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Synthesis and structures of lithium salts of two cluster iodoarsenate(III)s and a periodohexaantimonate(III)

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Treatment of the lithium β-diketiminate $\mathrm{Li[\{N(C_6H_3Pr^{\it i}_2\text{-}2,6)C(Me)\}_2CH]}$ with an equivalent portion of arsenic(III) iodide unexpectedly afforded $\mathrm{[Li(thf)_4]_2[As_8I_{26}]}$ (**1**) in modest yield. Another new cluster anion featured in $\mathrm{[Li(thf)_4]_2[Li(thf)_6][As_7I_{24}]\cdot 1.5(thf)}$ (**2**) was obtained in excellent yield from lithium iodide and four equivalents of $\mathrm{AsI_3}$ in thf. Using the same stoichiometry and solvent, but with $\mathrm{SbI_3}$ in place of $\mathrm{AsI_3}$, furnished in good yield $\mathrm{[Li(thf)_4]_4[Sb_6I_{22}]\cdot 2(thf)}$ (**3**). The structures of the new crystalline orange (**1**, **3**) or orange/red (**2**) salts was established by single crystal X-ray diffraction. Each anion of **1**–**3** may be factorised into respectively $\mathrm{[(AsI_2)_6(AsI)_2(\mu_2\text{-}I)_{10}(\mu_5\text{-}I)_2]^{2-}}$ (**1**), $\mathrm{[\{(AsI_2)(\mu_2\text{-}I)(\mu_3\text{-}I)\}_6As]^{3-}}$ (**2**) and $\mathrm{[(SbI_3)_2(SbI_2)_2(SbI)_2(\mu_2\text{-}I)_6(\mu_3\text{-}I)_4]^{4-}}$ (**3**). Each As atom in **2** and each Sb atom in **3** is the centre of a six-coordinate distorted octahedron, while the arsenic atoms in **1** have either four- or six-coordinate environments.

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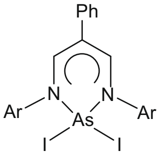
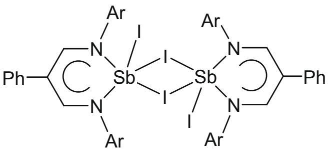
1. Introduction

This paper on unusual cluster iodides of arsenic and antimony derives from earlier recent studies dealing with the synthesis and structures of β-diiminato complexes of the group 15 elements: P(III) [1], As(0, I, II, III) [2], Sb(III, V) [3], and Bi(III) [4], and of the group 16 Te(IV) [4]. Particularly relevant in the present context was the preparation of the compounds **A** (as the $\mathrm{Et_2O}$ solvate) and **B** (as the 0.5 $\mathrm{Et_2O}$ solvate) [3], each obtained from *equivalent portions* of $\mathrm{K[\{N(Ar)C(H)\}_2CPh]}$ and (i) $\mathrm{AsI_3}$ in $\mathrm{Et_2O}$ or (ii) $\mathrm{SbI_3}$ in $\mathrm{Et_2O/thf}$ ($\mathrm{Ar = C_6H_3Pr^{\it i}_2\text{-}2,6}$).



A



B

2. Results and discussion

The initial objective of this research was to explore the outcome of the reactions between an alkali metal β-diketiminate M(**L**) (rather than as for **A** or **B** a β-dialdiminate) and $\mathrm{AsI_3}$ or $\mathrm{SbI_3}$ [$\mathbf{L}$ = $\mathrm{\{N(C_6H_3Pr^{\it i}_2\text{-}2,6)C(Me)\}_2CH}$]. In the event, from Li(**L**) and $\mathrm{AsI_3}$, there was obtained the **L**-free cluster compound **1**. As a consequence, the revised objective was to study reactions between lithium iodide and an excess of arsenic or antimony triodide.

2.1. Synthesis and structure of the lithium salt 1

The preparation of the crystalline lithium periodooctaarsenate(III) **1** is illustrated in Scheme 1 (1 Li:3 As stoichiometry of the reagents is assumed on the basis of the composition of **1**). However, surprisingly, by mixing equivalent portions of Li(**L**) and $\mathrm{AsI_3}$ in tetrahydrofuran at ambient temperature, removal of volatiles and extraction of the residue with toluene, orange crystals of the salt **1** were obtained in modest yield. The fate of the β-diketiminato ligand **L** was not established, but possibilities include [as well as unreacted Li(**L**)] As(**L**)$_3$ or [Li(thf)$_4$][AsI(**L**)$_3$] (both presently unknown).

The salt **1** was characterised by satisfactory C and H microanalysis and by its EI-mass spectrum showing strong signals for $\mathrm{[AsI_3]^+}$ and $\mathrm{[AsI_2]^+}$. The ^{1}H NMR spectrum in benzene-d$_6$ showed only the signals of coordinated thf ligands, confirming the absence of the β-diketiminato ligand **L** in the product. The molecular structure of the crystalline **1** was established by X-ray diffraction.

The structure of the anion of the crystalline lithium iodoarsenate **1** is illustrated in Fig. 1; selected bond distances are listed in Table 1 (Supplementary material, ESI, also includes geometric parameters for the cation, the thf groups of which were poorly defined). The mid-point of the As3–As3′ vector is the centroid of the $\mathrm{[As_8I_{26}]^{2-}}$ anion. Each of the eight arsenic atoms is in a pyramidal

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$$3\ \mathrm{Li}(\mathbf{L}) + 9\ \mathrm{AsI_3} \xrightarrow{\mathrm{thf}} [\mathrm{Li(thf)_4}]_2[\mathrm{As_8I_{26}}]$$

1, mp 100-102 °C, orange, 47%

$[\mathbf{L} = \{N(C_6H_3Pr^i{}_2\text{-}2,6)C(Me)\}_2CH]$

Scheme 1. Synthesis of the salt $[Li(thf)_4]_2[(AsI_2)_6(AsI)_2(\mu_2\text{-}I)_{10}(\mu_5\text{-}I)_2]$ (**1**).

bonding environment with the three As–I bonds ranging from 2.56 (As1–I3) to 2.66 Å (As3–I9) and the three I–As–I′ bond angles from 92.8 (I9–As3–I10) to 100.2° (I11–As4–I12); the I···As–I′ angles subtended at each arsenic atom also include one at As1 and three at each of As2, As3 and As4 in the range 160° (I1···As2–I5) to 171° (I6···As4–I13). Each of the As atoms also has longer As···I contacts: one for As1 and three for each of As2, As3 and As4, ranging from *ca.* 3.20 Å (As3···I1) to *ca.* 3.50 Å (As4···I10′). Of the 26 iodide ligands, the two central, five-coordinate I atoms (I1 and I1′) have only rather long contacts of 3.20–3.35 Å to arsenic atoms. Including non-bonding As···I distances, there are seven AsIAs′I′ rhomboids, the sum of the endocyclic bond angles being 358.1° (I1As1I2As2), 358.4° (I1As2I6As4), and 360° (I1As3I1′As3′).

As far as we are aware, there are just three precedents for crystalline iodoarsenate clusters: $[NHEt_3]_4[As_8I_{28}]$ (**C**) [5,6], $[\{(pyH)(AsI_4)\}_\infty]$ (**D**) [6] and $[AsPc]_2[As_4I_{14}]$ (**E**) [(AsPc) = (phthalocyaninato(2-)arsenic(III)] [7]. The centrosymmetric anion of **C** has each of its arsenic atoms in a quasi-octahedral coordination mode, involving a bonding pyramidal AsI_3 core with As–I bonds ranging from 2.61 to 2.73 Å and I–As–I′ angles from 92.7° to 98.9°, and three longer As···I contacts of 3.07–3.51 Å [5,6]. Each arsenic atom in the $[AsI_4{}^-]_\infty$ anion of **D** likewise has the arsenic atom in a similar six-coordinate environment, with the three pyramidal As–I bonds of 2.64, 2.68 and 2.87 Å and I–As–I′ angles of 89.4°, 94.3° and 96.2°, and three longer As···I contacts of 2.92, 3.16 and 3.26 Å [6]. The $[As_4I_{14}]^{2-}$ units of **E** are composed of two pairs of symmetrically equivalent AsI_3 and $AsI_4{}^-$ units; the five-coordinate arsenic atom in the former is the centre of a square pyramid having three short As–I bonds of 2.57 ± 0.015 Å and I–As–I′ angles of 99 ± 0.6°; while the six-coordinate quasi-octahedral arsenic atom of the latter has four short As–I bonds (2.76 ± 0.16 Å), four I–As–I′ angles (95.0 ± 4.7°) and one of 168.9°, and two long As···I contacts of 3.20 and 3.56 Å [7]. Another halogeno-octaarsenate anion is found in $[S_5N_5]_4[As_8Cl_{28}]\cdot 2S_4N_4$, which has an $[As_4Cl_{16}]^{4-}$ cubane-like core to which are attached four $AsCl_3$ moieties via $(Cl)_2$ bridges [8].

2.2. Synthesis and structure of the lithium salt 2

In the light of the unexpected formation of **1** from Li(**L**) and AsI_3, it was considered that a more rational synthesis would be from 2 LiI and 8 AsI_3 in tetrahydrofuran. However, by using this stoichiometry with thf as solvent at ambient temperature, the eventual surprising product, obtained in high yield (based on LiI), was the crystalline orange/red salt **2**, Scheme 2.

The salt **2** showed the appropriate signals of coordinated thf ligand in the ^1H and $^{13}C\{^1H\}$ NMR spectra in C_6D_6. The crystalline compound **2** was further characterised by the X-ray molecular structure, illustrated in Fig. 2; the As–I bond lengths of its anion are listed in Table 2.

The anion of **2** has as its core the As1-centred I1 to I6 octahedron, with the I1/I4, I2/I5 and I3/I6 pairs being mutually transoid, the As–I bonds ranging from 2.84 to 2.91 Å and the cisoid I–As–I’ angles from 88.4° to 91.6°. Each of the I1 to I6 ligands has long con-

Table 1
Bond lengths (Å) and angles (°) for the anion $[As_8I_{26}]^{2-}$ of **1**.

As(1)–I(3)	2.5624(13)	As(3)–I(8)	2.6057(11)
As(1)–I(4)	2.5946(15)	As(3)–I(0)	2.6302(12)
As(1)–I(2)	2.6098(13)	As(3)–I(9)	2.6619(11)
As(1)–I(1)	3.3310(12)	As(3)–I(1)	3.1956(11)
As(2)–I(7)	2.5813(12)	As(3)–I(1’)	3.3539(11)
As(2)–I(6)	2.6140(13)	As(4)–I(12)	2.5730(13)
As(2)–I(5)	2.6274(12)	As(4)–I(11)	2.5984(14)
As(2)–I(1)	3.2499(11)	As(4)–I(13)	2.6372(12)
As(2)–I(2)	3.3865(13)	As(4)–I(1)	3.2854(12)

Symmetry transformations to generate equivalent atoms: $-x + 1$, $-y + 1$, $-z + 1$.

$$3\ \mathrm{LiI} + 7\ \mathrm{AsI_3} \xrightarrow{\mathrm{thf}} [\mathrm{Li(thf)_4}]_2[\mathrm{Li(thf)_6}][\mathrm{As_7I_{24}}]\cdot 1.5(\mathrm{C_4H_8O})$$

2, mp 95-97 °C, orange/red, 93%

Scheme 2. Synthesis of the salt $[Li(thf)_4]_2[Li(thf)_6][\{(AsI_2)(\mu_2\text{-}I)(\mu_3\text{-}I)\}_6As]$ (**2**).

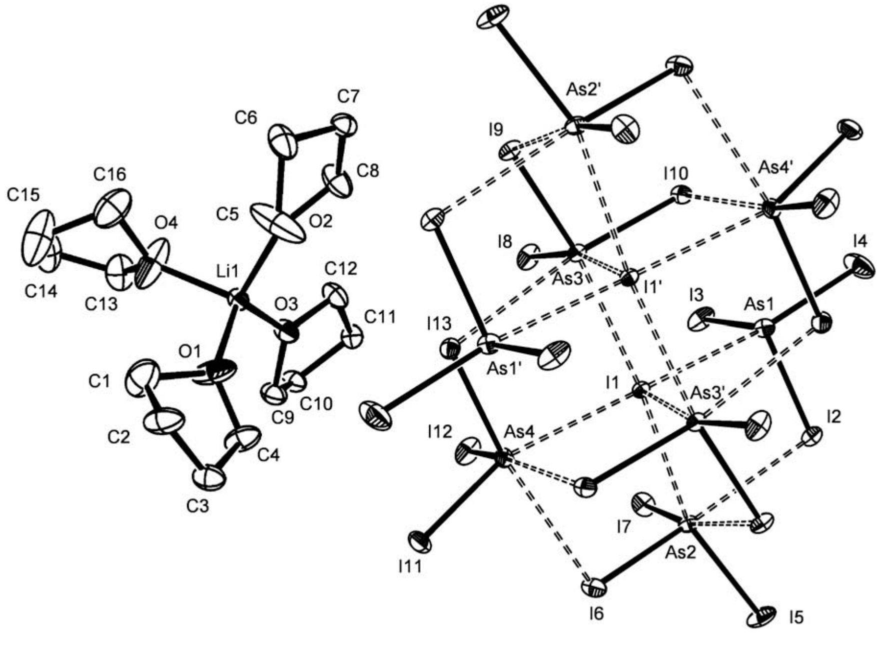

Fig. 1. The molecular structure of crystalline **1** with the atom labelling scheme (the second cation is omitted for clarity).

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