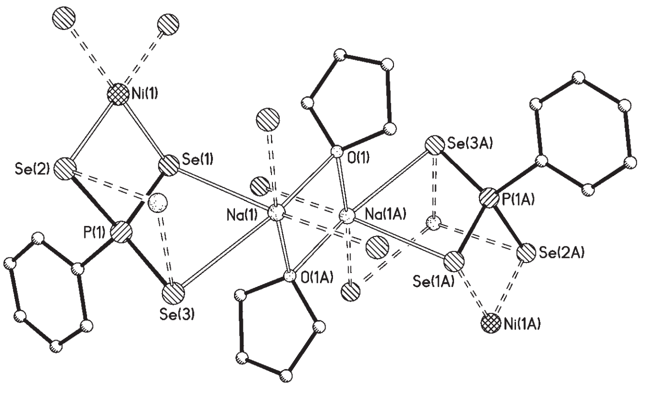

Figure 8. Section of polymeric **5** in the solid state. Label A denotes the symmetry operation $-x+2$, $-y+1$, $-z+1$. Selected bond lengths [Å] and angles [°]: Na(1)–O(1) 2.43(2), Na(1A)–O(1) 2.44(2), Na(1)–Se(1) 3.010(12), Na(1)–Se(3) 3.137(11), P(1)–Se(3) 2.135(7), P(1)–Se(2) 2.213(7), P(1)–Se(1) 2.213(7), Ni(1)–Se(1) 2.333(3), Ni(1)–Se(2) 2.343(3); O(1A)-Na(1)-Se(1) 93.4(6), O(1)-Na(1)-Se(3) 166.8(7), O(1A)-Na(1)-Se(3) 90.1(6), Se(1)-Na(1)-Se(3) 73.9(3), Se(3)-P(1)-Se(2) 115.3(3), Se(3)-P(1)-Se(1) 116.4(3), Se(2)-P(1)-Se(1) 95.2(3), Se(1)-Ni(1)-Se(2) 88.70(9), P(1)-Se(1)-Ni(1) 88.1(2), P(1)-Se(1)-Na(1) 85.7(3), Ni(1)-Se(1)-Na(1) 115.5(2), P(1)-Se(2)-Ni(1) 87.90(19), P(1)-Se(3)-Na(1) 83.8(3).

As in **1**–**3**, the alkali-metal ions in **5** form a one-dimensional polymer with $[PhPSe_3]^{2-}$ anions, however, these are now linked by the square-planar coordinated Ni(1) into a two-dimensional sheet. The Se atoms in the $[PhPSe_3]^{2-}$ anions bridge between Na atoms, whereas Ni(1) is chelated by two Se atoms belonging to anions of different one-dimensional polymeric strands (Figure 8).

The investigations in which tetrahedrally and octahedrally surrounded metal atoms are incorporated to give cross-linked organometallic polymers based on P–Se anions are still at an early stage. In this context, somewhat unpredictable results have been observed, as shown by the following example. The reaction of CuOAc with W.R. and successive treatment with PPh_3 afforded the crystalline compound $[Cu_4(PhSeP{-}O{-}PSePh)_2(PPh_3)_4]$ (**6**). In the solid state, **6** exhibits a cage arrangement of four distorted-tetrahedrally coordinated Cu^+ ions and the unusual dianion $[PhSeP{-}O{-}PSePh]^{2-}$ (Figure 9).

The formation of this anion indicates that reduction of P atoms has occurred during the reaction. It is likely that intermediates of the type $[Cu_2(PhSe_2P{-}O{-}PSe_2Ph)]$ are formed initially, together with Ac_2O. Subsequently, the PPh_3 present in solution acts both as ligand and reducing agent to give **6** and $P(Se)Ph_3$.[23,24] Reduction of W.R. in the presence of phosphines was also encountered in other investigations, and results of further studies in which this reaction was used will be reported shortly.

Conclusion

The characterisation of a series of compounds obtained from W.R. offers a novel approach to organometallic coordination polymers. The syntheses were achieved by nucleo-

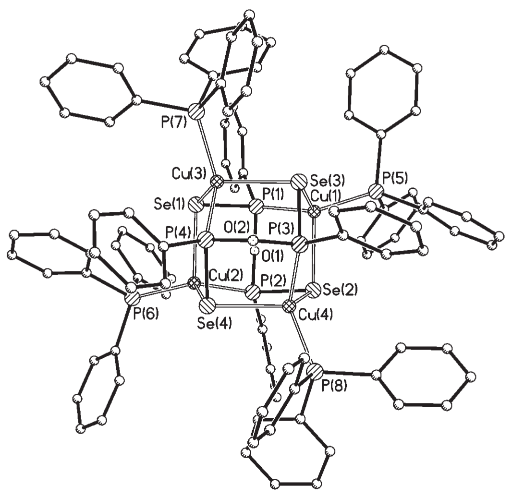

Figure 9. Molecular structure of **6** in the solid state. Selected bond lengths [Å] and angles [°]: Se−Cu 2.4353(9)–2.5077(9), Cu(1)−P(1) 2.2643(15), Cu(2)−P(2) 2.2573(17), Cu(3)−P(4) 2.2466(17), Cu(4)−P(3) 2.2407(15), Cu−P(PPh$_3$) 2.2331(16)–2.2462(16), Se(1)−P(1) 2.2363(17), Se(2)−P(2) 2.2380(14), Se(3)−P(3) 2.2394(15), Se(4)−P(4) 2.2414(16), P(1)−O(1) 1.662(5), P(2)−O(1) 1.658(4), P(3)−O(2) 1.657(4), P(4)−O(2) 1.676(4), O(1)−P(1)-Se(1) 103.67(15); O(1)-P(1)-Cu(1) 103.70(16), Se(1)-P(1)-Cu(1) 113.68(7), O(1)-P(2)-Se(2) 103.34(14), O(1)-P(2)-Cu(2) 103.63(17), Se(2)-P(2)-Cu(2) 114.71(6), O(2)-P(3)-C(13) 97.94(19), O(2)-P(3)-Se(3) 103.70(16), O(2)-P(3)-Cu(4) 104.00(15), Se(3)-P(3)-Cu(4) 115.26(6), O(2)-P(4)-Se(4) 103.41(16), O(2)-P(4)-Cu(3) 103.09(15), Se(4)-P(4)-Cu(3) 115.27(7), P(2)-O(1)-P(1) 114.8(2), P(3)-O(2)-P(4) 113.6(2).

philic ring-opening reactions of W.R. with metal salts and crystallisation using solvent-diffusion techniques. It is apparent that, regardless of the nature of the anhydrous alkali-metal salt used, one-dimensional coordination polymers are formed. The exact composition of the P−Se anions generated, however, remains unpredictable because not many examples of these compounds exist. We demonstrated that the dimensionality of the polymers can be influenced by using hydrated metal salts or by the construction of heterometallic compounds, and this will be the subject of future investigations. The reactivity of W.R. as a chalcogen-transfer reagent is described and this should be taken into account in performing similar investigations in the presence of tertiary phosphines or other reducing agents.

Experimental Section

All operations were carried out in an atmosphere of purified dinitrogen. Solvents were dried and were freshly distilled prior to use. W.R. and metal thiolates were prepared according to published procedures.[22,29]

Syntheses:

1: A mixture of W.R. (798 mg, 1.5 mmol) and KO*t*Bu (336 mg, 3.0 mmol) was dissolved in THF (15 mL). The yellow solution was stirred overnight at RT and then layered with 80 mL hexane. Storage of the solution at RT for two weeks produced yellow crystals of **1**. Yield 0.43 g (35 %); m.p. 131 °C (decomposed); ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): $\delta = 1.60$ (s, 18H; C(CH3)3), 1.78 (m, 4H), 3.64 (m, 4H), 7.22 (m, 6H; Ar-H), 8.26 ppm (m, 4H, Ar-H); ^{13}C{^{1}H} NMR (100 MHz, [D$_8$]THF, 25 °C): $\delta =$ 30.1, 30.1, 125.8, 126.0, 127.8, 129.7, 129.8, 147.5, 148.4 ppm; ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF, 25 °C, H$_3$PO$_4$): $\delta = 60.37$ ppm (s + d satellites, ^1J(P,Se) = −675 Hz); ^{77}Se NMR (76 MHz, [D$_8$]THF, 25 °C, SeMe$_2$): $\delta = 151.2$ ppm (d, ^1J(P,Se) = −675 Hz); IR (KBr): $\tilde{\nu} = 3047$ (m), 2970 (br s), 1433 (s) (P−C), 1304 (s), 1162 (s), 1091 (s), 928 (br s), 692 cm^{-1} (s); elemental analysis calcd (%) for $C_{24}H_{36}K_2O_3P_2Se_4$ (828.52): C 34.79, H 4.38; found: C 34.69, H 4.40.

2: THF (10 mL) was added to a mixture of W.R. (266 mg, 0.5 mmol) and NaSe*t*Bu (159 mg, 1.0 mmol). The mixture was stirred at RT overnight. The reaction was filtered and the filtrate (yellow solution) was layered with 40 mL hexane. Storage of the solution at RT for one week produced yellow crystals of **2**. Yield 0.1 g (28 %); m.p. 190 °C (grey), 215 °C (orange-brown); ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): $\delta = 1.76$ (m, 8H), 3.60 (m, 8H), 7.10 (m, 6H; Ar-H), 8.16 ppm (m, 4H; Ar-H); ^{13}C{^{1}H} NMR (100 MHz, [D$_8$]THF, 25 °C): $\delta = 25.1$, 67.0, 124.4, 126.3, 126.8, 127.6, 130.1, 134.8 ppm; ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF, 25 °C, H$_3$PO$_4$): $\delta = 46.8$ ppm (s + m, ^1J(P,Se) = −659 Hz, ^2J(P,Se) = 9 Hz, ^1J(P,P) = −146 Hz); ^{77}Se NMR (76 MHz, [D$_8$]THF, 25 °C, SeMe$_2$): $\delta =$ −20.8 ppm (dd, ^1J(P,Se) = −658 Hz, ^2J(P,Se) = 9 Hz, ^1J(P,P) = −144 Hz); IR (KBr): $\tilde{\nu} = 3047$ (m), 2958 (m), 1434 (s) (P−C), 1084 (s), 689 (s), 523 cm^{-1} (s); elemental analysis calcd (%) for $C_{24}H_{34}Na_2O_3P_2Se_4 \cdot C_4H_8O$: C 33.26, H 3.63; found: C 33.19, H 3.52.

3: THF (8 mL) was added to a mixture of W.R. (266 mg, 0.5 mmol) and KOAc (98 mg, 1.0 mmol). The mixture was heated to reflux for 5 h. The reaction was filtered and the filtrate (yellow solution) was layered with 20 mL hexane. Storage of the solution at RT for four weeks produced orange crystals of **3**. Yield 0.17 g (75 %); m.p. 148–150 °C (decomposed); ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): $\delta = 1.80$ (m, 8H), 3.64 (m, 8H), 7.22 (m, 6H; Ar-H), 8.22 ppm (m, 4H; Ar-H); ^{13}C{^{1}H} NMR (100 MHz, [D$_8$]THF, 25 °C): $\delta = 25.4$, 67.2, 126.1, 126.3, 128.8, 130.3, 145.8 ppm; ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF, 25 °C, H$_3$PO$_4$): $\delta = 12.7$ ppm (s + d satellites, ^1J(P,Se) = −655 Hz); ^{77}Se NMR (76 MHz, [D$_8$]THF, 25 °C, SeMe$_2$): $\delta = 138.0$ (d, ^1J(P,Se) = −655 Hz); IR (KBr): $\tilde{\nu} = 3045$ (m), 2964 (m), 1433 (s) (P−C), 1048 (s), 688 (s), 535 cm^{-1} (s); elemental analysis calcd (%) for $C_{20}H_{26}K_2O_2P_2Se_6$: C 26.33, H 2.87; found: C 26.39, H 2.81.

4: THF (8 mL) was added to a mixture of W.R. (266 mg, 0.5 mmol) and NaOAc·3H$_2$O (136 mg, 1.0 mmol). The mixture was heated for about 5 h, and then the filtrate (yellow solution) was layered with 25 mL hexane. Storage of the solution at RT for four weeks produced colourless crystals of **4**. Yield 0.2 g (50 %); m.p. 95–98 °C (decomposed); IR (KBr): $\tilde{\nu} = 3349$ (br s) (H$_2$O), 3052 (m), 2968 (m), 1433 (s) (P−C), 1040 (s), 689 cm^{-1} (s); elemental analysis calcd (%) for $C_{20}H_{42}Na_4O_{12}P_2Se_4 \cdot C_4H_8O \cdot 4H_2O$: C 24.02, H 3.28; found: C 23.81, H 3.32.

5: A mixture of W.R. (266 mg, 0.50 mmol) and NaS*t*Bu (112 mg, 1.00 mmol) was dissolved in THF (10 mL). The yellow, cloudy solution was stirred for about 5 h at RT, and then added to Ni(OAc)$_2$ (177 mg, 1.00 mmol). The mixture was stirred overnight and the filtrate was layered with 40 mL hexane. Storage of this solution at RT for two weeks produced brown crystals of **5**. Spectroscopic and analytical data are listed in ref. [25].

6: A mixture of W.R. (177 mg, 0.33 mmol) and CuOAc (164 mg, 1.33 mmol) was dissolved in THF (10 mL). The mixture was stirred for 3 h at RT, during which time the formation of a brown precipitate was observed. The mixture was filtered and the residue was added to a solution of PPh$_3$ (0.57 M in THF, 5 mL). Solvent diffusion within a double-Schlenk tube of Et$_2$O into the filtrate produced brown crystals after five weeks; yield 0.04 g (10 %). Despite repeated attempts, correct analysis could not be obtained.

Crystallography: Data were collected by using a STOE IPDS II and a STOE STADI IV (Kuma CCD detector) diffractometer, using Mo$_{K\alpha}$ radiation. The structures were solved by direct methods, and refined by full-matrix least-squares against F^2 using all data (see Table 1). Hydrogen atoms were placed in idealised positions.[30] Disordered C atoms of phenyl groups and THF were refined with isotropic temperature factors. CCDC 603361–603365 (**1**–**4**,**6**) and 606341 (**5**) 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 1. Details of X-ray data collection and refinements.

Compounds	1	2	3	4	5	6
formula	$C_{24}H_{36}K_2O_3P_2Se_4$	$C_{24}H_{34}Na_2O_3P_2Se_4$	$C_{20}H_{26}K_2O_2P_2Se_6$	$C_{10}H_{21}Na_2O_6PSe_2$	$C_{20}H_{26}Na_2NiO_2P_2Se_6$	$C_{104}H_{96}Cu_4O_4P_8Se_4$
formula weight	828.51	794.27	912.31	472.14	938.80	2227.57
T [K]	150(2)	120(2)	100(2)	150(2)	120(2)	100(2)
crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a [Å]	17.0055(10)	11.5501(8)	12.0394(6)	6.839(1)	7.6892(9)	14.0222(6)
b [Å]	10.0063(3)	24.8978(15)	23.4696(10)	7.748(1)	24.398(3)	14.2408(6)
c [Å]	19.1984(11)	11.7555(9)	12.0063(6)	18.691(3)	7.8155(9)	24.6917(11)
α [°]	90	90	90	101.55(1)	90	78.144(3)
β [°]	101.019(4)	116.901(5)	116.301(4)	93.41(1)	91.937(10)	87.007(3)
γ [°]	90	90	90	103.92(1)	90	82.187(3)
V [Å^3]	3206.6(3)	3014.7(4)	3041.3(3)	935.8(2)	1465.3(3)	4779.1(4)
Z	4	4	4	2	2	2
ρ_{calcd} [g cm^{-3}]	1.716	1.750	1.992	1.676	2.128	1.548
μ [mm^{-1}]	4.959	5.027	7.614	4.100	8.270	2.587
$F(000)$	1632	1560	1736	468	892	2248
2θ range [°]	3.56–56.48	3.28–54.14	3.48–56.56	8.16–52.00	3.34–54.08	3.34–56.42
reflns collected	14199	23625	26890	6604	8354	42640
unique data	7442	6591	7497	3591	3175	21721
R_{int}	0.0751	0.0664	0.0431	0.0703	0.1196	0.0439
parameters	316	316	289	209	134	486
$wR2$ (all data)	0.1874	0.1036	0.0701	0.2344	0.4385	0.1738
$R1$ [$I>2\sigma(I)$]	0.0634	0.0424	0.0293	0.0792	0.1345	0.0626
peak, hole [e Å^{-3}]	1.484, −1.403	0.758, −1.042	0.615, −0.909	2.906, −2.136	4.822, −1.941	1.344, −1.036

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