Yellow Arsenic

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Stabilization of Tetrahedral P_4 and As_4 Molecules as Guests in Polymeric and Spherical Environments**

*Christoph Schwarzmaier, Andrea Schindler, Claudia Heindl, Sabine Scheuermayer, Eugenia V. Peresypkina, Alexander V. Virovets, Maria Neumeier, Ruth Gschwind, and Manfred Scheer**

Chemistry as a science has originated from the exploration and handling of native elements such as sulfur or noble metals that allowed the formulation of the crucial concept of a chemical element. Despite great achievements of inorganic chemistry in the last century, the structural features of some simple substances are still not explicitly clear. It is remarkable that modern X-ray crystallography succeeded in crystal structure determination of proteins containing several thousands of atoms, yet it still faces obstacles in the characterization of some elementary compounds. For example, the extremely high aggressiveness of fluorine gas that was discovered in 1886 impeded its structural characterization for 78 years.[1] Another barrier is the instability and chemical reactivity of allotropic modifications such as O_3, whose crystal structure was not revealed until 2001,[2] or the molecular allotropes of phosphorus and arsenic. The high dynamic motion of tetrahedral P_4 molecules in white phosphorus led to a complete disorder of the cubic α-P_4 phase under ambient conditions.[3] To overcome this problem and obtain a convincing X-ray structural determination, single crystals of the ordered β-P_4 phase have to be grown at temperatures below $-77\,^{\circ}C$.[4] Arsenic exists in three allotropic modifications of which yellow arsenic, consisting of As_4 tetrahedral molecules, is the most toxic and the least stable one. It can be obtained in a time-consuming synthesis by heating gray arsenic to $750\,^{\circ}C$. The emerging As_4 is taken away by a constant flow of a carrier gas and can be discharged into a hot solvent. In contrast to white phosphorus, yellow arsenic cannot be stored as a solid. It is surprisingly poorly soluble in common organic solvents, and it readily polymerizes under ambient conditions to gray arsenic, especially when exposed to light or X-rays. Hence, until now no solid-state structure of yellow arsenic is known. Moreover, traces of gray arsenic accelerate the polymerization of As_4 even in solution. Yet, only scarce facts regarding its reactivity or coordination behavior are known.[5]

One of the ways to stabilize such unstable molecules is to include them as a guest in a molecular container or polymeric matrix.[6] Oxidation of P_4 in air was shown to be prevented by inclusion into the cavity of a supramolecular arrangement of a tetranuclear iron complex.[7] Moreover, the co-crystallization of P_4 in the lattice of solid C_{60} was reported.[8] Recently, Fujita et al. presented an elegant method for the X-ray structural characterization of organic compounds, only available in nanogram scale, based on their inclusion into single-crystalline, porous 3D coordination polymers.[9] Furthermore, our group succeeded in the stabilization of the unstable paramagnetic 16-electron complex, $[Cp^*Cr(\eta^5\text{-}As_5)]$, embedded as a guest in the giant $[Cu_{20}Cl_{20}\{Cp^*Fe(\eta^5\text{-}P_5)\}_{12}]$ molecule ($Cp^* = \eta^5\text{-}C_5Me_5$).[10] We reasoned that the use of host molecules could not only enhance the stability of the E_4 (E = P, As) molecules, especially of As_4, but would also decrease their molecular motion in the solid state. We have reported that the system $[Cp^*Fe(\eta^5\text{-}P_5)]$ and Cu^I-halides forms either polymeric structures[11] or large fullerene-like spherical molecules[10,12] capable of encapsulating guest molecules and, thus perhaps, the E_4 tetrahedra themselves. Herein we present the synthesis and X-ray molecular and crystal structure of polymeric host compounds that contain intact E_4 tetrahedra as guests. Furthermore we show that $[Ag(\eta^2\text{-}As_4)_2]^+[pftb]^-$ ($pftb = \{Al(OC(CF_3)_3)_4\}$)[5e] can be utilized for the release of As_4 as remarkably light-stable and highly concentrated solutions, making it an ideal storage medium for yellow arsenic. Finally these As_4 solutions, as well as solutions of P_4, were used to build up spherical macromolecules containing intact E_4 tetrahedra as guest molecules.

In the presence of P_4 or As_4, the reaction of CuCl with $[Cp^*Fe(\eta^5\text{-}P_5)]$ leads to the formation of the isostructural compounds $[Cu_2Cl_2\{Cp^*Fe(\eta^5\text{-}P_5)\}_2]_\infty\cdot(P_4)_n$ (**1**) and $[Cu_2Cl_2\text{-}\{Cp^*Fe(\eta^5\text{-}P_5)\}_2]_\infty\cdot(0.75As_4)_n$ (**2**), in which the tetrahedral voids are filled by perfectly adjusted E_4 molecules. Surprisingly, the crystals of **1** and **2** are light- and air-stable for days and are insoluble in common solvents. Crystal-structure analysis reveals that in **1** all the voids are totally occupied by P_4, while in **2** the As_4 molecules statistically occupy 75% of the available sites (Figure 1) probably a result of the low and rapidly decreasing concentration of As_4 in the reaction medium.

The E_4 tetrahedra are fixed between the polymeric chains by four pairs of $E\cdots P(P_5)$ intermolecular contacts of 3.98 and 4.00 Å in **1** and 3.98 and 4.04 Å in **2** (Figure 1), together with

[*] Dr. C. Schwarzmaier, Dr. A. Schindler, C. Heindl, S. Scheuermayer, Dr. M. Neumeier, Prof. Dr. R. Gschwind, Prof. Dr. M. Scheer
Universität Regensburg
93040 Regensburg (Germany)
E-mail: Manfred.Scheer@chemie.uni-regensburg.de
Dr. E. V. Peresypkina, Dr. A. V. Virovets
Institute of Inorganic Chemistry SB RAS
Ak. Lavrentiev prosp. 3, Novosibirsk 630090 (Russia)

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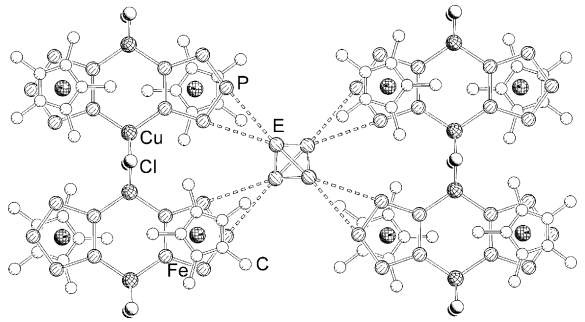


Figure 1. Molecular structure of E_4 in the crystal lattice of **1** and **2**. The E_4 molecule is locked between two polymeric chains. Dashed lines show noncovalent intermolecular E···P contacts. Hydrogen atoms are omitted for clarity.

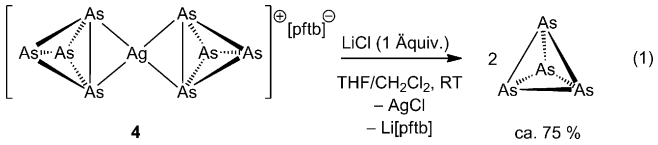
numerous CH_3···E contacts, all longer than 3.2 Å. According to the van der Waals radii of 1.80 and 1.85 Å for P and As,[13] respectively, the E···P(P_5) distances point to rather weak host–guest interactions. These interactions might take place between the LUMO (e_1) or LUMO + 1 (e_2) of [Cp*Fe(η^5-P_5)],[14] located at the *cyclo*-P_5 rings, and the lone pairs of the E_4 molecule,[15] contributing to the HOMO−5 (a_1). Additionally, the methyl groups of the Cp* ligands sterically lock the guest molecule in its orientation. A rotational disorder is therefore unlikely and not observed. The specific structures of **1** and **2** coerce the isolated E_4 molecules to be ordered, and thus allow a reliable determination of their molecular geometry at $T = 123$ K. In the case of As_4, it is the first molecular-structure determination based on single-crystal X-ray diffraction.

In the last decades, the P–P bond lengths in white phosphorus as a prototype of a covalent P–P single bond were determined using a variety of physical and theoretical methods, leading to inconsistent results. In the gas phase, electron diffraction shows P–P bond lengths of 2.21(1) Å[16] which agrees well with 2.223(1) Å suggested by Raman spectroscopy.[17] More recent electron diffraction studies at 100 °C lead to a value of 2.1994(3) Å.[18] The average P–P bond length in the low-temperature phase of white phosphorus, β-P_4 (−115 °C, ambient pressure) was investigated to give 2.182 Å (2.1756(5)–2.1920(5) Å) that was corrected for libration to a value of 2.204 Å (2.190–2.212 Å).[4] DFT calculations predict values of 2.194 Å[19] or 2.186 Å depending on the basis set.[18,20] The P–P bond lengths in **1** are 2.160(3)–2.165(3), average 2.162(2) Å, and thus are slightly shorter compared to bond lengths determined by other experimental methods but similar to the theoretical value of 2.186 Å.[18,20] A room-temperature structure determination of **1** showed significantly larger thermal motion of the P_4 guest molecule (cf. Supporting Information) that points to rather weak host–guest interactions and precluded us from determining precise P–P bond lengths at room temperature. The obtained values of 2.051(6)–2.077(4) (av. 2.06 Å) being averaged over very close positions of the disordered guest molecule, are even shorter than the values obtained at 123 K.

The As–As bond length in As_4 was determined by electron diffraction in the gas phase, resulting in values of 2.44(3) Å and 2.435(4) Å.[16,21] DFT calculations predict As–As distances of 2.4372 Å[5d] which agrees well with the experimentally obtained ones. Owing to the extreme X-ray sensitivity of yellow arsenic, only one study on X-ray diffraction from As films reports As–As bond lengths to be 2.42(2) Å at 30 K.[22] In **2**, the As–As bond lengths vary in the range of 2.3907(12)–2.3998(15) (av. 2.396(5) Å) which is slightly shorter than earlier data.

To exclude possible influence of strong host–guest interactions that could be responsible for the E–E bond lengths, we performed additional spectroscopic investigations on **1** and **2**. The solid-state MAS-NMR spectrum of **1** shows one sharp resonance at $\delta = -506$ ppm which is reminiscent of the chemical shift of white phosphorus in benzene solution ($\delta = -520$ ppm) and in the gas phase ($\delta = -551$ ppm).[23] In contrast, solid or liquid white phosphorus show one sharp singlet at $\delta = -461.5$ ppm or $\delta = -460$ ppm, respectively.[23] The downfield shift indicates strong interactions between the P_4 molecules in the condensed phase that are not observed in **1**. In case of **2**, MAS-NMR investigations failed because of the large quadrupole moment of the ^{75}As nucleus. Therefore a Raman spectrum of **2** was compared to those of the original polymer $[Cu_2Cl_2\{Cp^*Fe(\eta^5\text{-}P_5)\}_2]_\infty \cdot CH_2Cl_2$ (cf. Supporting Information).[11b] The Raman bands for the embedded As_4 molecules at $\tilde{\nu} = 202$ (broad), 259, and 347 cm^{-1} agree well with those calculated for As_4 in the gas phase at $\tilde{\nu} = 203$ (two-fold degenerate), 259 (three-fold degenerate), and 349 cm^{-1}. For both **1** and **2**, spectroscopic investigations indicate only minor interactions between the embedded E_4 molecules and the polymeric host matrix. Hence, the E_4 molecular structure is almost unaffected by the solid-state environment and the E–E bond lengths can be reliably used as reference for the E_4 molecules.

Besides the formation of polymeric structures, we have also shown the potential of the CuX/[Cp*Fe(η^5-P_5)] system (X = Cl, Br) for the template-controlled formation of spherical structures.[10,12,24] Interestingly, we never obtained similar spherical host–guest compounds by using CuI as the starting material. Surprisingly, in the presence of P_4 we succeeded in the preparation of $P_4@[\{Cp^*Fe(\eta^5\text{-}P_5)\}_{10}Cu_{30}I_{30}(MeCN)_6]\cdot 2\,MeCN$ (**3**), a first CuI-containing cage molecule not following the Fullerene-topology. However, we failed upon using unstable solutions of As_4 made by a classical synthetic route. Therefore, we searched for less direct ways to generate As_4 solutions. Recently, we reported on the synthesis of the homoleptic silver complex $[Ag(\eta^2\text{-}As_4)_2][pftb]$ (**4**) in which two As_4 tetrahedra coordinate side-on at the silver cation.[5e]



4 (1)

The reaction of **4** with one equivalent of LiCl leads to the formation of AgCl as well as Li(pftb), both precipitate almost quantitatively from the reaction mixture within 20 min [Eq. (1)]. To confirm the release of As_4 from **4**, ^{75}As NMR spectroscopy was performed. While solutions of As_4, obtained from gray arsenic, show a broad signal at $\delta = -892$ ppm

($\omega_{1/2}$=2060 Hz), **4** does not show any signals in the range from $\delta = 0$ to -1200 ppm owing to quadrupole relaxation and the associated line broadening together with the low local symmetry of the coordinated As_4 tetrahedra. When LiCl is added, a signal at $\delta = -908$ ppm ($\omega_{1/2} = 2364$ Hz) is detected which clearly indicates the successful release of As_4 from **4**. The As_4 solutions obtained contain about 75% of the initially used arsenic and show a unique stability to light (over 4 h). A reason for this stability might be the lack of gray arsenic seeds that autocatalyze the As_4 polymerization. In addition, the As_4 solutions are about five-times more concentrated than those obtained from high-temperature synthesis.

Using these more stable As_4 solutions in the reaction of CuI with [Cp*Fe(η^5-P_5)], we succeeded in the formation of As_4@[{Cp*Fe(η^5-P_5)}$_{10}$$Cu_{30}I_{30}$(MeCN)$_6$]·2 MeCN (**5**), the arsenic analogue of the P_4-containing supramolecular **3**. These unique supramolecular species consist of two half shells that are connected by a copper iodide scaffold not observed in spherical supramolecular species based on CuCl and CuBr.[12] The belt region is formed by four bowl-like {Cu_4(μ_4-I)(μ_3-I)(μ_2-I)$_3$} units. They connect four pentaphosphaferrocene {Cp*Fe(P_5)} entities of each hemisphere (Figure 2) that in turn are attached to a capping {Cu_2-(μ_2-I)$_2$(MeCN)CuI} framework by two {CuI} and two {Cu(MeCN)} units. Each half shell is completed by a dangling pentaphosphaferrocene unit with a 1,2-coordination pattern. In total, the inorganic frameworks of **3** and **5** consist of 100 atoms. The supramolecular species **3** and **5** have similar dimensions of 2.08 nm × 3.33 nm and 2.09 nm × 3.41 nm, respectively.[25]

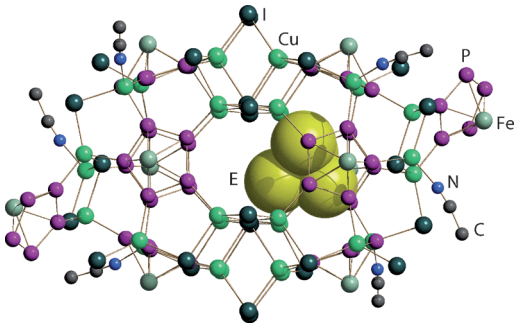


Figure 2. The E_4 (E = P, As) tetrahedron encapsulated in an ellipsoid shaped host molecule of **3** and **5**. Only one position of the disordered E_4 molecule is shown and Cp* ligands are omitted.

The supramolecular species have an elongated cavity 10.3 Å in length, divided into two parts by four iodine atoms of the middle belt (Figure 2). In each part, the distance between two opposing *cyclo*-P_5 rings is about 4.9 Å providing enough space to enclose an E_4 molecule. The parts are statistically occupied by the E_4 guest with a probability of 50%. Moreover, they show an orientational disorder over two or more close positions because of the inappropriate cuboid-like shape of the cavity. Despite the disorder, host–guest interactions are more significant than those in **1** and **2**, since the E_4 molecule forms shortest intermolecular contacts of 3.68 Å for E = P and 3.55 Å for E = As with the *cyclo*-P_5 rings, and of 3.71 for E = P and 3.64 Å for E = As with nearby iodine atoms. In the case of **3** the P–P bond lengths of the P_4 unit vary from 1.94 to 2.28 Å. For the As_4 tetrahedron in **5**, the As–As bond length had to be restrained during structure refinement. In both cases the bond lengths are determined only with low precision as a result of the disorder but still satisfactorily agree with those found in **1** and **2**.

In conclusion, we successfully incorporated tetrahedral P_4 and As_4 molecules in the tetrahedral voids of the polymeric matrix of [Cu_2Cl_2{Cp*Fe(η^5-P_5)}$_2$]$_\infty$. In the resulting products [Cu_2Cl_2{Cp*Fe(η^5-P_5)}$_2$]·$(E_4)_x$ (E = P, $x = 1$; E = As, $x = 0.75$) the E_4 guests only interact very weakly with the polymeric matrix. Hence, a precise molecular structure for the intact E_4 molecules by single-crystal X-ray diffraction is accomplished. In the case of As_4, it is the first structure determination based on single-crystal diffraction methods. In both cases, the E–E bonds are shorter than others reported but agree with calculated values. Furthermore, we also succeeded in inclusion of the E_4 molecules in giant ellipsoid-like cage molecules based on a novel strategy for the generation of stable and highly concentrated As_4 solutions that uses [Ag(η^2-As_4)$_2$][pftb] as an arsenic source. Because this unique salt is light-stable as well as storable, it appears to be an unprecedented As_4 storage material that will open new directions in the chemistry of yellow arsenic.

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[25] The outer dimensions of ellipsoidal supramolecules were determined as the sum of the distances between the H atoms of the most distant opposing Cp* ligands and doubled van der Waals radii of H atoms (1.20 Å).

