Tetraphenylphosphonium Hexaazidoarsenate(v): The First Structurally Characterized Binary As^{V}–Azide Species**

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Dedicated to Professor Heinrich Vahrenkamp on the occasion of his 60th birthday

The chemistry of covalent arsenic–azide species was opened by Revitt and Sowerby[1] with the reported synthesis, spectroscopic properties, and thermal decomposition of some organoarsenic(III) azides. However, very little is known about their reactivity or structures. To our knowledge, only two molecular arsenic(III) azides have been structurally characterized: the perfluoroalkyl species bis(trifluoromethyl)arsenic azide, $((CF_3)_2AsN_3)$,[2a] and trifluoromethylarsenic diazide, $CF_3As(N_3)_2$,[2b] which were investigated by gas-phase electron diffraction. Recently we reported on the reaction between $AsCl_3$ and $[AsCl_4][AsF_6]$ with activated sodium azide, which resulted in the formation of the first binary arsenic azide, $As(N_3)_3$, and the first reported As^{V}–azide species, $[As(N_3)_4]^+$.[3a,b] As far as we are aware, prior to this study there has been no report on a hexacoordinated arsenic–azide compound nor has the structure of any arsenic–azide species through X-ray analysis been determined experimentally.[4a,b] Herein, we report on the formation and the crystal structure[5] of the extremely nitrogen rich, binary hexaazidoarsenate(v) anion $[As(N_3)_6]^-$.

In contrast to the synthesis of $As(N_3)_3$ and $[As(N_3)_4]^+$, which were prepared from NaN_3 and the corresponding As–Cl compound, in this study we used trimethylsilylazide, $(CH_3)_3SiN_3$, as the azide group-transferring agent. The compound $[PPh_4][AsCl_6]$ was prepared as described in the literature[6] and treated with an excess of trimethylsilylazide in a solution of CH_2Cl_2 at room temperature to yield tetraphenylphosphonium hexaazidoarsenate(v) **1** [Eq. (1)].

$$[PPh_4][AsCl_6] + 6\,Me_3SiN_3 \longrightarrow [PPh_4][As(N_3)_6] + 6\,Me_3SiCl \qquad (1)$$

Compound **1** was isolated and fully characterized by elemental analysis, IR, Raman, and multinuclear NMR spectroscopies, and the molecular structure was determined by single crystal X-ray diffraction.

The IR and Raman spectra of **1** show, in addition to the expected vibrations which can be attributed to the $[PPh_4]^+$ ion, all the characteristic modes of a covalently bound azide species. The covalent nature of the $[As(N_3)_6]^-$ ion is indicated by both the simultaneous appearance of the asymmetric ($2110-2084\ cm^{-1}$) and the symmetric ($1270-1279\ cm^{-1}$) azide stretch modes and by the presence of a strong As–N vibration at $416\ cm^{-1}$ in the IR and the Raman spectra.[7] An exact assignment of the normal modes of the $[As(N_3)_6]^-$ ion, which has idealized S_2 symmetry, was not possible due to lowering of the symmetry in the solid state.

Compound **1** was characterized by ^{1}H, ^{13}C, ^{14}N, ^{31}P, and ^{75}As NMR spectroscopy. The most suitable NMR method for the characterization of covalent azides is undoubtedly the ^{14}N NMR spectroscopy. The ^{14}N NMR spectrum (Figure 1) shows

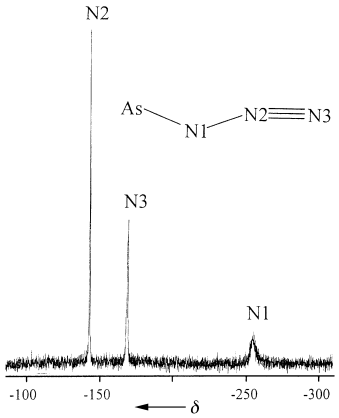

Figure 1. ^{14}N NMR spectrum of **1**.

three well resolved resonances, which can be assigned to the chemically inequivalent nitrogen atoms of the covalently bound azide group. The assignment was made on the basis of examples given in the literature.[8] The N2 atom shows a sharp signal at $\delta = -141.1$, the N3 atom at $\delta = -165.4$, and the N1 atom, as expected, gives a very broad resonance at $\delta = -256.2$. In the ^{75}As NMR spectrum, **1** shows a resonance at $\delta = +4$ (standard: $KAsF_6$, $\delta = 0$) and appears at significantly lower shift compared to the starting material $[PPh_4][AsCl_6]$ ($\delta = -392$).[9d] The relatively sharp signal in the ^{75}As NMR spectrum of $[As(N_3)_6]^-$ indicates a very symmetrical environment around the central As atom, since the large quadrupolar moment of the ^{75}As nucleus means this element can be detected only in very symmetrical environments.[9a–d]

The X-ray structure analysis of **1** (Figure 2)[5] revealed the presence of an ionic compound with $[PPh_4]^+$ cations and $[As(N_3)_6]^-$ anions which do not show any significant cation–anion interaction. The arsenic atom, which exhibits a slightly

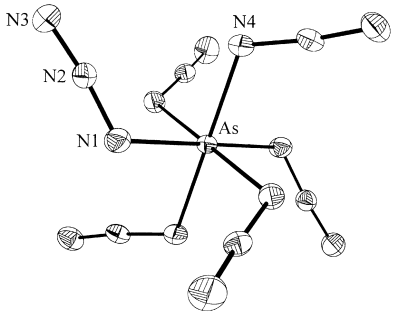

Figure 2. The molecular structure of **1** (the counterions are omitted for clarity). The thermal ellipsoids represent a 25% probability. Selected bond lengths [Å] and angles [°]: As-N1 1.931(2), N1-N2 1.229(3), N2-N3 1.123(3); As-N1-N2 115.6(2), N1-N2-N3 173.6(3), N1-As-N4 91.5(1).

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distorted octahedral environment with idealized S_2 symmetry, is bound to six nitrogen (N1) atoms. The As–N1 distances span 1.920(3) – 1.938(2) Å and the N1-As-N4 angles lie between 88.2(1) – 91.8(1)°. While the N1–N2 bond lengths range 1.222(3) – 1.238(3) Å, the terminal N2–N3 lengths range 1.120(3) – 1.123(3) Å and are both in good accord with the bond lengths of bis(trifluoromethyl)arsinic azide[2a] and trifluoromethylarsinic diazide.[2b] The N1-N2-N3 angle lies within 173.6(3) – 176.3(3)° and in good agreement with N-N-N angles of other previously reported covalent azides.[10] The angle between the arsenic atom and the azide group (As-N1-N2) is 116.2(2)°.

Compound **1** shows only moderate impact, friction, and electrostatic sensitivity but explodes when subject to a thermal shock test.[11] The relatively high kinetic stability of **1** can be explained by the fact that the large and bulky $[PPh_4]^+$ ions separate the $[As(N_3)_6]^-$ ions in the solid state and therefore cause a high activation barrier for the overall exothermic decomposition. This phenomenon has also been observed for the $[I(N_3)_2]^-$ ion, which is kinetically stable as the $[PPh_4]^+$ salt but highly explosive as the $[NMe_4]^+$ salt.[12]

Experimental Section

Caution: Covalent and ionic azides as well as arsenic compounds are very toxic and covalent azides are potentially explosive. Appropriate safety precautions should be taken.

Apparatus: NMR: Jeol EX400 Delta (^{1}H, ^{13}C: relative to $\delta_{TMS} = 0.00$; ^{31}P: relative to $\delta_{H_3PO_4} = 0.00$; ^{14}N: relative to $\delta_{CH_3NO_2} = 0.00$; ^{75}As: relative to $\delta_{KAsF_6} = 0.00$). IR: Nicolet 520 FT IR. Raman: Perkin Elmer Spectrum 2000R NIR FT. Elemental (C, H, N) analysis: Analysator Elementar Vario EL.

Compound **1** was synthesized under an inert gas atmosphere at 25 °C by the slow addition of neat $(CH_3)_3SiN_3$ (0.53 mL, 4 mmol) with stirring to a solution of $[PPh_4][AsCl_6]$ (0.314 g, 0.5 mmol) in CH_2Cl_2 (25 mL). After 5 hours the solvent and $(CH_3)_3SiCl$ were removed by a dynamic vacuum. Colorless crystals were obtained after recrystallization from CH_2Cl_2 at –25 °C. Yield: 0.237 g (71 %, based on $[PPh_4][AsCl_6]$); elemental analysis for $C_{24}H_{20}AsN_{18}P$: calcd: C 43.25, H 3.02, N 37.83; found: C 42.89, H 2.91, N 37.44; IR (powder between CsI plates): $\tilde{\nu}$: 2085 (vs, $\nu_{as}(N_3)$), 1585 (w), 1481 (m), 1434 (s), 1270 (s, $\nu_s(N_3)$), 1108 (s), 996 (w), 888 (m), 783 (s), 688 (s, $\delta(N_3)$), 526 (s), 416 (s, ν(AsN)), 305 cm^{-1} (s); Raman (525 scans, 200 mW, 180° geometry, 25 °C): $\Delta\tilde{\nu}$: 3068 (6.5), 2110 ($\nu_{as}(N_3)$ in plane, 3.5), 2084 ($\nu_{as}(N_3)$ out of plane, 1.5), 1587 (4.5), 1279 ($\nu_s(N_3)$, 3.5), 1187 (0.5), 1163 (0.5), 1099 (1.5), 1027 (2.5), 1001 (6.5), 681 ($\delta(N_3)$, 1.5), 669 ($\delta(N_3)$, 1.5), 416 (ν(AsN), 10), 267 (1.5), 252 (1.5), 116 (8) cm^{-1}; ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): $\delta = 117.5$ (d, C1), 130.8 (d, C2), 134.4 (d, C3), 135.9 (d, C4); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 6.8 – 7.5$ (Ph); ^{31}P NMR (109 MHz, $CDCl_3$, 25 °C): $\delta = 23.9$ (s); ^{14}N NMR (29 MHz, $CDCl_3$, 25 °C): δ = -141.1 (N2), -165.4 (N3), -256.2 (N1); ^{75}As NMR (46 MHz, $CDCl_3$, 25 °C): $\delta = 4$.

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[5] X-ray structure analysis: Siemens CCD Area Detector, hemisphere scan type, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 183$ K, range $3.72° < 2\theta < 58.48°$ in $-27 \le h \le 12$, $-7 \le k \le 8$, $-24 \le l \le 24$, 8213 measured reflections, 2869 independent reflections ($R_{int} = 0.0343$), 2399 observed reflections ($F > 4\sigma(F)$). Structure solution program: SHELXS-97 (G. M. Sheldrick, University of Göttingen, Germany, **1997**), solution with direct methods, data to parameter ratio 11.9:1 (10.0:1 [$F > 4\sigma(F)$]), $R1 = 0.0375$, $wR2 = 0.0922$, $R1 = 0.0501$, $wR2 = 0.0986$ (all data), GOF(F^2) = 1.035, max./min. residual electron density 0.574, –0.436 e Å^{-3}, structure refinement program: SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany, **1997**). Crystal data for **1**: $C_{24}H_{20}AsN_{18}P$ ($M_r = 666.47$), colorless prisms, $0.20 \times 0.10 \times 0.05$ mm, monoclinic, space group $C2/c$, $a = 22.147(3)$, $b = 7.1943(8)$, $c = 18.766(2)$ Å, $\alpha, \gamma = 90.00$, $\beta = 98.635(2)°$, $V = 2956.1(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.498$ g cm^{-3}, $\mu = 1.255$ mm^{-1}, $F(000) = 1352$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140555. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Preparation of Bioconjugates through an Ugi Reaction**

Thomas Ziegler,* Sonja Gerling, and Martin Lang

Dedicated to Professor Franz Effenberger on the occasion of his 70th birthday

The specific preparation of bioconjugates, which is, in general, the covalent linking of a low molecular weight compound to a protein or an oligonucleotide or bond formation between two proteins, can be regarded as one of the most important methods in modern biochemistry.[1] Conjugates which are constructed out of a protein or oligonucleotide (for example, an enzyme or a DNA fragment) and a pigment or a radioactive compound are widely used for

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