

A New Arsenic-rich Polyaniion. Synthesis and Structure of $[(\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3)\text{NiI}]_2[\text{As}_6\text{I}_8]$

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The reaction of AsI_3 with $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ and $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ yields the new arsenic iodide anion $[\text{As}_6\text{I}_8]^{2-}$ the structure of which has been determined by X-ray crystallography.

It is well known that elements of Main Group V are capable of forming homo- and hetero-atomic clusters.¹ As far as arsenic is concerned, besides homopolyatomic anions, some hetero-atomic compounds of different stoichiometries and structures have recently been reported.¹⁻⁴ These latter generally contain as heteroatoms transition metals or chalcogens. We now report the synthesis and the structure of the first example of a cubane-like arsenic-iodine polyaniion.

The reaction of AsI_3 with the system $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2/\text{triphos}$, where triphos is the tripod-like phosphine $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$, molar ratio 3:1, in tetrahydrofuran-butanol solution, under nitrogen atmosphere, affords brown well-shaped crystals of analytical composition $\text{C}_{41}\text{H}_{39}\text{As}_3\text{I}_5\text{NiP}_3$, (**1**). The complex, which slowly decomposes in air, is paramagnetic with μ_{eff} 3.25 B.M. at room temperature.

The molecular structure[†] of (**1**) consists of $[\text{As}_6\text{I}_8]^{2-}$ cluster

[†] Crystal data for $[(\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3)\text{NiI}]_2[\text{As}_6\text{I}_8]$: $M = 3085.37$, monoclinic, space group $C2/c$, $a = 22.500(8)$, $b = 19.092(5)$, $c = 24.912(12)$ Å, $\beta = 109.29(4)^\circ$, $U = 10\,100.6$ Å³, $Z = 4$, $D_c = 2.028$ g cm⁻³, monochromatic Mo- K_α radiation, $\lambda = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 54.8$ cm⁻¹. The intensity data were collected within $2\theta \leq 40^\circ$ on an ENRAF-NONIUS CAD4 diffractometer using ω - 2θ scan technique at 295 K. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedure. The phenyl rings were treated as rigid groups and the hydrogens were included in their calculated positions but not refined. The R and R_w factors are 0.053 and 0.052, respectively, for 2161 absorption corrected observed reflections having $I \geq 3\sigma(I)$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

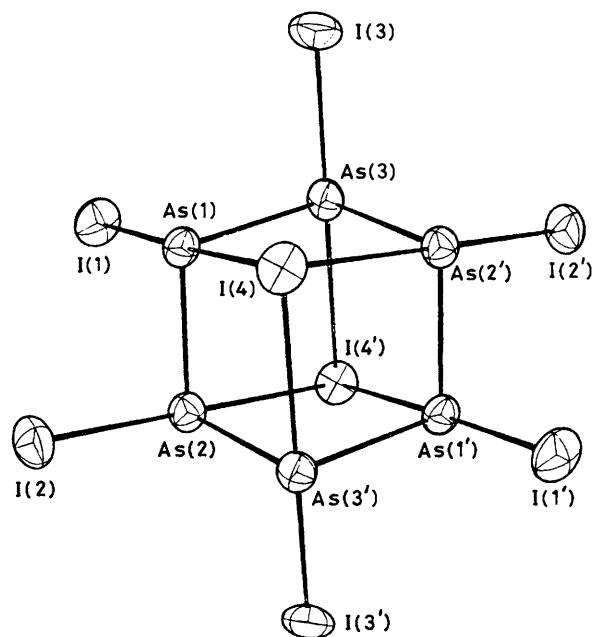


Figure 1. Perspective view of the cluster anion $[\text{As}_6\text{I}_8]^{2-}$. ORTEP drawing with 30% probability ellipsoids. Selected bond distances (Å) and angles (deg.): As-As (av.) 2458(4), AsI_{term} (av.) 2.69(2), $\text{As-I}_{\text{bridg}}$ (av.) 3.10(3), As-As-As 99.9(4), As-As- I_{term} (av.) 89.4(5), As-As- I_{bridg} (av.) 91.4(5), I-As-I (av.) 177.8(10), As-I-As (av.) 74.7(4).

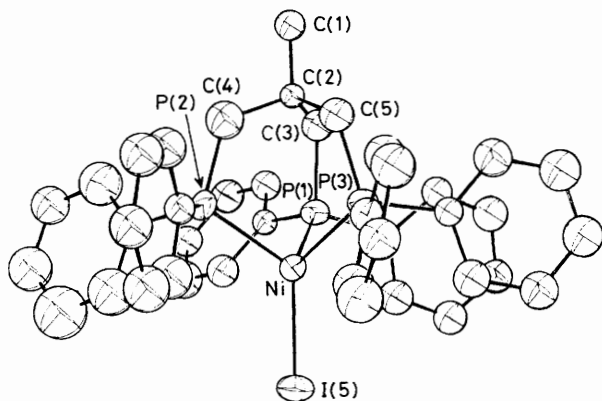


Figure 2. Perspective view of the complex cation $[(\text{triphos})\text{NiI}]^+$. ORTEP drawing with 30% probability ellipsoids. Selected bond distances (Å) and angles (deg.): Ni–P (av.) 2.244(4), Ni–I 2.414(4), P–Ni–P (av.) 92.8(7), P–Ni–I (av.) 123.0(11).

anions and $[(\text{triphos})\text{NiI}]^+$ complex cations, perspective views of which are given in Figures 1 and 2, respectively.

Two interesting features characterize the results of the X-ray analysis of (1): the achievement of the new, hitherto unknown, polyanionic cluster species $[\text{As}_6\text{I}_8]^{2-}$ and the isolation of a tetrahedral nickel(II) complex with the unprecedented P_3X set of donor atoms.

The cluster anion $[\text{As}_6\text{I}_8]^{2-}$, which possesses crystallographic imposed C_i symmetry, displays a distorted cubane-like structure, where six vertices of the cube are occupied by the arsenic atoms and two diagonally opposite corners by two iodine atoms. The cluster unit could be conceptually derived from a chair-conformed As_6 ring with two iodine atoms as caps. Distortions from the limit geometry seem mainly due to the presence of the bridging iodine atoms, which displaying As–I distances of 3.10(3) Å (av.), [the As–As average 2.458(4) Å], allow a stretching of the cube along the I(4)–I(4') diagonal, with the As–I–As bond angles ranging from 73.9(1) to 75.4(1)°.

Each arsenic atom, which is linked to two other arsenic and to one iodine atoms, completes its four co-ordination by being additionally bound to a terminal iodine atom. It is noteworthy that the metal centres are far from having a tetrahedral geometry: as a matter of fact the terminal iodine atoms are *trans* to the bridging ones, so that the co-ordination around the arsenic atoms is more consistent with an incomplete octahedral geometry [the bond angles involved are: As–As–As (av.) = 99.9(4), As–As–I_{term} (av.) = 89.4(5), As–As–I_{bridg} (av.) = 91.4(5), I–As–I (av.) = 177.8(10)°].

The As–As bond distances [range 2.450(5)–2.463(5) Å] fall well in the range of values reported for the free As_4 molecule,⁵ the homocyclic As_3 unit,⁶ the two forms of As_4S_3 ,⁷ and the polyarsenic species As_7^{3-8} and As_{11}^{3-9} .

The As–I_{term}, averaging 2.69(2) Å, are markedly shorter than the As–I_{bridg}, whose range goes from 3.051(4) to 3.166(4) Å.

In the complex cation‡ the nickel atom is surrounded in a distorted tetrahedral geometry by the phosphorus atoms of the triphos ligand and by an iodine atom. The distortion from the limit geometry is well evidenced by the values of the P–N–P angles [range 91.6(3)–94.1(3)°] as well as of the P–Ni–I angles [range 121.0(3) to 124.6(3)°]. Such a distortion seems mainly due to the steric constraints of the triphos ligand, which prevents the achievement of the ideal values. An interesting comparison of the $[(\text{triphos})\text{NiI}]^+$ cation can be made with the molecular unit $[(\text{triphos})\text{NiI}]$,¹¹ where a major difference has been observed in the Ni–I bond distances: 2.414(4) and 2.546(2) Å in the Ni^{II} and Ni^I species, respectively.

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‡ The series of the tetrahedral complexes $[(\text{triphos})\text{NiX}](\text{ClO}_4)$, X = Cl, Br, I, can easily be prepared by reaction of the appropriate halide ion with $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ and triphos.¹⁰