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[{(η^5-C$_5$Me$_5$)$_2$Sm}$_4$P$_8$]: A Molecular Polyphosphide of the Rare-Earth Elements

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Monocyclic and polycyclic phosphines and their corresponding anions have been studied for decades.[1] One of the most prominent examples in this series is the heptaphosphanotricyclane anion P_7^{3-}, which can be understood by the Zintl−Klemm−Busmann concept (Figure 1). Nevertheless, there is still a huge interest in the coordination and functionalization of white phosphorus and polyphosphide anions. Thus, only very recently, the aromatic P_4^{2-} anion was reported.[2,3] Cummins et al. reported on the activation of P_4 by a niobium complex leading to a P_2 synthon.[4] Fryzuk et al. worked on the reduction of [ZrCl$_2${PhP(CH$_2$SiMe$_2$NSiMe$_2$CH$_2$)$_2$PPh}] in the presence of P_4.[5] Other examples are the activation of P_4 by cyclic alkylaminocarbenes[6] or other low-valent group 13[7] or group 14 compounds.[8] Also, in transition metal chemistry the coordination and functionalization of P_4 and polyphosphide anions is still under investigation[9−13] and has been reviewed recently.[14,15] In contrast to those activities, there is to the best of our knowledge no known P_4 or polyphosphide derivative in the coordination chemistry of the rare-earth metals. Only some lanthanide phosphine Ln-PR$_3$[16−18] and phosphide Ln-PR$_2$[19,20] derivatives had been known for more than two decades. In this contribution, we now report on [{(η^5-C$_5$Me$_5$)$_2$Sm}$_4$P$_8$], which is the first molecular polyphosphide of the rare-earth elements.

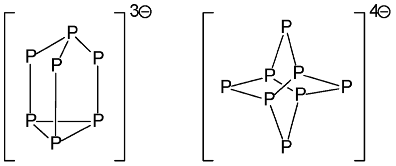
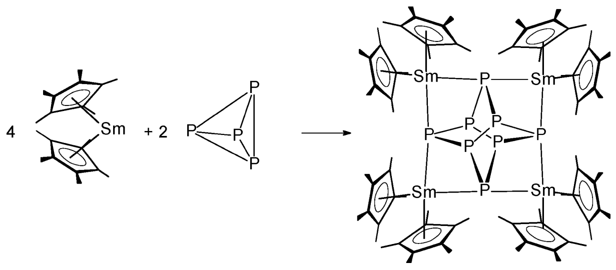


Figure 1. Structures of the polyphosphide anions P_7^{3-} and P_8^{4-} .

Diffusion of P_4 vapor into a toluene solution of solvate-free samarocene, [(η^5-C$_5$Me$_5$)$_2$Sm], over a period of several days resulted in the formation of [{(η^5-C$_5$Me$_5$)$_2$Sm}$_4$P$_8$] (**1**) as red crystals (Scheme 1). Compound **1** is a very pyrophoric compound. In the center of the molecule a P_8 unit is located, which possesses a realgar-type homoatomic structure. This unit can formally be considered as P_8^{4-} (Figure 1), which is the larger analogue of the well-established Zintl anion P_7^{3-}.[21] According to this analogy, in compound **1** each {(η^5-C$_5$Me$_5$)$_2$Sm} unit is bound to two coordinated phosphorus atoms of the P_8 cage. Obviously during the reaction each metal atom in the samarocene molecules is oxidized from divalent to trivalent samarium, and thus one electron is transferred from each samarocene molecule to the phosphorus atoms.

Scheme 1



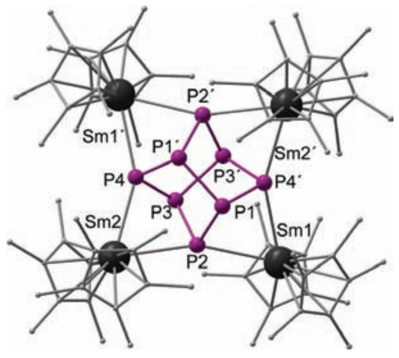


Figure 2. Solid-state structure of **1**, omitting hydrogen atoms. Selected distances [Å] and angles [°]: Sm1−P2 3.100(2), Sm1′−P4 3.018(2), Sm2−P2 3.073(2), Sm2−P4 2.997(2), P1−P1′ 2.289(4), P1−P2 2.195(3), P1−P4 2.189(3), P1′−P4 2.189(3), P2−P3 2.201(3), P3−P3′ 2.292(5), P3−P4 2.196(3); Sm1−P2−Sm2 160.72(7), Sm1−P4−Sm2 154.10(7), P2−Sm1−P4 63.55(5), P2−Sm2−P4′ 64.27(5), P2−P1−P4 94.60(10), P1′−P1−P4 101.40(10), P1′−P1−P2 103.36(10), P1−P2−P3 95.29(10), P2−P3−P2 94.51(10), P4−P3−P4 101.31(11), P2−P3−P3′ 103.12(12), P1−P4−P3′ 96.42(11).

The solid-state structure was established by single-crystal X-ray diffraction (Figure 2). The Sm−P distances within compound **1** range from 2.997(2) Å to 3.100(2) Å, and the Sm−P−Sm angles are Sm1−P2−Sm2 160.72(7) and Sm1−P4−Sm2 154.10(7)°. Each {(η^5-C$_5$Me$_5$)$_2$Sm} unit bridges the central P_8 cage giving P−Sm−P angles of P2−Sm1−P4 63.55(5) and P2−Sm2−P4′ 64.27(5). In the center of the P_8 cage, a crystallographic C_2 axis through the P1−P1′ and P3−P3′ bond is observed. The angles within the P_8 cage range from 94.51(10)° to 103.36(10)°. The P−P distances range from 2.292(5) Å to 2.189(3) Å. Owing to the paramagnetic character and the low solubility of compound **1** in toluene, the NMR spectra are not very conclusive. By using solvents such as THF, decomposition is observed.

The realgar-type P_8 structural motif is very rare. To the best of our knowledge, it was only reported in the transition metal compounds [(η^5-C$_5$H$_4$Me)$_4$Fe$_4$(CO)$_4$P$_8$],[22] [(η^5-C$_5$H$_4$Me)$_4$Fe$_6$(CO)$_{13}$P$_8$],[22] and [{(η^5-C$_5$Me$_5$)Ir(CO)}$_2${Cr(CO)$_5$}$_3$P$_8$][23] but not in rare-earth chemistry. Since it has been established for a long time that the dimerization of P_4 to P_8 is enthalpically disfavored,[24] we suggest that the formation of

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compound **1** is induced by an electron transfer from the divalent samarium atom onto a P_4 molecule. There are some recent reports in which P_4 was dimerized to P_8 cages. Examples are $[\{Nb(OC[^2Ad]Mes)_3\}_2(P_8)]$ (^{2}Ad = 2-adamantylidene, Mes = 2,4,6-trimethylphenyl)[13] and $[K([18]crown\text{-}6)(thf)_2]^+$ $[P_8\{Si(SiMe_3)_3\}_2K([18]crown\text{-}6)]$.[12] In contrast to compound **1**, which has a realgar-type structural motif, these structures consist of a nortricyclic P_7 core, with a single branched phosphorus atom bonded exo to the ring.

As observed earlier, the P_8^{4-} anion is in contrast to the P_7^{3-} anion as an isolated salt not stable, and octaphosphorus tetrahydride, P_8H_4, has been identified solely by mass spectrometry.[25] As a reason for the instability of the α-P_8^{4-} anion, the unfavorable steric interactions between endo-oriented sets of planar phosphorus orbitals was discussed.[22] This theory is supported by the observations of the abnormally long P−P bond length in the isostructural and isoelectronic α-P_4S_4 molecule.[26] As pointed out by Baudler et al. the P_8 unit observed in **1** is an essential building block of the violet phosphorus, but it could be stabilized in larger P_n frameworks or in the few metal complexes reported until now.[27] Thus, the alkyl polyphosphine P_8iPr_4 could be isolated in a homonorbornane structure,[27] which was also observed in the two mentioned molecules $[\{Nb(OC[^2Ad]Mes)_3\}_2(P_8)]$[13] and $[K([18]crown\text{-}6)(thf)_2]^+$ $[P_8\{Si(SiMe_3)_3\}_2K([18]crown\text{-}6)]$.[12]

The bonding in **1** has been investigated by quantum chemical RI-DFT calculations on the model compound $[\{(\eta^5\text{-}C_5H_5)_2Sm\}_4P_8]$ (**2**) using the program system TURBOMOLE.[28,29] The calculations were performed using the BP86 functional[30−32] by means of the R-IJ approximation.[33] The basis sets for C, H, and P were of def-SV(P) quality.[34,35] For Sm, a relativistic corrected effective core potential has been used to simulate the 51 inner electrons (ECP-51).[36] The inclusion of the 5 f electrons into the ECP is allowed due to the expected ionic nature of the complex containing Sm in the formal oxidation state +III.[37] The geometry optimization by means of analytically derived gradients using redundant internal coordinates[38] leads to a molecule of D_{2d} symmetry. The theoretical vibrational spectrum of **2** was obtained by calculation of the second derivatives using the module AOFORCE.[39] The structural results obtained by means of the crystallographic study were principally confirmed by our theoretical calculation ($d(Sm-C) = 276.5 \pm 1.2$, $d(P-P) = 224.6, 236.0$, $d(Sm-P) = 298.4$ pm). To gain insight into the bonding in this molecule, a population analysis based on occupation numbers has been performed (Roby−Davidson−Ahlrichs−Heinzmann population analysis).[40] Partial charges (Q) to interpret the iconicity of the bonds were obtained. Shared electron numbers (SEN) served as a measure for the covalent bond strength. The analysis confirmed the realization of a strongly ionic complex ($Q(Sm) = +1.51$, $Q(P) = -0.26$, $Q(P_{naked}) = +0.10$). The covalent strengths of the P−P bonds of the P_8 fragment ($SEN(P-P_{naked}) = 0.90$, $SEN(P_{naked}-P_{naked}) = 1.14$) were comparable to those in the P_4 molecule ($SEN(P-P) = 1.08$). The strong polar character of the Sm−P bond was confirmed by its SEN value of 0.35. The interpretation of a P_8^{4-} unit being stabilized by four countercations was convincingly confirmed by a test calculation (RI-DFT, BP86, SV(P)) on the isostructural compound $(Na^+)_4P_8^{4-}$ (**3**) ($d(P-P) = 225.0, 243.9$, $d(Na-P) = 268.8$ pm, $SEN(P-P_{naked}) = 0.84$, $SEN(P_{naked}-P_{naked}) = 1.15$, $Q(Na) = 0.34$, $Q(P_{naked}) = -0.01$, $Q(P) = -0.33$). The energy for its formation ($4Na_g + 2P_{4g} = (Na^+)_4P_8^{4-}$) was calculated to be −658 kJ/mol. From a comparison of the experimental Raman spectrum of **1** (most intense band at 389 cm^{-1}; cf. Supporting Information) with the theoretically calculated spectra of the model compounds **2** and **3**, this band at 389 cm^{-1} can be attributed to the totally symmetric breathing mode of the P_8^{4-} cluster core (symmetry D_{2d}, a_1 representation, **2**: 401, **3**: 397 cm^{-1}).

In summary, we succeeded in synthesizing the first lanthanide polyphosphide by a one-electron redox reaction of divalent samarocene and white phosphorus.

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Supporting Information Available: Crystallographic data of **1** and experimental preparations for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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