Phosphorus Chemistry

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Mineralization Routes to Polyphosphides: Cu_2P_{20} and Cu_5InP_{16}**

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The element chemistry of phosphorus is one the most complex but also one of the most exciting of all chemical elements. Both the element and the binary and ternary derivatives show a great diversity in terms of reactivity, structural chemistry, and physical properties,[1] such as polymorphism, magnetism, and superconductivity, and are applied, for example, as thermoelectrics, catalysts, or in precipitation hardening. Four allotropic modifications of phosphorus are known to date at standard conditions, namely white, violet, fibrous, and black phosphorus, besides the amorphous red phosphorus.[2–6]

White phosphorus comprises molecular P_4 units, and black phosphorus is a layered compound, whereas violet and fibrous phosphorus are characterized by polymeric phosphorus stands of tubular $[P_{20}]^{2-}$ units connected via P_2 bridges. Structural fragments of these units have been identified in amorphous red phosphorus by vibrational spectroscopy and in KP_{15} by structural analysis.[7] Some theoretically predicted allotropes[8] featuring polymeric phosphorus units were successfully isolated from a copper halide matrix.[9a] $P_{15}Se$ and $P_{19}Se$ are two examples of heteroatomic polymer chains that have similar but not identical structural motifs to $[P_{20}]^{2-}$.[9b] In the past decades elemental phosphorus was used to prepare a plethora of binary and multinary phosphides and polyphosphides.[1] Thermodynamically and also kinetically controlled reactions[10] were developed to derive new compounds from elemental phosphorus. Surprisingly none of the developed methods led to a binary derivative of violet or fibrous phosphorus with retention of the polyphosphide substructure. Only one ternary compound featuring a $[P_{20}]^{2-}$ unit, the direct subunit of the element structure, embedded in a copper(I) halide matrix, was reported.[11]

Recently we prepared the novel polyphosphide $AgSbP_{14}$, the first pure inorganic material containing a covalent Sb–P interaction,[12] and developed a low-pressure route to black phosphorus,[13] making this phosphorus modification commercially available[14] and accessible for applications. Both compounds have been synthesized by a kinetically controlled reaction route using main group metal halides such as SbI_3 or SnI_4 as reaction promoters (mineralizers). The general reaction principle is closely related to the well-known concept of mineralization reactions described by Schäfer.[15]

Phosphides and polyphosphides such as Zn_3P_2, Cu_3P, $LiCu_2P_2$, and $Li_7Cu_5P_8$ are considered to be promising materials for electrodes in rechargeable batteries,[16–19] and a carbon–phosphorus composite was successfully tested as an electrode material.[20] The ongoing interest in new energy storage materials on the one hand and the still not completely solved material and engineering problems with present battery systems on the other hand are stimulating the development of new synthesis routes to new materials. Polyphosphides with anisotropic subunits (2D layers) are potential candidates for intercalation reactions, as shown in case of black phosphorus. Herein we report on the CuI-mediated synthesis of Cu_2P_{20} and Cu_5InP_{16} as well as on their structures and physical properties.

X-ray powder diffraction and EDX analyses for both polyphosphides substantiated the phase purity of the bulk phases and the composition of the single crystals selected for the structure determinations.[21] The crystal structure of Cu_2P_{20} was solved from single-crystal X-ray data at room temperature (Figure 1, top).[22a] Tubular $[P_{20}]^{2-}$ units are stacked parallel to each other and connected through tetrahedrally coordinated copper(I) ions; the Cu–P bond lengths range between 2.271(3) and 2.317(3) Å. The P–P bond lengths (2.154(4)–2.322(3) Å) within the tubular $[P_{20}]^{2-}$ unit lie in the range reported for covalently bonded phosphorus (2.15–2.30 Å).[1b] The $[P_{20}]^{2-}$ unit, built up by P_2 dumbbells, P_3 units, and P_8 units, can be regarded as a fragment of the polymeric structure of violet or fibrous phosphorus. Baudler introduced a set of rules,[23] which were extended by Häser, to describe the unique and complex phosphorus substructures in terms of subunits and their links.[8] According to these rules the $[P_{20}]^{2-}$ unit can be written as $^{1}_{\infty}$([P8]P2[P3]P2[P3]P2[) and can be regarded as a condensation of a [P8]P2[and two [P3]P2[fragments. Both fragments are two of the possible repeating units of the Baudler set for polymers. A high Baudler index of 9, which is derived from the number of five-membered rings minus the number of three-membered rings, is a good indicator of a highly stable polymer unit. The close relationship to violet and fibrous phosphorus can easily be derived from the Baudler/Häser scheme $^{1}_{\infty}$([P8]P2[P9]P2[) for violet phosphorus by abstraction of the P_2 link located in the [P9] unit. A [P3]P2[P3] fragment for each strand (Figure 2) results.

The parallel stacking of the polyphosphide strands is forced by the cations coordinating one three-bonded (3b)P

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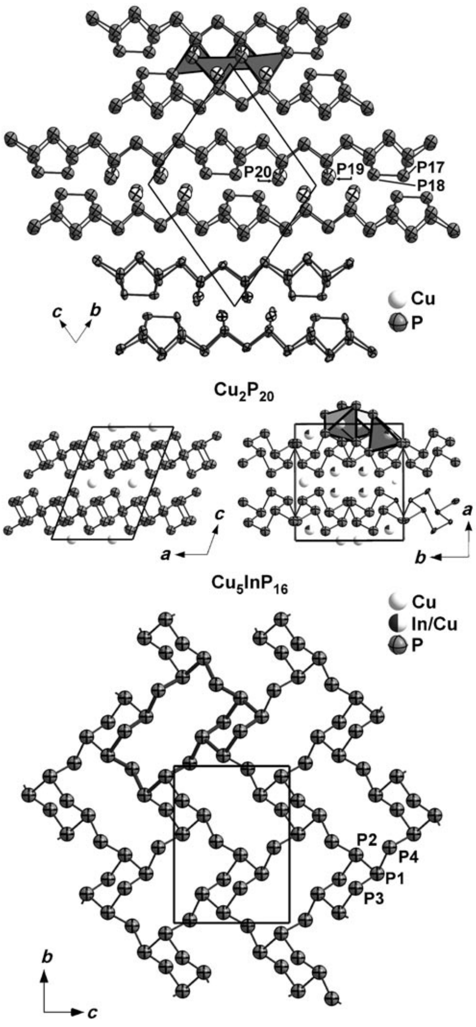

Figure 1. Crystal structures of Cu_2P_{20} (top) and Cu_5InP_{16} (bottom). Anisotropic displacement parameters at 95% probability. Cu and Cu/In coordination spheres are illustrated by polyhedra.

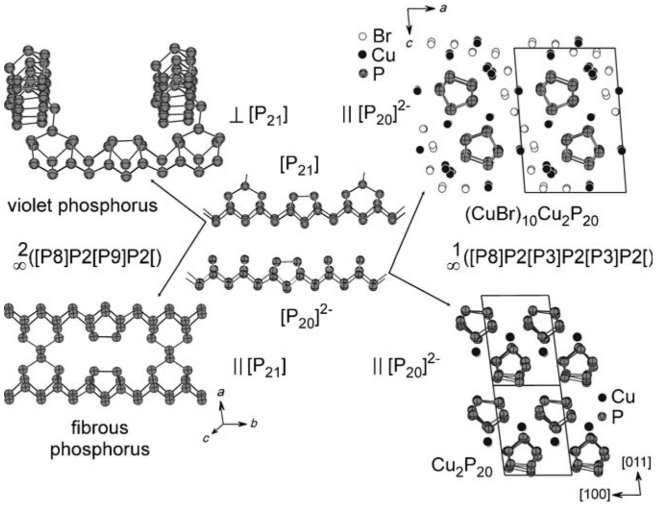

Figure 2. Structure relationships between Cu_2P_{20}, violet P,[4] fibrous P,[5] and $(CuBr)_{10}Cu_2P_{20}$.[11] The orientation of the tubular units relative to each other and the Baudler nomenclature is given.

position (P18) and the bridging two-bonded (2b)P atoms P19 and P20. Cu_2P_{20} represents the direct link between the element chemistry and the huge field of phosphides and polyphosphides. Despite a plethora of polyphosphides described so far, no binary polyphosphide has been reported in which the structural features of the tubular element allotropes are retained. Cu_2P_{20} is diamagnetic, in good agreement with the two d^{10} ions connecting the covalently bonded polyphosphide substructure.[24] Band structure calculations at the DFT level (GGA) revealed that Cu_2P_{20} is a semiconductor with a band gap of 1.58 eV, which is consistent with the dark red/violet color of the compound.[25]

Within the polyphosphide substructure a “weak” bond is located between P17 and P18 in the P_8 unit. Compared to that in violet (d(P–P) = 2.30 Å)[4] or fibrous phosphorus (d(P–P) 2.31 Å), this bond in slightly elongated to 2.322(3) Å.[26] From Mulliken population analyses (MPA) of the polyphosphide substructure, we found the highest overlap of 0.31 a.u. for the (2b)P positions to the neighboring P positions (d(P–P) ca. 2.15 Å). A MPA of 0.25 a.u. is observed for this “weak” bond compared with the average MPA of 0.29 a.u. for the remaining bonds. We hope to be able to break this slightly activated bond by intercalation or electrochemical reactions, to reduce the tubular polyphosphide strand to a $[P_5^-]$ unit, which would correspond to a polymer of the Bauder set unit [P3]P2[.

The mineralization concept was successfully transferred to ternary polyphosphides, which substantiated the high potential of the general method. Cu_5InP_{16} crystallizes monoclinic in the space group $C2/c$.[22b] It contains a previously unknown polyphosphide substructure built up by P_6 rings in the chair conformation, connected to each other in 1-, 2-, 5-, 6-position through (2b)P bridges. Alternatively, the polyphosphide substructure can be described by condensed corrugated P_{14} and P_6 rings, which form a polyphosphide layer. This unique arrangement has not previously been found in polyphosphide chemistry, but it has a topological pendant in ultraphosphate chemistry as regards the phosphorus substructure.[27] NiP_4O_{11} and MgP_4O_{11} show similar but not identical 14/6 ring subunits.[28] The polyphosphide layers in Cu_5InP_{16} are connected through a tetrahedrally coordinated Cu and through a [3+1] coordinated mixed occupied Cu/In position (Figure 1, bottom).

Both Cu_2P_{20} and Cu_5InP_{16} can be regarded as electron-precise compounds with Cu^+, In^{3+}, (2b)P^-, and (3b)P^0 resulting in $Cu_2^+[(3b)P_{18}^0(2b)P_2^-]$ and $Cu_5^+In^{3+}[(3b)P_0^0(2b)P_2^-]$ following the Zintl–Klemm concept.

Our studies confirm that the mineralization principle, which is based on the use of small amounts of metal halides as reaction promoters, is a powerful tool in polyphosphide chemistry. The application of the method ranges from element chemistry (low-pressure route to black phosphorus) over binary compounds such as Cu_2P_{20}, the first example of a polyphosphide with complete retention of the structural features of the element, to ternary compounds with previously unknown polyphosphide substructures (Cu_5InP_{16}). It can also be used to make some of the elements such as Hg, Pb, Sb, Bi, or Te, which are known to be less or nonreactive with phosphorus, more accessible as starting materials for the synthesis of new compounds. These elements and do not form binary phases with phosphorus and only a handful of ternary compounds of Hg or Te have been stabilized as phosphide halides,[29] BaP_4Te_2,[30] and Ti_2PTe_2.[31] Recently we reported on $AgSbP_{14}$, the first purely inorganic compound with a covalent Sb–P interaction, and we have preliminary experimental evidence for a compound in which Pb is the only cationic species stabilizing a polyphosphide substructure. Currently we are looking to increase the number of mineralization agents and trying to generalize and transfer the principle to other polyanionic frameworks. A first successful step was the transfer of this principle to polytellurides.[32]

Experimental Section

Cu_2P_{20} was synthesized by the reaction of Cu_3P and red P (Chempur, 99.999+ %) in the molar ratio of $^{1}/_{3}$:$9^{2}/_{3}$ in evacuated silica ampoules. A total of 300 mg of powdered starting materials were placed in the ampoule together with CuI (4 mg, Sigma Aldrich, 98 %) as mineralization promoter. Cu_3P was prepared from the elements at 1023 K in evacuated silica ampoules and checked for phase purity by X-ray powder diffraction and EDX analyses. The starting materials were heated to 820 K within 10 h and kept at that temperature for one week. Cu_2P_{20} was obtained as a dark red powder, on top of which needle-shaped crystals grew. When the reaction was carried out without adding CuI under the above-mentioned conditions, a mixture of Cu_2P_7 and elemental phosphorus was obtained.

Cu_5InP_{16} was synthesized by reacting Cu (Chempur, 99.999 %, In (Chempur, 99.99 %) and red P (Chempur, 99.999+ %) in a molar ratio of 5:1:16 in evacuated silica ampoules. CuI (10 mg) was added to a total of 500 mg of starting materials. After an initial heating step to 550 K for 8 h, the mixture was kept at 823 K for 14 days.

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[22] a) Crystallographic data for Cu_2P_{20}: $M = 746.6$ g mol^{-1}; dark red, nontransparent crystals, $0.01 \times 0.02 \times 1.0$ mm^3, triclinic, space group $P\bar{1}$, $a = 7.131(4)$, $b = 11.437(4)$, $c = 11.750(4)$ Å, $\alpha = 68.53(3)$, $\beta = 83.60(4)$, $\gamma = 84.39(4)°$, $V = 884.6(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.80$ g cm^{-3}, Stoe IPDS II, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, $F(000) = 716$, $\mu = 4.2$ mm^{-1}, $T = 293(1)$ K, 2487 independent reflections between $1.87 < \theta < 26.74°$, 1939 reflections ($I > 3\sigma I$), and 199 parameters, $R_{int.} = 0.0321$, numerical absorption correction, full-matrix least-squares refinement against F^2 with Jana 2000,[22c] $R1 = 0.0585$, $wR2 = 0.0818$ for $I > 3\sigma I$ and $R1 = 0.0792$, $wR2 = 0.0837$ for all data. b) Crystallographic data for Cu_5InP_{16}: refined composition $Cu_{4.9(1)}In_{1.1(1)}P_{16}$; $M = 933.9$ g mol^{-1}; dark red, nontransparent crystal $0.45 \times 0.40 \times 0.18$ mm^3, monoclinic, space group $C2/c$, $a = 11.124(3)$, $b = 9.663(3)$, $c = 7.533(2)$ Å, $\beta = 109.96(1)°$, $V = 761.1(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 4.07$ g cm^{-3}, Stoe IPDS II, $Mo_{K\alpha}$-radiation ($\lambda = 0.71073$ Å), graphite monochromator, $F(000) = 872$, $\mu = 10.0$ mm^{-1}, $T = 293(1)$ K, 642 independent reflections

between $2.87 < \theta < 29.17°$, 362 reflections ($I > 3\sigma I$), and 53 parameters, $R_{\text{int.}} = 0.0450$, numerical absorption correction, full-matrix least-squares refinement against F^2 with Jana 2000,[22c] $R1 = 0.0240$, $wR2 = 0.0386$ for $I > 3\sigma I$ and $R1 = 0.0402$, $wR2 = 0.0403$ for all data. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-418805 (Cu_2P_{20}) and CSD-418806 (Cu_5InP_{16}); c) V. Petricek, M. Dusek, L. Palatinus, JANA2000, The Crystallographic Computing System; Institute of Physics: Praha, Czech Republic, **2000**.

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