Ag_3SnP_7: A Polyphosphide with a Unique ${}^{1}_{\infty}(P_7)$ Chain and a Novel Ag_3Sn Heterocluster**

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The numerous polyphosphides known to date exhibit a variety of compositions and structures.[1] The combination of two different metals, which leads into the realm of ternary phases, is deemed an effective approach for seeking novel structure types. Here we describe the new polyphosphide Ag_3SnP_7, which possesses a unique crystal structure composed of infinite one-dimensional ${}^{1}_{\infty}(P_7)$ chains which are interconnected by discrete Ag_3Sn heteroclusters (Figure 1). Both structural fragments were previously unknown. The compound was unexpectedly obtained during investigations of the possibility to partially substitute silver for tin in tin-based clathrates.[2] The composition Ag_3SnP_7 was established by single-crystal X-ray diffraction[3] and further confirmed by a stoichiometric synthesis of the monophase product in an ampoule.

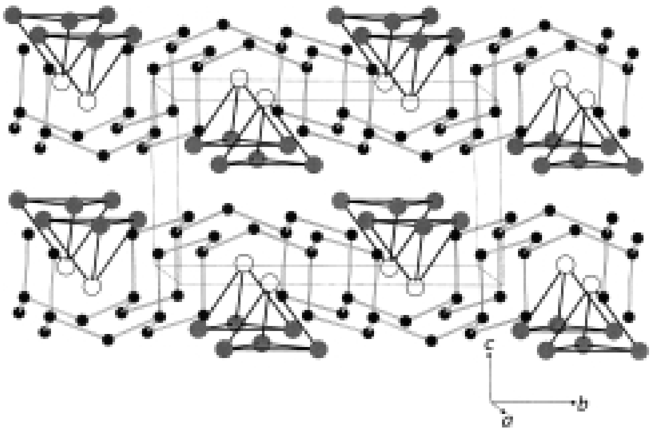

Figure 1. A view of the crystal structure of Ag_3SnP_7. Dark circles: P, white circles: Sn, shaded circles: Ag. The M–P bonds are omitted for clarity.

The ${}^{1}_{\infty}(P_7)$ chains are built up from P_6 chair fragments that are interlinked by additional two-bonded P atoms. The linkage occurs at opposite sides of each P_6 ring. Hence, there are two three-bonded and five two-bonded phosphorus atoms per formula unit (Figure 2a). The interatomic distances within the chain lie in the range 2.18–2.20 Å, which is characteristic of conventional P–P bonding.[1] The phosphorus partial structure is therefore consistent with the formulation ${}^{1}_{\infty}(P_7^{5-})$: $P_7^{5-} = (3b)P_2^{0}(2b)P_5^{1-}$. Consequently, the formal charge on the Ag_3Sn heterocluster is +5. The tetrahedral coordination of each phosphorus atom is completed by metal atoms.

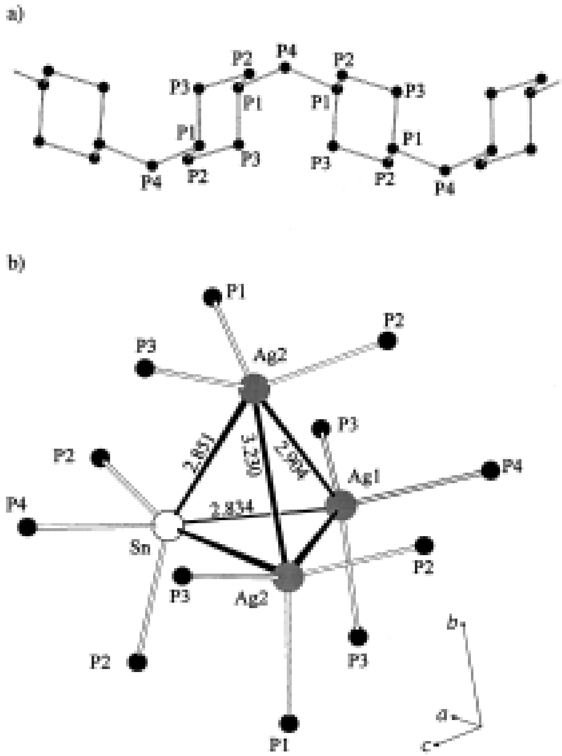

Figure 2. Fragments of the crystal structure of Ag_3SnP_7: a) a section of the polyphosphide chain; b) the $(Ag_3Sn)^{5+}$ cluster and its surrounding by phosphorus atoms. The M–P distances vary from 2.59 to 2.62 Å (Sn–P) and from 2.49 to 2.58 Å (Ag–P).

The distorted tetrahedral heterocluster $(Ag_3Sn)^{5+}$ is elongated along one of its edges (Ag2–Ag2 3.23 Å) towards a butterfly shape (Figure 2b). The other edges correspond to three Sn–Ag bonds (two of 2.85 Å and one of 2.83 Å) and two Ag–Ag bonds (2.90 Å). The Ag–Ag and Sn–Ag distances are comparable with those of $SrAg_2Sn_2$[4] and Ag_3Sn.[5] The coordination number of six for each metal atom is achieved by three Sn–P or Ag–P bonds, which complete the distorted octahedral environments around the metal atoms. The M–P distances are similar to those of Ag_3P_{11}[6] and NaSnP.[7] The coordination of Ag and Sn is quite usual, and the formal oxidation states of +1 and +2, respectively, are reasonable. With such a formal charge distribution, semiconducting behavior is expected. Indeed, according to conductivity measurements, Ag_3SnP_7 is a narrow-gap semiconductor ($E_g \approx 0.2$ eV).

Molecular orbital calculations[8] at the Extended Hückel level on the discrete $(Ag_3Sn)^{5+}$ heterocluster reveal that mainly the s orbital of Sn and d orbitals of Ag contribute to bonding between the metal atoms. The contribution from the closed-shell d^{10} silver centers should not be exaggerated, even though the Ag–Ag distance of 2.90 Å, which is 0.02 Å shorter than in the metal, suggests that the d^{10}–d^{10} interactions are attractive,[9] and d electrons should be considered in the electron count. Evidently, the p orbitals of Sn and the s and p orbitals of Ag are involved predominantly in twelve external M–P bonds per cluster. Twelve electron pairs are thus

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donated from the 32-electron heterocluster to provide the closed-shell eight-electron configuration of the phosphorus atoms. This leaves eight electrons for internal bonding and is consistent with four 3c–2e bonds in the (distorted) tetrahedral cluster.

The only previously reported example of a mixed polyphosphide with a transition/post-transition metal heterocluster is Cu_4SnP_{10}.[10] Its crystal structure also contains distorted tetrahedral units (towards pyramidal Cu_3Sn). However, the phosphorus partial structure consists of discrete adamantane-like P_{10} cages, which are interconnected by Cu_3Sn heteroclusters and additional copper atoms. The discovery of Ag_3SnP_7 indicates that the nature of the metal atoms may play a crucial role in defining the structure of phosphorus structural fragments and their interconnection.

Experimental Section

Ag_3SnP_7: silver, tin, and red phosphorus in the stoichiometric ratio were used as starting materials (1 g in total). A few crystals of SnI_4 (ca. 0.01 g) were added to the mixture to provide effective vapor-phase transport. Annealing twice in an evacuated silica ampoule (inner diameter 6 mm; length 5 cm; 823 K for 7 d, slow cooling to ambient temperature) with intermediate grinding of the products gave a black monophase product. No impurities were detected by X-ray diffraction (as a small amount of SnI_4 was added to the original mixture this observation means that formation of iodine-containing substances is negligible). All attempts to synthesize Ag_3SnP_7 without the use of SnI_4 led to low yields.

A single crystal for the X-ray structure determination was found among the products of annealing a mixture of tin, silver, tin(IV) iodide, and red phosphorus in the ratio $Sn:Ag:SnI_4:P = 17.5:4.5:2:22$ (conditions were as above).

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[3] Crystal structure of Ag_3SnP_7: monoclinic, space group $P2_1/m$ (no. 11), $a = 6.360(1)$, $b = 11.071(2)$, $c = 6.518(1)$ Å, $\beta = 108.17(1)^\circ$, $V = 436.1(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 5.020\,g\,cm^{-3}$. 1430 reflections, 1329 of which were independent ($R_{int} = 0.0285$), $T = 294$ K, $\omega/2\theta$ scans, $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, $2\theta_{max} = 60.0^\circ$, crystal dimensions $0.12 \times 0.05 \times 0.05\,mm^3$, semiempirical absorption correction (ψ scans of seven reflections, min./max. transmission: 0.6936/0.9969, $\mu = 10.668\,mm^{-1}$). Structure solution: direct methods (SHELXS-86),[11a] refinement against F^2 (1186 reflections with $F > 4\sigma(F)$) by full-matrix methods (SHELXL-97)[11b] with 56 free parameters; $R1 = 0.0425$, $wR2 = 0.0930$; max./min. residual electron density: $3.775/-2.127\,e\,Å^{-3}$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-411041.
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Fixation of Dinitrogen to a Mesoscale Solid Salt Using a Titanium Oxide/Conducting Polymer System**

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Since Schrauzer and Guth[1] reported the photocatalytic reduction of dinitrogen on titanium oxides under mild conditions, efforts have been devoted to prepare more effective catalysts and to understand the reaction mechanism;[2] such N_2 fixation under mild conditions is an important goal of many research groups.[3] However, the products of this reaction are gaseous ammonia (major) and hydrazine (trace); solid products which are easily isolated, manipulated, and characterized, have not been synthesized by this process. Herein, we describe a system to fix N_2 as an ammonium perchlorate salt, which has a structure of mesoscale needles. Dinitrogen fixation to this salt occurs upon white-light irradiation of a titanium oxide/conducting polymer system under ambient temperature and pressure conditions. The needles grow from the conducting polymer matrix and increase in size and abundance with irradiation time and intensity. The formation of such structures as a result of N_2 fixation is explained on the basis of ammonia synthesis on the oxide coupled with perchlorate dedoping of the conducting polymer.

The system used here is a composite of poly(3-methylthiophene) (P3MeT) and a titanium oxide, both of which were prepared electrochemically. A solution of 3-methylthiophene (3MeT, 0.08 M) and tetrabutylammonium perchlorate ($TBA^+ClO_4^-$, 0.1 M) in dichloromethane was subjected to galvanostatic electrooxidation at a temperature T of 13 °C for a time t of 400 s with a constant current density j of $1.5\,mA\,cm^{-2}$ in a one-compartment cell.[4] The cell was equipped with a titanium oxide anode ($2.14\,cm^2$) and a Pt plate cathode ($2.14\,cm^2$). An electrochemically synthesized titanium oxide (ETO) layer on the anode was formed by the anodic oxidation[5] of a Ti plate in a CH_2Cl_2 solution containing 0.1 M of $TBA^+ClO_4^-$ under galvanostatic conditions of $j = 0.7\,mA\,cm^{-2}$, $T = 20\,°C$, and $t = 970$ s. The Ti plate (>99.5 % purity) contained impurities such as Fe (0.250 %), K (0.013 %), O (0.200 %), and N (0.050 %); prior to the anodic oxidation the plate was degreased and etched by dipping in aqueous HF (5 %, 5 min) and then in an HF (1 %)/HNO_3 (3 %)/H_2O_2 (10 %) mixture for 30 s. In addition, prior to the deposition of P3MeT, the ETO layer was washed in trichloro-

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