A recipe for new organometallic polymers and oligomers? Synthesis and structure of an oligo- and a polymeric arrangement of P–S anions†‡

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A route to organometallic polymers and oligomers is described using metal complexes with P/S-ligands as examples.

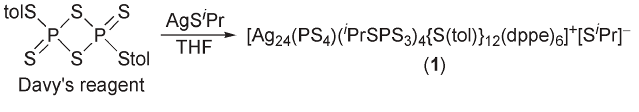
The principle that weak interactions between atoms can be used for the formation of highly ordered structures is a key to synthetic bottom-up approaches to larger well-defined arrangements of atoms.[1–3] Having chosen a weak interaction (*e.g.*, hydrogen-bonding, weak ionic interactions,…) another important issue is the choice of the chemically suitable building blocks, that are assembled into compounds ranging from larger molecules to colloidal or even macroscopic particles. Finally, crystallization of products is required, providing insight on the atomic level into what was formed and to what extent chosen interactions and building blocks are suitable for a specific synthetic goal. In the area of group 15–chalcogenide chemistry, current activities in the field make use of these considerations in different ways with great success, as far as precursor chemistry for materials in the form of thin films or particles with tunable properties is concerned.[4–6] In this communication significant developments relevant to synthesis and characterization of clusters and coordination polymers containing P–S anions are described. These include the first structural evidence for an interstitial $[P(\mu_3\text{-}S)_4]^{3-}$ anion that is encapsulated in a large cluster cation and the characterization of a new P–S anion type. This work focuses on weak coulombic interactions between constituting units. As building blocks the neutral molecules $[\{(tol)S\}P(S)(\mu\text{-}S)]_2$ (tol = 4-methylphenyl, Davy's reagent) and P_2S_5 and metal salts [AgSR, NaSR (R = organic group)] were chosen.[7] In the course of the reactions they are converted to novel P–S anions. Subsequent organization of ionic building blocks into larger aggregates may indicate potential applicability of the synthetic route to a broader variety of coordination polymers or clusters.[8,9] These hopes were based on recent results where the potential of readily available P/S and P/Se reagents to serve as building blocks for various kinds of metal coordination oligomers and polymers has been demonstrated.[10–15] When Davy's reagent is suspended in THF and reacted with silver thiolates in the presence of dppe (dppe = 1,2-bis(diphenylphosphino)ethane), a clear solution is obtained. Within three weeks colourless crystals of $[Ag_{24}(PS_4)(^iPrSPS_3)_4\{S(tol)\}_{12}(dppe)_6)](S^iPr)$ (**1**) (tol = 4-methylphenyl) were formed (Scheme 1).

Complex **1** crystallizes in the cubic space group *F*23. The cluster cation present in **1** consists of 24 Ag^+ ions, one central $[PS_4]^{3-}$, four $[^iPrSPS_3]^{2-}$ and twelve $[(tol)S]^-$ (Fig. 1).§ Although it was impossible to directly identify the counteranion (ESI-MS failed; statistic orientation of the anion relative to the cluster cation in the extended crystal lattice), correction with SQUEEZE for remaining unallocated electron density indicates the presence of $^iPrS^-$ as the anion in **1**.[16] The $^{31}P\{^1H\}$ NMR spectrum of **1** shows that the solid-state structure **1** in solution is not retained. The resonances at δ 130–115 indicate rearrangements of the P/S-anions in solution similar to those observed in $(PPh_4)_3[(NiPS_4)_3]$ and oxidation of dppe to sulfur-functionalised derivatives occurred.[17–19] In the solid state the cluster cation of **1** consists of a remarkable assembly of generated anions and the silver cations (Fig. 1). Starting from the middle of the cluster cation in **1**, twelve silver cations (Ag2) are arranged around the $[P(\mu_3\text{-}S)_4]^{3-}$ anion. The outer layer consists of a mix of twelve phosphine-stabilized Ag cations (Ag1) and the remaining anions. Four $[^iPrSPS_3]^{2-}$ (P6, S1, S2) and twelve $[(tol)S]^-$ anions (S5) are coordinated to both the twelve inner and the twelve outer Ag atoms. **1** represents a unique example of a cluster compound containing an encapsulated thiophosphato $[P(\mu_3\text{-}S)_4]^{3-}$ anion among a variety of metal thiophosphates.[17,20–22] Also structural data for an anion of the general type $[RSPS_3]^{2-}$ (R = ^{i}Pr) has not been reported so far.

In the following, another attempt to generate further examples of P/S anions is described. When the filtrate of a reaction of P_2S_5 and NaS^tBu was layered with hexane, crystals of the 2D-polymer $^1_\infty[Na_2(S_3PS^tBu)(dme)]_\infty$ **2** were obtained (Scheme 2, Fig. 2 and 3).

In the solid state, the generated $[^tBuSPS_3]^{2-}$ anions in **2** coordinate metal atoms *via* three edges and one face of a PS_4-tetrahedral building block. The auxiliary ligand DME coordinates in the common chelating mode but O(1) and O(3) are additionally bridging Na atoms (Fig. 2, top).[23] The Na atoms are six-coordinated (Fig. 2, bottom) and act as flexible multiacceptor centres in the extended solid-state structure of **2**. A section of the aesthetic arrangement of polymeric **2** is displayed in Fig. 3.

The honeycomb-like architecture of **2** in the solid state consists of six $[^tBuSPS_3]^{2-}$ anions held together by Na^+ ions. In the $^{31}P\{^1H\}$ NMR of a $[D_8]$-THF solution of **2**, a singlet resonance at



Scheme 1 Synthesis of **1**.

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† Dedicated to Professor Joachim Strähle on the occasion of his 70th birthday.

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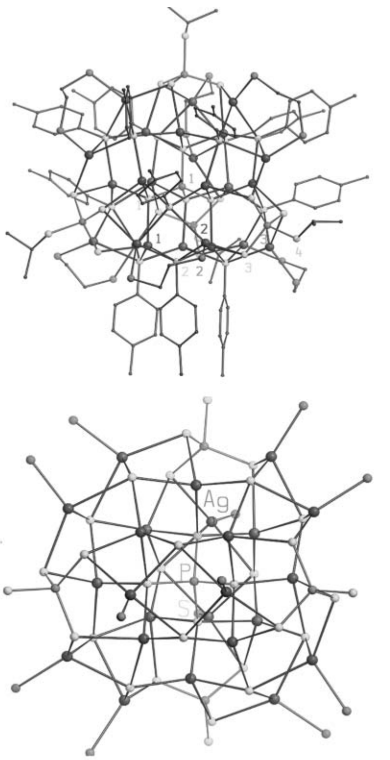

Fig. 1 Solid-state structure of the $[Ag_{24}(PS_4)(^iPrSPS_3)_4\{S(tol)\}_{12}(dppe)_6)]^+$ cation in **1** (tol = 4-methylphenyl, dppe = 1,2-bis(diphenylphosphino)ethane; without phenyl groups of dppe; only one of the three orientations of ^{i}Pr substituents is shown) (top). Representation of the [P,S,Ag]-core in **1** (bottom). Selected bond lengths (Å) and angles (°): Ag(1)–S(1) 2.5482(8), Ag(1)–S(2) 2.4861(14), Ag(2)–S(3) 2.628(2), Ag(2)–S(2) 2.7048(14), other Ag–S distances 2.4861(14)–2.7369(14), Ag(2)–P(2) 2.4334(17), P(1)–S(1) 2.0465(17), P(3)–S(3) 2.016(2), P(3)–S(4) 2.085(4); S(1)–Ag(1)–S(2) 112.15(4), other S–Ag–S 82.78(4)–137.04(6), P(2)–Ag(2)–S(3) 121.22(7), P(2)–Ag(2)–S(2) 121.07(5), S–P(1)–S *ca.* 109.5, S(3)–P(3)–S(4) 105.33(9).

$$P_2S_5 \xrightarrow{NaS^tBu,\ DME} 1/\infty[Na_2(S_3PS^tBu)(dme)]_\infty\ (\mathbf{2})$$

Scheme 2 Synthesis of **2** (DME = 1,2-dimethoxyethane).

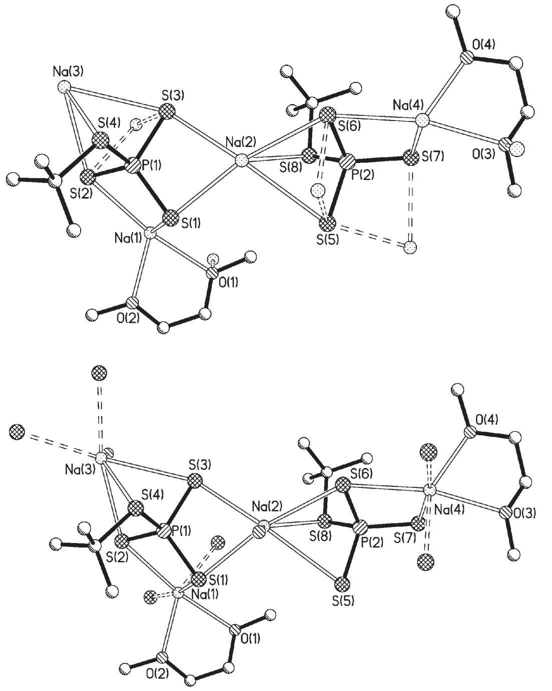

Fig. 2 Two representations of the asymmetric unit of **2** in the solid state. Environments of S and O donor centers are indicated by dashed bonds to Na (top). Coordination environment of Na cations with dashed bonds to donor centers of adjacent units (bottom). Selected bond lengths (Å) and angles (°): Na–S 2.8150(7)–3.2191(8), Na(1)–O(2) 2.3453(12)–2.5157(14), S(4)–P(1) 2.1347(6), S(8)–P(2) 2.1291(6), S–P 2.0187(6)–2.0228(6), S(4)–C 1.8636(16), S(8)–C 1.8626(16); O–Na–O 72.35(4), 72.31(4), O–Na–S 77.08(3)–161.84(4), S–Na–S 59.031(16)–171.53(2), S(3)–P(1)–S(4) 96.33(2), S(5)–P(2)–S(8) 96.48(2), S–P–S 109.00(2)–113.56(2).

δ 93.3 for the P atom in the $[^tBuSPS_3]^{2-}$ anion was observed. The investigation illustrates the potential of neutral precursor molecules to undergo fragmentation into ions and subsequent organisation into clusters or polymers using neutral P/S compounds as an example. The absence of classical leaving groups (metal halides, volatile compounds) complicates matters and at the same time is exciting because *lattice-energy of products* seems to represent the thermodynamical driving force of the reactions. Further investigations, aimed at understanding reactions mechanisms leading to the formation of **1** and **2** will focus on synthesising more examples of P/S metal complexes at a variety of reaction conditions. Related reactions, applying the described synthetic strategy to other proligands will be reported in a subsequent full paper.

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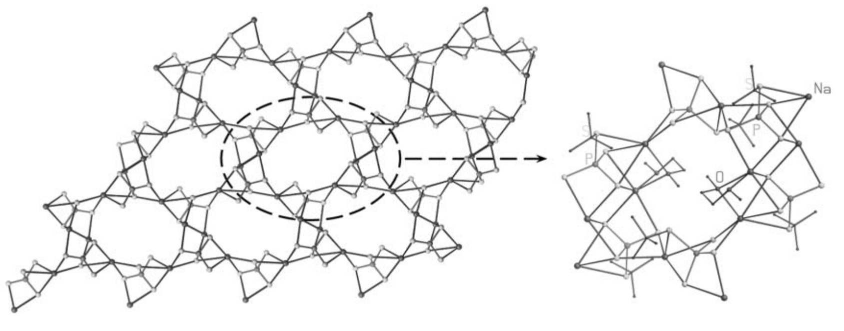

Fig. 3 Section of the 2D polymeric structure of **2** and a representation of the constituting cyclic hexamer of $[^tBuSPS_3]^{2-}$ anions Na atoms and DME in **2**.

Notes and references

§ *Crystal data* for **1**: $C_{255}H_{263}Ag_{24}P_{17}S_{33}$, M = 7501.00, cubic, space group $F23$ (no. 196), a = 31.215(4), U = 30417(6) Å^3, T = 100(2) K, Z = 4, μ(Mo-Kα) = 1.866 mm^{-1}, 26 709 reflections measured, 5565 unique (R_{int} = 0.0352) which were used in all calculations. wR_2 (all data) = 0.1068, R_1 [$I > 2\sigma(I)$] = 0.0360. One disordered $[{}^{i}\text{PrS}]^{-}$ anion per cluster could not be refined, and was corrected for using the SQUEEZE option in PLATON (160 e$^-$ per cell calculated; 164 e$^-$ per cell expected for C_3H_7S).[16,24] S atoms of ^{i}PrS groups are located (and were left) on a three-fold axis and exhibit slightly larger temperature factors than other S atoms. One phenyl group of dppe was disordered over two positions. Disordered C atoms were refined using isotropic temperature factors. *Crystal data* for **2**: $C_{16}H_{38}Na_4O_4P_2S_8$, M = 704.84, triclinic, space group $P\bar{1}$ (no. 2), a = 10.8600(6), b = 11.8116(7), c = 13.6914(7) Å, α = 89.670(4), β = 82.780(4), γ = 83.450(5)°, U = 1739.89(17) Å^3, T = 100(3) K, Z = 2, μ(Mo-Kα) = 0.679 mm^{-1}, 13 736 reflections measured, 7000 unique (R_{int} = 0.0303) which were used in all calculations. wR_2 (all data) = 0.0549, R_1 [$I > 2\sigma(I)$] = 0.0235. The graphic representations of crystal structures were prepared using Schakal99 by E. Keller and MiKTeX 2.5. CCDC 623841 and 623842. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617177j

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