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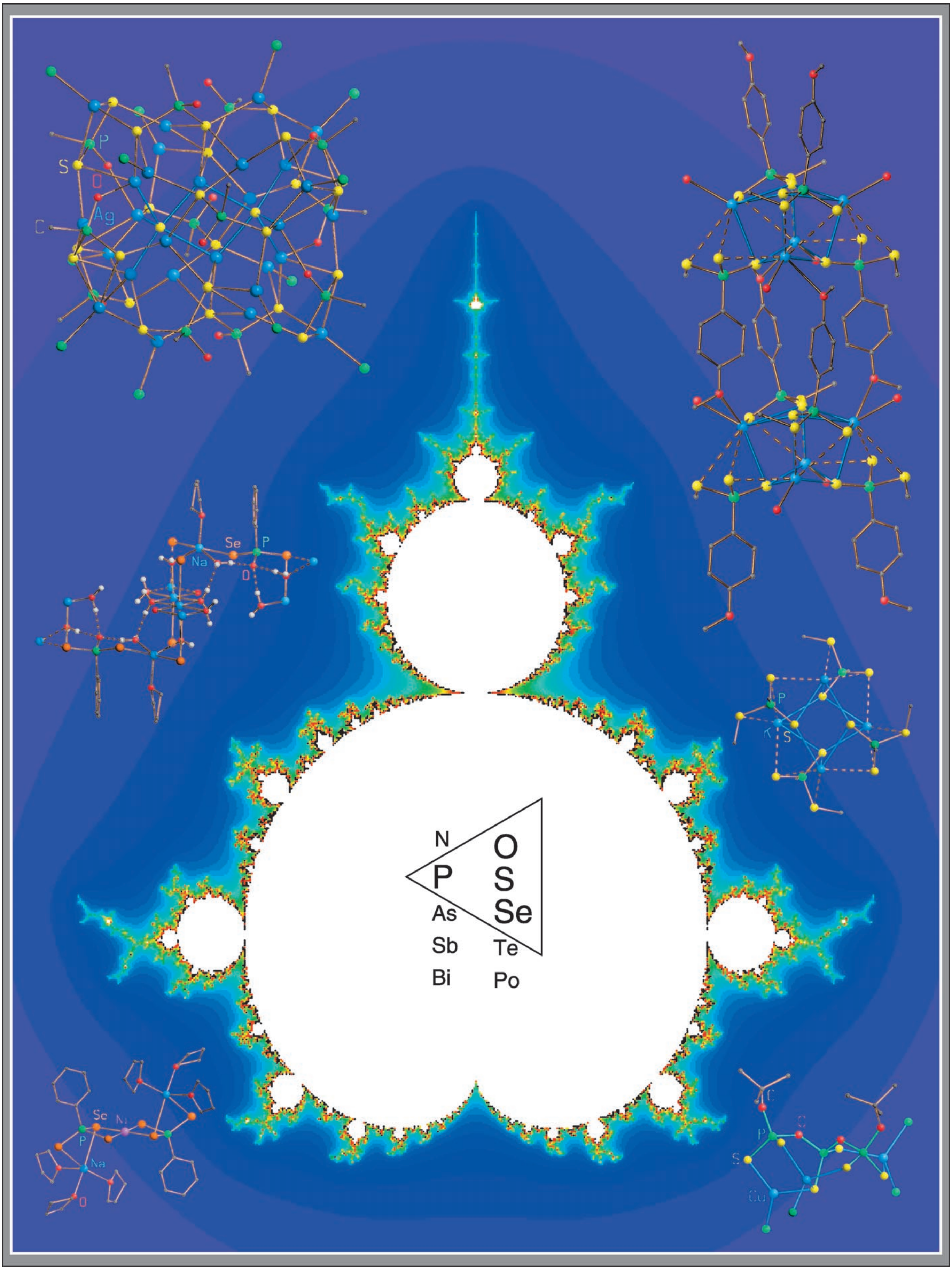

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# The Anhydride Route to Group 15/16 Ligands in Oligomeric and Polymeric Environments: From Metal Complexes to Supraionic Chemistry

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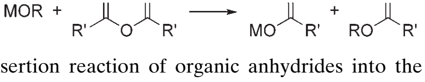
*Dedicated to Professor Dieter Fenske on the occasion of his 65th birthday*

**Abstract:** The aim of this paper is to introduce a synthetic concept suitable for the preparation of a broad variety of compounds. The so-called anhydride route (in this article the term *anhydride* is used for compounds derived from corresponding acids by formal loss of $H_2O$, $H_2S$ and $H_2Se$) has so far led to a range of unusual Group 15/16 ligands in oligomeric and polymeric environments. Commonly, reactions of neutral precursor molecules, for example, $[\{RP(S)(\mu\text{-}S)\}_2]$ (R = 4-anisyl) Lawesson's reagent or $[\{PhP(Se)(\mu\text{-}Se)\}_2]$ Woollins's reagent and metal salts are performed to result in novel coordination compounds in which ligands and metal atoms form coordination oligomers and polymers. An attempt is made to relate the outcome of the investigations to the type of metal used. By relating the strength of ionic interactions, which correspond to metal–donor distances, to phenomena observed in the solid-state structures, an aspect of supraionic chemistry is described. Chemistry of and beyond novel Group 15/16 anions is further discussed using a novel approach in coordination chemistry where the chemical nature of ligands is unknown prior to the experiment despite the use of a range of similar starting materials.

**Keywords:** coordination polymers • main group chemistry • phosphorus ligands • supraionic chemistry

## Introduction

The interest in the synthesis of inorganic/organic hybrid materials with their potential applications as storage devices for gases, as matrices for catalytic transformations and for a variety of other purposes prompted intense investigations.[1] Nevertheless, it is still desirable to develop synthetic routes for molecular complexes suitable for any of these or other applications and the characteristics of a useful synthetic approach are clear: 1) A variety of metal atoms with specific properties can be easily introduced. 2) The ligand to be incorporated into metalorganic frameworks with functional groups, for example, carboxylates, sulfonates, and phosphonates, is variable in order to influence the properties, for example, stability, porosity or other features of the assembly. A contribution to this field could be the exploration of insertion reactions of organic anhydrides into the metal–O bond of late transition metal alkoxides. This reaction allows a range of transition metals to be incorporated and at the same time to modify the involved organic ligand by selecting different alkoxy groups or organic anhydrides with various topologies (Scheme 1).[2]



Scheme 1. Insertion reaction of organic anhydrides into the M–O bond of metal alkoxides (M = transition metal, R, R′ = organic group).

Originally applied by Bergman and co-workers to probe the reactivity of metal–O bonds in late transition metal alkoxides, it was recently shown that the investigations can be extended to a larger variety of metal alkoxides and anhydrides.[3,4]

Remembering the fact that much of the Earth's constituting matter is of anhydride nature there is large potential to pick out any of the abundant classes of compounds (e.g., metal silicates, oxides, sulfides) and develop a field of

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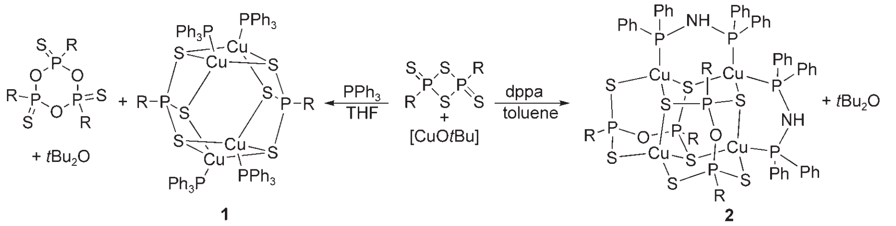


Scheme 3. Surprising findings in the reaction of $[\{RP(S)(\mu\text{-}S)\}_2]$ with [CuO$t$Bu] (R = 4-anisyl, dppa = 1,2-bis-diphenylphosphinoamine).

chemistry based on the particular class. These efforts have led to the development of important industrial processes involving anhydride materials in the broadest sense. For molecular chemists, however, there are two obvious routes to make use of anhydrides in synthesis. One is to generate models for naturally occurring anhydrides and investigate their chemistry as it has been recently described, for example, for metal silicates by Roesky et al.[5] The second route involves the use of anhydride derivatives of inorganic acids (instead of carboxylic acids) and their transformations with metal salts. The fact that the latter approach can be used as a synthetic concept is illustrated in the following for novel Group 15/16 anions derived from thiophosphonic and selenophosphonic acid anhydrides (in this article the term *anhydride* is used for compounds derived from corresponding acids by formal loss of $H_2O$, $H_2S$ and $H_2Se$). Since investigations with the compounds $[\{RP(S)(\mu\text{-}S)\}_2]$ (R = 4-anisyl, Lawesson's reagent, L.R.) and $[\{PhP(Se)(\mu\text{-}Se)\}_2]$ (Woollins' reagent, W.R.), so far produced the most complete set of results, the synthetic concept is demonstrated with the focus on novel P/S and P/Se anions.[6,7] The efforts to be described add on to the research area of Group 15/16 anions for which numerous compounds containing the structural fragments [Group 15 element–Group 16 element E metal] are known (e.g., N–E,[8–10] P–E,[11–14] As–E,[15–19] Sb–E,[20–23] Bi–E[24–28]).

## Group15/16 Ligands in Oligomeric Complexes

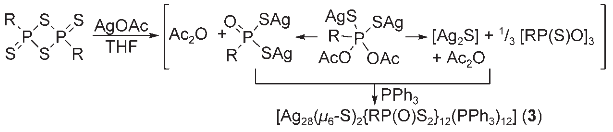
In an analogous way to the reaction described in Scheme 1, metal alkoxides open in a nucleophilic attack the anhydrides L.R. and W.R. (Scheme 2).

Scheme 2. Reaction of the anhydride $[\{RP(E)(\mu\text{-}E)\}_2]$ with alkali metal (M) alkoxides (E = S, Se; R = 4-anisyl, phenyl; R' = organic group).

The intermediate alkali metal phosphorodithioato or -diselenolato complexes can subsequently be used in metathesis reactions with metal halides to give numerous compounds in which ligands of the general type $[RP(OR)E_2]^-$ chelate metal ions through sulphur or selenium donor centres.[29,30] An entirely different outcome is observed when L.R. is treated with [CuO$t$Bu] (Scheme 3). Depending on the type of solvent used, the dianionic ligands $[RS_2P\text{-}O\text{-}PS_2R]^{2-}$ (in **2**) or $[RPS_3]^{2-}$ (in **1**) are formed and it was possible to unequivocally characterise them in oligomeric environments with phosphane-stabilised $Cu^I$ centres.[31,32]

It was assumed that the different metal ions involved in the reactions displayed in Schemes 2 and 3 have an influence on the nature of the P/S anion formed.

The results from these investigations prompted attempts to synthesize larger cluster complexes by the fragmentation of P=S bonds in sulfur analogues to phosphorus or phosphonous acid anhydrides. For this purpose, metal salts with oxygen-containing anions, for example, metal carboxylates and alkoxides were chosen with the assumption that the strong P=O bond versus the weaker P=S bond would provide the thermodynamic driving force for the investigations. This novel approach to P/S containing ligand systems is illustrated by a reaction of AgOAc with L.R. When $PPh_3$ was used to dissolve the precipitate obtained from the reaction of L.R. and AgOAc, $[Ag_{28}(\mu_6\text{-}S)_2\{RP(O)S_2\}_{12}(PPh_3)_{12}]$ (**3**), the largest cluster so far containing $[RP(O)S_2]^{2-}$ ligands, was obtained (Scheme 4).[33]



Scheme 4. Synthesis of **3** (R = 4-anisyl).

Structural features of **3** include the two central $\mu_6$-S atoms coordinating the 10 inner Ag atoms. This arrangement is surrounded by an outer layer of 12 $[RP(O)S_2]^{2-}$ ligands and 18 Ag atoms (Figure 1). The generation of both $S^{2-}$ and $[RP(O)S_2]^{2-}$ ligands in the course of the reaction between AgOAc and L.R. was observed for the first time and the formation of two different anions was explained by decomposition reactions of the proposed intermediate $[RP(SAg)_2(OAc)_2]$ in the presence of tertiary phosphanes (Scheme 4).

At this stage it is clear that the anhydride route offers a new approach to the coordination chemistry of P/S based ligands. Here and in other investigations it was demonstrated that the oxophilicity of phosphorus and the thiophilicity of coinage metal atoms allow facile transformation of readily available precursors, for example, L.R., $P_4S_{10}$ and metal salts into elaborate molecular architectures.[34]

In other words, the synthetic concept presented herein makes use of the HSAB principle and is thus not restricted to the class of compounds used here for description.[35] As far as the synthesis of transition metal complexes from

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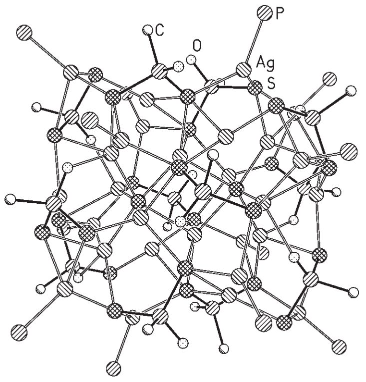


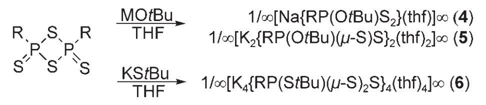
Figure 1. Molecular structure of **3** in the solid state (without phenyl groups of $PPh_3$ ligands; only α-C atoms of 4-anisyl substituents are displayed).

metal carboxylates and alkoxides is concerned, at the early stage of the investigations no prediction of generated Group 15/16 anions is possible and hence the design of a particular complex is impossible.[36] Furthermore, the synthesis of **1**–**3** illustrates an explorative approach to coordination chemistry based on Group 15/16 ligands, which is entirely different to coordination chemistry of well-defined ligands and metal ions. In the following section some developments from the above considerations that base on recently synthesized oligomeric complexes with P/S ligands are discussed.

## Group 15/16 Ligands in Polymeric Environments

A general approach to all kinds of new metal complexes with Group 15/16 ligands includes initial functionalisation of, for example, a P/S or P/Se anhydride with an alkali metal salt (see Scheme 2 for an example). For alkoxides and L.R., alkali metal phosphorodithioate salts are generated, which are commonly prepared in situ and used in subsequent metathesis reactions.[29] Until recently, however, no structural evidence for alkali metal phosphorodithioate salts existed. In that sense the synthesis and characterisation of **4** and **5** formed the basis of a potentially emerging structural chemistry of alkali metal phosphorodithioate coordination polymers (Scheme 5).[37]

In the solid state **4** exists as a polymer of $[RP(OtBu)S_2]^-$ ions held together by Na atoms (Figure 2). It becomes clear that the shape and composition of the 1D polymeric arrangement can easily be influenced by changes in alkali metal ions and the anions that come with them. Larger $K^+$ ions for example, turn out to have a significant influence on the solid-state structure of polymeric alkali metal phosphorodithioates. The main difference between **4** and **5**, are an increased coordination number of the metal cation and longer K–S and K–O distances in **5** in comparison to Na–S and Na–O distances observed in **4**. As a consequence a higher-ordered structure held together by more and weaker electrostatic interactions is found in **5** (Figure 2). A striking feature of **5** is the fact that coordination of $[RP(OtBu)S_2]^-$ ions to the alkali metal involves all donor centres resulting in $[K_2\{RP(OtBu)(\mu\text{-}S)S\}_2(thf)_2]$ constitutional units linked into a polymetallacyclophane by coordination of O atoms of 4-anisyl substituents to potassium ions.



Scheme 5. Reaction of $[\{RP(S)(\mu\text{-}S)\}_2]$ L.R. with metal alkoxides (M = Na, K; R = 4-anisyl).

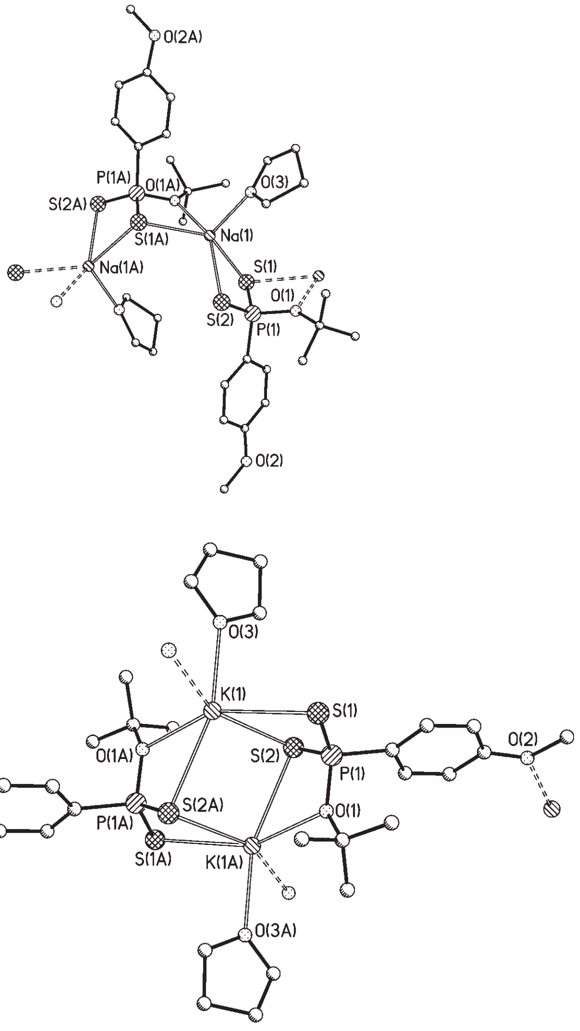


Figure 2. Molecular structure of a section of **4** (top) and **5** (bottom) in the solid state (connections to adjacent units are indicated).

With **4**, **5** and a number of similar complexes in hand, the question arose if higher-ordered coordination polymers than those of **4** and **5** can be made by introducing more and weaker electrostatic interactions. As an answer to this question (and most likely to similar questions in other areas of research), the development of a chemistry beyond the ion is necessary, which may be called "supraionic chemistry" (in analogy to the term for supramolecular chemistry as a chemistry beyond the molecule[38]). In compound **6** (Scheme 5, Figure 3), which in the solid state consists of a tetrameric arrangement of $[RP(S\textit{t}Bu)S_2K]$ units, the number of weaker interactions was increased with all the ingredients necessary for unusual supraionic architectures, for example, a heavier alkali metal and weak electrostatic interactions to S-donor centres in $[RP(S\textit{t}Bu)S_2]^-$ anions.

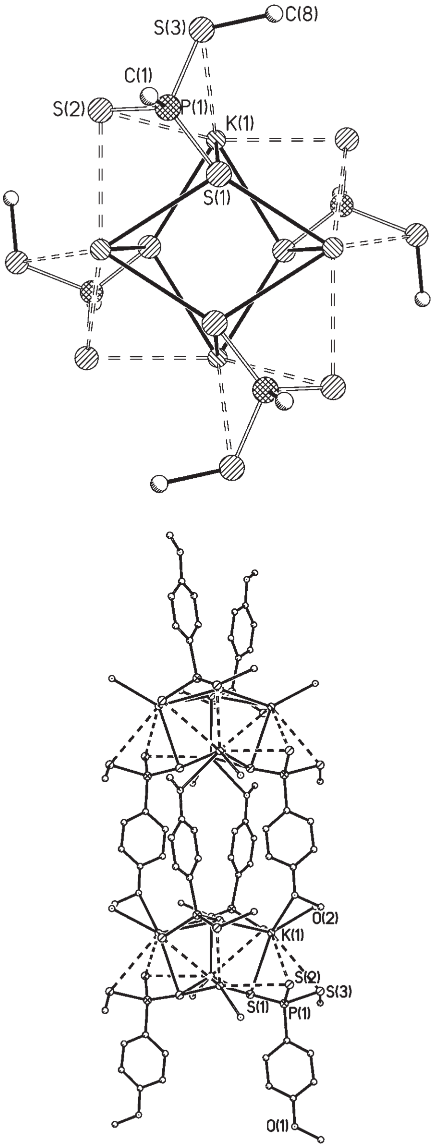
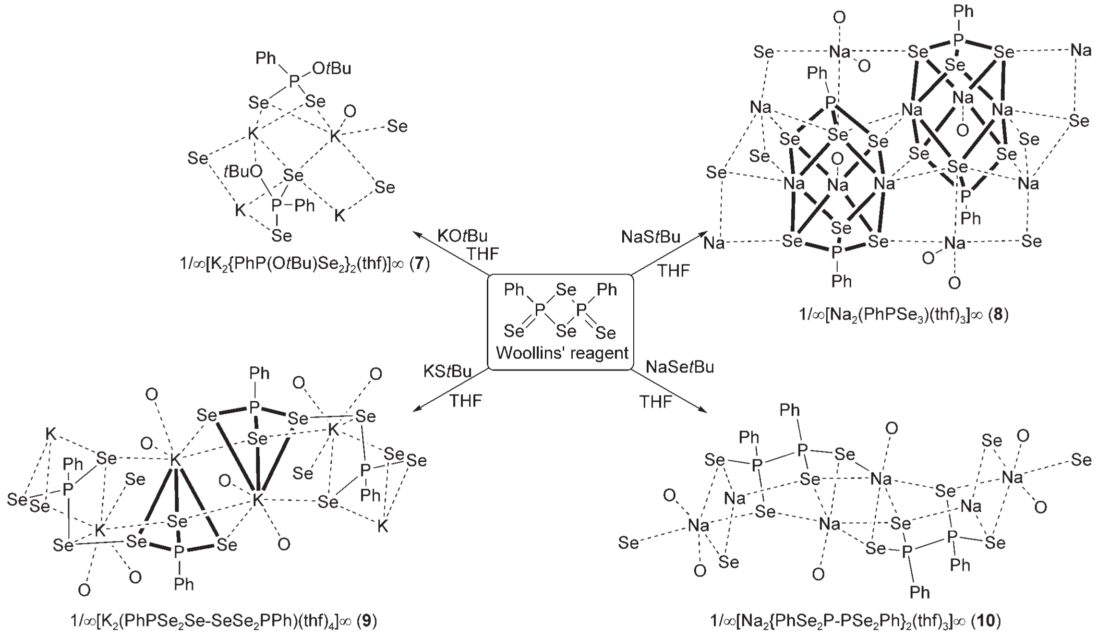


Figure 3. Tetrameric units and stacks of them are found in the solid-state structure of **6**.

In addition to the attempt to rationalize the increasing order within the solid-state structures in the row **4** (1D polymer) < **5** (1D polymer of dimeric units) < **6** (1D polymer of tetrameric units) the discussion of solid-state structural trends can be extended to P/Se anions derived from the perselenophosphonous acid anhydride Woollins' reagent and alkali metal salts (Scheme 6).

Commonly, polymeric arrangements of generated anions and alkali metal cations are formed and in the case of **7** the asymmetric unit contains two independent $[\{PhP(O\textit{t}Bu)Se_2]$ anions held together by two $K^+$ ions. A closer look at the structure of a section of **7** reveals that anions bridge the $K^+$ cations in different modes (Scheme 6). As in **4**–**6** the arrangement in **7** is held together by electrostatic interactions of various strengths resulting in an unusual coordination mode for $[PhP(OR)Se_2]^-$ ligands (R = alkyl), which commonly are bidentate and chelate metal atoms through chalcogen atoms.[30] Electrostatic interactions holding together polymeric arrangements of P–Se anions can again be modified by employing a range of alkali metal salts. Interestingly, this does not seem to result in huge changes of the polymeric arrangements. So far, 1D-polymeric architectures are predominant. In the case of P–Se anions, however, slight changes in metal salt anions and even cations result in different chemical reactions to occur and as a consequence in different P/Se anions formed (Scheme 6).

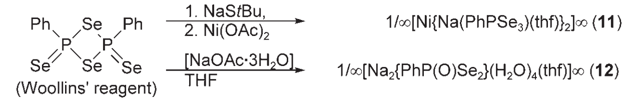
When NaS*t*Bu is treated with W.R. $1/\infty[Na_2(PhPSe_3)(thf)_3]_\infty$ (**8**) is obtained in moderate yield as colorless crystals together with $PhPSe(S\textit{t}Bu)_2$ (Scheme 6). The principal building block for polymeric **8** consists of two $[PhPSe_3]^{2-}$ anions, forming a cage arrangement with three sodium ions located between $[PhPSe_3]^{2-}$ tripodal ligands. "Outer-cage" $Na^+$ ions act as templates for the arrangement of cages in the extended solid-state structure of **8**. This represents a rare example of cage complex units with tripodal ligands that are connected by alkali-metal ions to a one-dimensional polymer. With KS*t*Bu, yellow crystals of $1/\infty[(PhPSe_2Se{-}SeSe_2PPh)K_2(thf)_4]_\infty$ (**9**) are obtained (Scheme 6). The unusual dianion $[PhPSe_2Se{-}SeSe_2PPh]^{2-}$ does not form cage complex units anymore as observed in **8**. Instead $[PhPSe_3]$ units of $[PhPSe_2Se{-}SeSe_2PPh]^{2-}$ anions act as tridentate ligand to one potassium cation and as bidentate ligands to one potassium atom of an adjacent unit (Scheme 6). Remarkably, $[PhPSe_3]$ units are covalently linked by a Se–Se bond, which was formed in the course of the reaction by formal oxidation of intermediate $[PhPSe_3]^{2-}$ anions.[39] The extended solid-state structure of **9** can be described as a corrugated ladder of two dimerized KSe strands. In an attempt to rationalize the reaction mechanism involved in the formation of **9**, both $PhP(Se)(S\textit{t}Bu)_2$ and $PhP(S\textit{t}Bu)_2$ were identified as soluble by-products and their identity checked by separate targeted synthesis.[40] A similar observation was made in the presence of $Rb^+$ ions which resulted in the formation of $[Rb_2(PhPSe_2Se{-}SeSe_2PPh)(thf)_4]$, which is isostructural to **9**. Along this line of research, the reaction of NaSe*t*Bu and W.R. resulted in the formation of $[PhSe_2P{-}PSe_2Ph]^{2-}$, which is known for some time (Scheme 6, **10**).[41] Although the reaction mechanism leading to the formation of **10** has not been investigated in detail, it seems likely that mixtures of W.R. and NaSe*t*Bu initially form sodium complexes of $[PhP(Se\textit{t}Bu)Se_2]^-$ anions that decompose into $(\textit{t}BuSe)_2$ and the $[PhSe_2P{-}PSe_2Ph]^{2-}$ anion observed in **10**.[39] A decomposition reaction with a similar outcome represents the reaction of $PhPS(SSiMe_3)_2$ with $Ag(CF_3CO_2)$, in



Scheme 6. Reaction of the anhydride [{PhP(Se)(μ-Se)}$_2$] W.R. with metal salts and sections of the solid-state structures of **7**–**10** (only O atoms of thf ligands are displayed.

which the 1D polymer 1/∞[$Ag_2(PhS_2P{-}PS_2Ph)(dppe)_2$]$_\infty$ was formed (dppe = 1,2-bis(diphenylphosphino)ethane).[42]

A challenge resulting from these findings is to try to connect polymeric assemblies by incorporating metal ions with "fixed" coordination geometries and thereby to apply a "building-block" approach to polymers of different dimensionality. A synthetic strategy could be to carry out metathesis reactions of the alkali metal complexes **4**–**10**. With [$Na_2(PhPSe_3)(thf)_3$] (**8**) this was demonstrated and the first result from this strategy is 2D-polymeric 1/∞[Ni{Na($PhPSe_3$)(thf)}$_2$]$_\infty$ (**11**) that was isolated together with [Ni{Na($PhPSe_3$)$(thf)_3$}$_2$] (Scheme 7, Figure 4).[39,40] Similar to **4**–**10** the alkali-metal ions in **11** form a one-dimensional polymer with [$PhPSe_3$]$^{2-}$ anions. 1D polymeric strands are, however, now linked by square-planar coordinated nickel atoms into a two-dimensional sheet. The Se atoms in the [$PhPSe_3$]$^{2-}$ anions bridge between Na atoms and two sets of Se atoms belonging to anions of different one-dimensional polymeric strands chelate the nickel atoms (Scheme 6).



Scheme 7. Synthesis of the 2D polymeric compounds (in the solid state) **11** and **12**.

To investigate potentially broader applications of nucleophilic ring-opening reactions of W.R. or other Group 15/16 anhydrides 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/∞[$Na_2(PhPSe_2O)(H_2O)_4(thf)$]$_\infty$ (**12**) were obtained (Scheme 7, Figure 5).

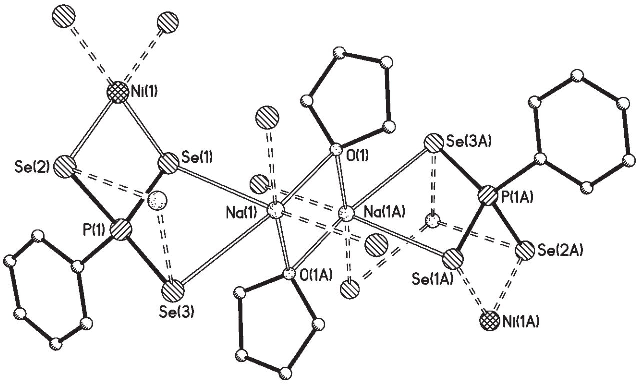


Figure 4. Structure of a section of the 2D polymer **11** in the solid state.

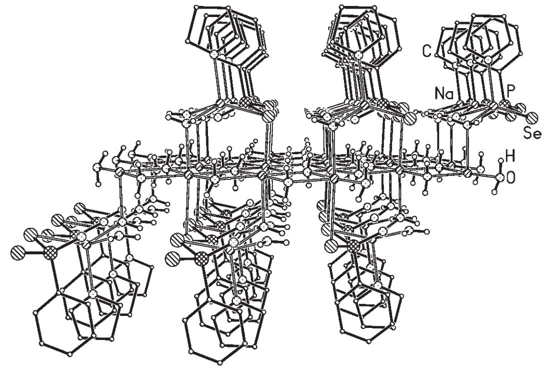


Figure 5. Section of the 2D polymeric arrangement found in **12** with a mikado arrangement of interconnected 1D coordination polymers.

The solid-state structure of **12** shows that Na atoms are held together by an elaborate arrangement of $[PhP(O)Se2]^{2-}$ anions and hydrogen-bonded water. Sodium cations in the two lipohilic outer layers in the extended packing diagram of **12** are coordinated by Se-donor centers and oxygen atoms of THF and water. The one-dimensional strands within lipophilic outer layers are connected by a perpendicular arrangement of sodium atoms connected by μ-$H_2O$ ligands. Altogether, this results in the formation of a 2D arrangement with a lipophilic surface and a polar inner layer.

## Conclusion and Outlook

By choosing a few examples of recently prepared compounds it was shown that the anhydride route has the potential to produce a range of novel compounds by the nucleophilic break-up of neutral proligands (anhydrides) with metal salts. The synthetic concept was demonstrated for Group 15/16 ligands in oligomeric and polymeric environments. Despite the fact that it is still early days and not many experimental results exist, some trends have become evident. These include the observation that oligomeric compounds with Group 15/16 ligands are predominantly formed with coinage metals that exhibit rigid coordination geometries (**1**–**3**) in comparison to alkali metals. Alkali metals favor polymeric arrangements of Group 15/16 ligands. Compounds **4**–**6** showed the potential of emerging supraionic chemistry in which weak ionic interactions of different strength are used as an ordering principle for new compounds in the solid state. The P/S and P/Se anions generated by the anhydride route are an example of a novel area of coordination chemistry, where the chemical nature of ligands is unknown before the experiment is carried out. Particularly the syntheses of **7**–**10** illustrate the latter point. Ligands are generated in situ and despite chemically similar starting materials, the formation of entirely different solid-state structures with different Group 15/16 anions was observed. Finally, recent developments of the anhydride route are described. These include a potentially rational approach to coordination polymers of different dimensionality by incorporating transition metal ions with “fixed” coordination geometries, for example, square-planar $Ni^{2+}$ in **11** or octahedral metal ions in future. Also the controlled hydrolysis (rehydration of anhydrides) of neutral precursors provides great prospects (see compound **12**). In future the synthetic principles outlined here may be useful for the preparation of a broad range of yet unknown main group ligands. In particular as far as the heavier elements are concerned, many new discoveries are likely to be made.

## Acknowledgements

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[1] A. K. Cheetham, G. Ferey, T. Loiseau, *Angew. Chem.* **1999**, *111*, 3466–3492; *Angew. Chem. Int. Ed.* **1999**, *38*, 3268–3292.
[2] J. R. Fulton, A. W. Holland, D. J. Fox, R. G. Bergman, *Acc. Chem. Res.* **2002**, *35*, 44–56.
[3] L. Ponikiewski, A. Rothenberger, *Inorg. Chim. Acta* **2005**, *358*, 1322–1326.
[4] C. E. Anson, R. Langer, L. Ponikiewski, A. Rothenberger, *Inorg. Chim. Acta* **2005**, *358*, 3967–3973.
[5] H. W. Roesky, G. Anantharaman, V. Chandrasekhar, V. Jancik, S. Singh, *Chem. Eur. J.* **2004**, *10*, 4106–4114.
[6] B. S. Pedersen, S. Scheibye, K. Clausen, S. O. Lawesson, *Bull. Soc. Chim. Belg.* **1978**, *87*, 293–297.
[7] I. P. Gray, P. Bhattacharyya, A. M. Z. Slawin, J. D. Woollins, *Chem. Eur. J.* **2005**, *11*, 6221–6227.
[8] R. Fleischer, D. Stalke, *Coord. Chem. Rev.* **1998**, *176*, 431–450.
[9] T. Chivers, F. Edelmann, *Polyhedron* **1986**, *5*, 1661–1699.
[10] T. Chivers, R. T. Oakley, *Top. Curr. Chem.* **1982**, *102*, 117–147.
[11] T. Chivers, *Dalton Trans.* **1996**, 1185–1194.
[12] A. Clearfield, *Prog. Inorg. Chem.* **1998**, *47*, 371–510.
[13] I. Haiduc, *J. Organomet. Chem.* **2001**, *623*, 29–42.
[14] T. S. Lobana, J. C. Wang, C. W. Liu, *Coord. Chem. Rev.* **2007**, *251*, 91–110.
[15] Y. Wu, C. Nather, W. Bensch, *Inorg. Chem.* **2006**, *45*, 8835–8837.
[16] R. Langer, W. Shi, A. Rothenberger, *Dalton Trans.* **2006**, 4435–4437.
[17] T. Berrocal, J. L. Mesa, J. L. Pizarro, M. K. Urtiaga, M. I. Arriortua, T. Rojo, *J. Solid State Chem.* **2006**, *179*, 1659–1667.
[18] T. Soumahoro, E. Burkholder, W. Ouellette, J. Zubieta, *Inorg. Chim. Acta* **2005**, *358*, 606–616.
[19] T. M. Martin, P. T. Wood, G. L. Schimek, W. T. Pennington, J. W. Kolis, *Inorg. Chem.* **1995**, *34*, 4385–4391.
[20] S. S. Dhingra, R. C. Haushalter, *J. Am. Chem. Soc.* **1994**, *116*, 3651–3652.
[21] L. M. Opris, A. Silvestru, C. Silvestru, H. J. Breunig, E. Lork, *Dalton Trans.* **2004**, 3575–3585.
[22] D. M. Smith, C.-W. Park, J. A. Ibers, *Inorg. Chem.* **1996**, *35*, 6682–6687.
[23] J. M. Tanski, B. V. Kelly, G. Parkin, *Dalton Trans.* **2005**, 2442–2447.
[24] T. Amitsuka, H. Seino, M. Hidai, Y. Mizobe, *Organometallics* **2006**, *25*, 3034–3039.
[25] J. Beck, M. Dolg, S. Schlüter, *Angew. Chem. Int. Ed.* **2001**, *40*, 2287–2290.
[26] M. W. DeGroot, J. F. Corrigan, *Dalton Trans.* **2000**, 1235–1236.
[27] W. Henderson, B. K. Nicholson, H. Zhang, T. S. A. Hor, *Inorg. Chim. Acta* **2006**, *359*, 221–227.
[28] M. Mehring, D. Mansfeld, S. Paalasmaa, M. Schurmann, *Chem. Eur. J.* **2006**, *12*, 1767–1781.
[29] I. P. Gray, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2004**, 2477–2486.
[30] I. P. Gray, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2005**, 2188–2194.
[31] W. Shi, A. Rothenberger, *Eur. J. Inorg. Chem.* **2005**, 2935–2937.
[32] W. Shi, M. Shafaei-Fallah, C. E. Anson, A. Rothenberger, *Dalton Trans.* **2005**, 3909–3912.
[33] W. Shi, R. Ahlrichs, C. E. Anson, A. Rothenberger, C. Schrodt, M. Shafaei-Fallah, *Chem. Commun.* **2005**, 5893–5895.
[34] A. Rothenberger, M. Shafaei-Fallah, W. Shi, *Chem. Commun.* **2007**, 1499–1501.
[35] R. G. Pearson, *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.
[36] M. Jansen, J. C. Schön, *Angew. Chem.* **2006**, *118*, 3484–3490; *Angew. Chem. Int. Ed.* **2006**, *45*, 3406–3412.
[37] W. Shi, M. Shafaei-Fallah, C. E. Anson, A. Rothenberger, *Dalton Trans.* **2006**, 3257–3262.
[38] J.-M. Lehn, *Chem. Soc. Rev.* **2007**, *36*, 151–160.
[39] W. Shi, M. Shafaei-Fallah, L. Zhang, C. E. Anson, E. Matern, A. Rothenberger, *Chem. Eur. J.* **2007**, *13*, 598–603.
[40] W. Shi, M. Shafaei-Fallah, C. E. Anson, A. Rothenberger, *Dalton Trans.* **2006**, 2979–2983.

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[41] R. P. Davies, M. G. Martinelli, A. E. H. Wheatley, A. J. P. White, D. J. Williams, *Eur. J. Inorg. Chem.* **2003**, 3409–3416.

[42] D. Fenske, A. Rothenberger, M. Shafaei-Fallah, *Eur. J. Inorg. Chem.* **2005**, 59–62.

[43] P. F. Kelly, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *Chem. Soc. Rev.* **1992**, *21*, 245–252.

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