$[\text{PbAsSi}i\text{Pr}_3]_6$ − the First Structurally Characterized Compound with Chemical Bonds between Lead and Arsenic

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Received October 30th, 2003.

Abstract. The compound $[\text{PbAsSi}i\text{Pr}_3]_6$ (**1**) could be obtained by the reaction of PbCl_2 with $i\text{Pr}_3\text{SiAs}(\text{SiMe}_3)_2$ in THF at 0°C. Central structural motif is a hexagonal prism built by six lead and six arsenic atoms. The average Pb−As bond length is 281 pm. The cluster crystallizes in the monoclinic space group *C*2/*c*, the lattice constants are: $a = 4460.8(9)$ $b = 2296.6(5)$, $c = 2734.4(6)$ pm, $\beta = 117.57(3)°$. The thermogravimetric analysis in vacuum shows the tendecy of **1** to decompose under formation of elementary lead and volatile arsenic compounds.

Keywords: Lead; Arsenic; Cage compounds; Cluster compounds

Parallel to the intensively investigated field of molecular 13/15 compounds [1], several research groups have worked on the synthesis of cyclic and cage-like compounds built by the elements of group 14 and 15 [2]. In the past few years the interest in both fields has increasingly focused on the synthesis of compounds which consist of the heavier main group elements. Recently, the first molecules with aluminium-bismuth and gallium-bismuth bonds $[\text{Me}_2\text{MBi}(\text{SiMe}_3)_2]_3$ (M = Al, Ga) have been obtained from the reactions of $\text{Bi}(\text{SiMe}_3)_3$ with Me_2AlH and Me_2GaH [3]. The reaction of $\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$ with $\text{H}_2\text{AsSi}i\text{Pr}_3$ yields the first tin-arsenic cage compound $[\text{SnAsSi}i\text{Pr}_3]_6$ [4a]. Lead compounds with the heavier elements of group 15, however, have not been studied much so far. The crystal structures of such compounds are hardly known. Only the crystal structures of cyclic lead(II) phosphorus compounds as well as the carben homologous compound $\text{Pb}(\text{PRR}')_2$ (R, R′ = sterically demanding silyl groups) have been reported to date [5, 6]. Furthermore *Schumann* and coworkers described the lead(IV) arsenic compounds $\text{As}(\text{PbR}_3)_3$ (R = Me, Ph) and $\text{Ph}_2\text{AsPbPh}_3$ several years ago. However none of these Pb/As compounds have been structurally characterized by X-ray diffraction methods [7].

Besides the Zintl-anions Pb_9^{n-} (n = 2, 4) [8], the only other known cluster compounds of lead are those with bridging oxygen or halogenide ligands such as $[\text{Pb}_7\text{O}_2(\text{OSiMe}_3)_{10}]$ or $[\text{NBu}_4]_8[\text{Pb}_{18}\text{I}_{44}]$ [9]. Furthermore, the transition metal complexes $[\text{PPh}_4]_2[\text{Pb}\{\text{Cr}(\text{CO})_5\}_3]$ and $[\text{PPh}_4]_2[\text{Pb}_2\{\text{W}(\text{CO})_5\}_4]$, in which the lead atoms act as ligands are noteworthy [10].

We have succeeded in synthesizing the first lead(II)-arsenic compound by the reaction of the arsenic species $i\text{Pr}_3\text{SiAs}(\text{SiMe}_3)_2$ [11] with PbCl_2. These starting materials react in THF at 0°C to yield a deeply red solution. Black crystals form during a period of two days if the solution is kept at 0°C. These crystals are always associated with small amounts of elementary lead. The crystal structure analysis shows that the cage compound $[\text{PbAsSi}i\text{Pr}_3]_6$ (**1**) has been formed in this reaction [12]. **1** crystallizes in the monoclinic space group *C*2/*c* with two independent molecules. These two independent molecules differ only slightly. Therefore only one will be discussed in detail. The central structural motif of **1** is a distorted Pb_6As_6 hexagonal prism. This cage is built by two Pb_3As_3 rings in chair conformation. In these rings the Pb−As bonds come to 280.0 pm on average. Between the rings these bonds are approximately 282.0 pm long. These values are slightly longer than the sum of the covalent radii of lead and arsenic (276 pm). The arsenic atoms in **1** show a distorted tetrahedral surrounding by three lead atoms and one silyl group. The lead atoms possess no exocyclic ligands and consequently have only coordination number three. The molecular structure of **1** is mostly analogous to the tin compounds $[\text{SnESi}i\text{Pr}_3]_6$ (E = P, As) [4].

Table 1 Crystallographic data of **1**. STOE-IPDS2 (Mo-K$_\alpha$ radiation, $\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by full-matrix least-squares techniques against F^2 (Pb, As, Si, C refined anisotropically, H atoms were calculated at ideal positions, the C atoms of one $i\text{Pr}_3\text{Si}$ group were calculated with split positions (isotropically), at these C atoms no H atom positions were determined) [12].

Formula	$\text{C}_{54}\text{H}_{126}\text{As}_6\text{Si}_6\text{Pb}_6$
Space group	*C*2/*c*
Formula units	12
Temperature	200 K
Lattice constants	$a = 4460.8(9)$ pm
	$b = 2296.6(5)$ pm
	$c = 2734.4(6)$ pm
	$\beta = 117.57(3)°$
Volume	24832(9) Å^3
density	2.105 g/cm^3
2° range	4−45°
Reflections measured	29835
Independent reflections	13925 ($R_\text{int} = 0.0649$)
Ind. reflections with $F_0 > 4\sigma(F_0)$	9643
Parameter	948
$\mu(\text{Mo}_{\text{K}\alpha})$	14.656 mm^{-1}
*R*1	0.0388
*wR*2 (all data)	0.0962
Residual electron density	1.337 e/Å^3

Thermogravimetric analysis of compound **1** in vacuum shows a one step decomposition in the temperature range from 160 to 190°C with a poorly distinguishable shoulder at 177°C. The overall mass loss is 49.9 % (calculated for the formation of pure lead: 52.85 %). Considering the unavoidable contamination of **1** with elementary

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DOI: 10.1002/zaac.200300387

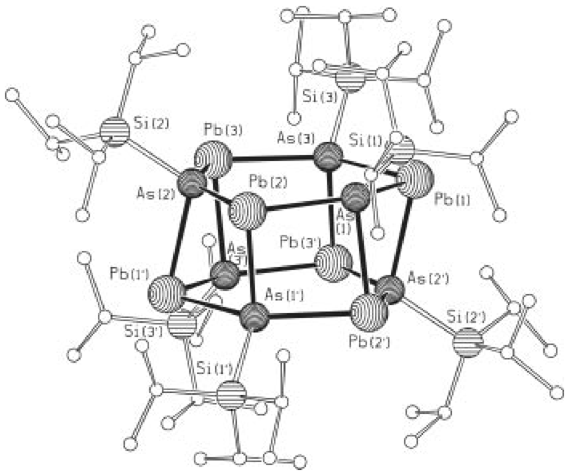

Figure 1 Molecular structure of **1**, selected bond lengths/pm and angles/°:

As(1)−Pb(1) 280.6(1), As(1)−Pb(2) 279.4(1), As(2)−Pb(2) 280.2(1), As(2)−Pb(3) 280.4(1), As(3)−Pb(1) 279.6(1), As(3)−Pb(3) 280.2(1), As(1)−Pb(2′) 283.7(2), As(2)−Pb(1′) 281.7(2), As(3)−Pb(3′) 283.2(2), As(1)−Si(1) 236.0(4), As(2)−Si(2) 236.5(3), As(3)−Si(3) 236.5(4); Pb−As−Pb (four-membered ring): 90.78(5)−92.69(4), Pb−As−Pb (six-membered ring): 139.28(4)−140.37(5), As−Pb−As (four-membered ring): 83.86(3)−85.76(5), As−Pb−As (six-membered ring): 99.34(4)−100.29(4).

lead, this corresponds to a complete loss of the silyl groups and the arsenic. This is further confirmed by powder X-ray diffraction measurements on the gray residue obtained, which display only the reflexes of elementary lead. The tendency of **1** to decompose under formation of volatile arsenic compounds can be observed also by EI mass spectrometry. No lead containing fragments can be observed. Instead signals of the decomposition products $(\mathrm{AsSi}i\mathrm{Pr}_3)_4$, $(\mathrm{AsSi}i\mathrm{Pr}_3)_3$ and As_4 appear in the mass spectra.

Experimental Section

All manipulations were performed under rigorous exclusion of oxygen and moisture using a Schlenk line and nitrogen atmosphere. Solvents were dried and freshly distilled before usage. $i\mathrm{Pr}_3\mathrm{SiAs(SiMe}_3)_2$ was prepared according to literature [11], PbCl_2 (98 %) was obtained from Aldrich and used as received.

1: A solution of 0.16 g $i\mathrm{Pr}_3\mathrm{SiAs(SiMe}_3)_2$ (0.42 mmol) in 10 ml THF is added to a suspension of 0.12 g (0.42 mmol) PbCl_2 in 15 ml of THF at 0°C. Subsequently the solution is warmed to room temperature while stirring and then agitated for additional 20 hours due to low solubility of PbCl_2 and heterogeneous character of the reaction. Thereby a red solution as well as a grey residue of lead and lead chloride (characterised by powder X-Ray diffraction) forms. After filtration and cooling of the solution to 0°C, black crystals of **1** and small amounts of elementary lead are obtained during a period of two days. Yield: 0.05 g (28 %). Elemental analysis calc. for $\mathrm{C}_{54}\mathrm{H}_{126}\mathrm{As}_6\mathrm{Si}_6\mathrm{Pb}_6$ (2636.84): C 24.60, H 4.82; found: C 22.03, H 4.27 %.

^{1}H-NMR(THF-D_8): δ = 1.144 (d, $3J_{\mathrm{HH}}$ = 7.3 Hz, $\mathrm{CH(C}H_3)_2$, 108H), 1.422 (hep, $3J_{\mathrm{HH}}$ = 7.3 Hz, $\mathrm{C}H\mathrm{(CH}_3)_2$, 18 H); **MS** (EI, 70 eV, 190°C) m/z (%): 928 (2) $[(\mathrm{AsSi}i\mathrm{Pr}_3)_4{}^+]$, 771 (2) $[\mathrm{As}_4(\mathrm{Si}i\mathrm{Pr}_3)_3{}^+]$, 696 (30) $[(\mathrm{AsSi}i\mathrm{Pr}_3)_3{}^+]$, 421 (100) $[\mathrm{As}_2\mathrm{Si}_2(i\mathrm{Pr}_5)^+]$, 379 (100) $[\mathrm{As}_2\mathrm{Si}_2\mathrm{H}(i\mathrm{Pr})_4{}^+]$, 337 (100) $[\mathrm{As}_2\mathrm{Si}_2\mathrm{H}_2(i\mathrm{Pr})_3{}^+]$, 300 (53) $[\mathrm{As}_4{}^+]$, 157 (100) $[i\mathrm{Pr}_3\mathrm{Si}^+]$.

This work was supported by the Strategiefonds of the Helmholtz Foundation. We thank *Dr. P. Kramkowski* for his valuable help with the manuscript.

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[12] CCDC-214659 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).