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A Metalloid Al_{14} Cluster with the Structure of a "Nano-Wheel"[**]

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Hansgeorg Schnöckel[*]

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

Solutions of metastable aluminum(I) halides[1] can be prepared by condensation of the high-temperature molecules AlX (X = Cl, Br, I) with suitable donor-containing solvents. The thermodynamically favored disproportionation of these compounds to aluminum metal and the trihalide can be controlled kinetically by the choice of halide, donor, and temperature. Thus, with NEt_3 as donor a planar Al_4 species (for example, $Al_4Br_4 \cdot 4NEt_3$[2]) is obtained, whereas with THF the polyhedral subhalide $Al_{12}(AlBr_2 \cdot THF)_{10} \cdot 2THF$ forms as a result of "internal" disproportionation.[3]

An additional variation of the disproportionation is acheived by replacement of the halide with suitable bulky substituents. Use of the $N(SiMe_3)_2$ group proved to be especially successful: Reaction of $LiN(SiMe_3)_2$ with a solution of AlI provided a $Al_{77}R_{20}^{2-}$ compound with the largest *metalloid* cluster yet characterized by diffraction methods. This compound can be viewed as an intermediate on the way

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to aluminum metal.[4] Recently, utilizing the more reactive AlCl solutions, two further *metalloid* clusters with the same substituents—$Al_7R_6^-$[5] and $Al_{12}R_8^-$[6]—could be isolated as intermediates in the formation of the Al_{77} unit.

In these clusters (Al_7, Al_{12}, Al_{77}) the number of direct metal–metal contacts exceeds the number of metal–ligand interactions. We classify such species as *metalloid* clusters,[5] to distinguish them from the variety of "metal clusters" included in Cotton's original definition.[7] In the search for further intermediates on the way to the metal, the title compound $[Al_{14}\{N(SiMe_3)_2\}_6I_6Li(OEt_2)_2]^-[Li(OEt_2)_4]^+ \cdot$ Tol (**1**; Tol = toluene), a mixed (I, $N(SiMe_3)_2$) metalloid cluster, could be isolated and structurally characterized for the first time.

Compound **1** was synthesized by slight variation of the reaction conditions under which the Al_{77} cluster was formed. After addition of solid $LiN(SiMe_3)_2$ to a pretreated $AlI \cdot Et_2O$ solution, the mixture was warmed to 55 °C several times and slowly cooled. After a few weeks **1** crystallized at +7 °C as dark red-brown platelets. The novel formation of the mixed substituted compound **1** appears to be plausible, as only the less reactive AlI reacts in the way described here. Treatment of the more reactive AlCl with the same starting material $LiN(SiMe_3)_2$ leads to $Al_7R_6^-$ and $Al_{12}R_8^-$ clusters with complete substitution of the halide. It is possible that a $Al_7R_3X_3^-$ species is a common precursor that is rapidly substituted in the case of X = Cl. For X = I the substitution is so slow that dimerization to form **1** is kinetically preferred.

Figure 1 presents the results of the X-ray structure analysis[8] of **1**. The $[Li(OEt_2)_4]^+$ ion, which fills the voids resulting from packing of Al_{14}^{2-} cluster units, is not shown.[9]

The main structural unit is represented by two staggered, approximately Al-centered Al_6 rings. The central Al atoms deviate somewhat from the planes of the rings and are separated by 2.728 Å. The other Al–Al distances range from 2.570 Å (between Al atoms with iodine ligands) to 2.910 Å (between Al atoms with $N(SiMe_3)_2$ ligands); that is, the values are in the range expected from other polyhedral or metalloid Al clusters.[10]

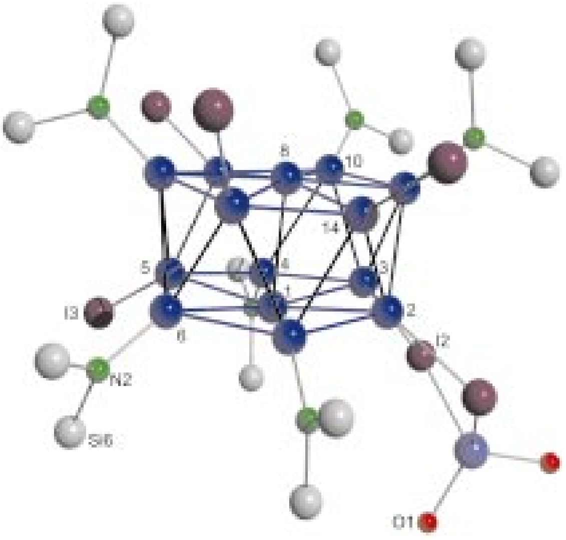
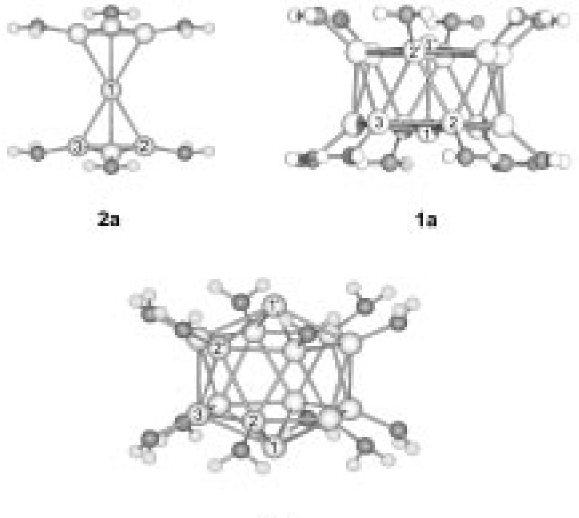


Figure 1. Molecular structure of **1**; for reasons of clarity the C and H atoms have been omitted. Blue: Al atoms. Selected distances [Å]: Al1–Al5 2.623(2), Al1–Al4 2.758(2), Al2–Al3 2.597(2), Al4–Al5 2.763(2), Al1–Al8 2.728(2), Al4–Al10 2.910(3), Al2–Al14 2.570(2), Al6–N2 1.855(5), Al5–I3 2.550(2), Al3–I2 2.636(2).

In the case of the $Al_7R_6^-$ cluster **2** as well as **1** the average oxidation state for the Al atoms is 0.71, which is in contrast to 0.23 for the Al_{77} cluster. The disproportionation of the initially monovalent Al species to aluminum metal is therefore equally far advanced for **2** and **1**. To be able to discuss the bonding situation in the two species with aluminum in the same average oxidation state, we carried out density functional theory (DFT) calculations[11] on the model compounds $Al_7R_6^-$ (**2a**; R = NH_2) and $Al_{14}R_{12}^{2-}$ (**1a**; R = NH_2). These calculations indicated that the dimerization **2a** → **1a** is exothermic (−275 kJ mol^{-1}). The geometrical parameters of **2a** and **1a**, which are shown in Figure 2, correspond at a first glance to the experimentally determined values for **2** and **1**. Additionally, calculations were carried out on the isomer **1b**, which is also shown in Figure 2. In this case the central Al–Al distance is highly elongated and an approximately polyhedral structure results, as found for M_{14} Frank–Kasper polyhedra, for example $Mg_{23}(Al,Zn)_{49}$.[12] However, the central atom is missing in **1b**.



2a **1a**

1b

Figure 2. The model compounds $Al_7(NH_2)_6^-$ (**2a**), $Al_{14}(NH_2)_{12}^{2-}$ (**1a**), and polyhedral $Al_{14}(NH_2)_{12}^{2-}$ (**1b**). The following characteristic Al–Al distances [Å] were obtained by DFT calculations:[10] **2a**: Al1–Al2 2.760, Al2–Al3 2.543; **1a**: Al1–Al2 2.721, Al2–Al3 2.713, Al2–Al2′ 2.690, Al1–Al1′ 2.693; **1b**: Al1–Al2 2.908, Al2–Al3 2.638, Al2–Al2′ 2.808, Al1–Al1′ 4.903.

Although the polyhedral structure of **1b** leads one to expect a bonding situation as described by Wade for a *precloso* or *nido* structure,[13] the calculations showed that **1b** is clearly destabilized with respect to **1a** (+123 kJ mol^{-1}); that is, a metalloid cluster is energetically favored over a polyhedral cluster.[14] As already discussed for other metalloid clusters (Al_7,[5] Al_{12},[6] Al_{77},[4] Ga_{22}[15]), the experimental and theoretical findings presented here confirm that Wade's rules are not appropriate for describing bonding situations of this type.

To obtain a deeper understanding of the exceptional bonding situation in **2** and **1**, we calculated the ^{27}Al NMR shifts for the central (**2a**, **1a**) and apical Al atoms (**1b**).[16] The results for **2a** ($\delta = 652$), **1a** ($\delta = 358$), and **1b** ($\delta = -313$) show—as already discussed for **2**[5]—that for **2a** and **1a**, but not for polyhedral **1b**, the central Al atoms approach the bonding situation in aluminum metal ($\delta = 1640$).[17]

The geometry of the partially preformed metal structure present in metalloid clusters is rationalized for **1** in Figure 3. Closest packing as in the metal structure results from rotation by 30° and subsequent translation.

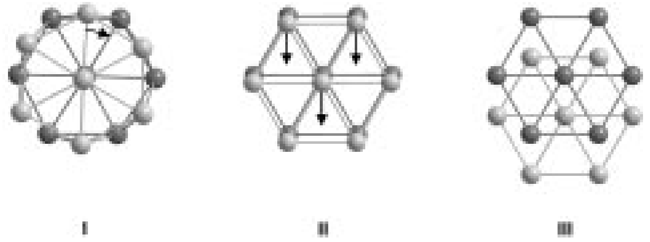


Figure 3. Rotation of the upper ring by 30° about the z axis—which incorporates the two central Al atoms of the two six-membered rings in the Al_{14} cluster (**I**)—leads to AA stacking, as found in hexagonal-primitive packing (**II**). If the upper ring is shifted in the layer of the page by ($\frac{1}{4}$,$\frac{1}{4}$, 0)—based on the basis vectors of the aluminum metal lattice—one obtains AB stacking (**III**), which represents one section of the closest packing of aluminum metal.

The results presented here have again demonstrated the large synthetic potential of AlX/AlR solutions for the experimentally challenging preparation of metalloid clusters in a well defined form. These clusters should probably play a key role in understanding the mechanism of metal formation.

Experimental Section

Gaseous AlI (40 mmol) was condensed at −196 °C with toluene (64 mL) and diethyl ether (16 mL) according to the method described in ref. [1]. An aliquot (6 mL) of the ca. 0.30 M dark red-brown $AlI \cdot Et_2O$ solution was concentrated at −78 °C under vacuum and dried. The residue was dissolved in toluene (12 mL), and the solution obtained was again concentrated to 6 mL and added to donor-free $LiN(SiMe_3)_2$ (150 mg). The reaction mixture was allowed to warm to −25 °C within 2 d. After a further 2 d at 7 °C, the amide had dissolved and LiI precipitated, which was subsequently redissolved in Et_2O (1 mL). The solution was warmed for 1.5 h at 55 °C and then kept at room temperature for 1 d. This temperature cycle was repeated several times, and then the warm solution was allowed to cool slowly within 3 d to room temperature. During this process disproportionation of Al^I species led to the formation of aluminum metal. The filtered solution was again warmed to 55 °C and allowed to cool slowly. After 3 d at 7 °C, 1 h at −80 °C, and several weeks at 7 °C, **1** crystallized as dark red-brown platelets that are chemically and mechanically very labile (yield: ca. 2%).

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[8] Crystal structure analysis of $[Al_{14}\{N(SiMe_3)_2\}_6I_6Li(OEt_2)_2]^-$-$[Li(OEt_2)_4]^+ \cdot$Tol (**1**): STOE-IPDS “Image Plate” diffractometer, 55 kV, 50 mA, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$), measurement temperature 200(2) K. Crystal dimensions $0.8 \times 0.1 \times 0.1$ mm, monoclinic I, space group $P2_1/n$, $a = 14.5638(5)$, $b = 37.546(5)$, $c = 23.266(4)$ Å, $\beta = 94.775(7)^\circ$, $V = 12678(1)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.390$ Mg m^{-3}, $\mu_{Mo} = 1.720$ mm^{-1}, $\theta_{min} = 1.93^\circ$, $\theta_{max} = 25.99^\circ$; of 78033 reflections measured, 24071 were independent, $16967 > 2\sigma(I)$, $5127 > 3\sigma(I)$; 788 parameters, empirical absorption correction, $R_1 = 0.0623$, $wR_2 = 0.1595$; max./min. residul electron density 1.805/−0.968 e Å^{-3}. The structure was solved by direct methods and refined against F^2 for all observed reflections. Software programs used: Shelxs-86, Shelxl-93 (G. M. Sheldrick, Universität Göttingen). 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-136893. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). The asymmetric unit contains an $[Al_{14}\{N(SiMe_3)_2\}_6I_6]^{2-}$ ion which is coordinated to a $[Li(OEt_2)_2]^+$ ion through two of the I ligands. Several of the methyl groups are disordered over two positions. Furthermore, a Li^+ ion coordinated to four Et_2O molecules was found along with a toluene molecule whose atoms could be refined with common isotropic temperature factors. All hydrogen atoms were placed in calculated positions and refined according to a riding model.

[9] As a supplement to the structure analysis, the presence of an even number of electrons could be confirmed by the lack of an ESR signal. The ESR measurement on crystalline **1** was carried out by Dr. B. Pilawa, Physikalisches Institut, Universität Karlsruhe.

[10] For purposes of comparison the Al–Al distances [Å] of selected substances are listed: $[Al_7\{N(SiMe_3)_2\}_6]^-$ 2.540 (in the $Al_3\{N(SiMe_3)_2\}_3$ ring; cf. Figure 2) and 2.737 (Al–Al contacts to the central Al atom);[5] $[Al_{12}\{N(SiMe_3)_2\}_8]^{2-}$ 2.542–2.759;[6] $Al_{12}(AlBr_2 \cdot THF)_{10} \cdot 2THF$ 2.526–2.762;[3] Al_{metal} 2.860.

[11] All quantum-chemical calculations were carried out with the RIDFT module (B-P86 functional) of the program TURBOMOLE with SV(P) basis sets. a) TURBOMOLE: O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346; b) B-P86 functional: A. D. Becke, *Phys. Rev. A* **1998**, *38*, 3098; J. P. Perdew, *Phys. Rev. B* **1996**, *33*, 8822; c) RIDFT: K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652; K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119.

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[13] An analysis of the MOs of **1b** (however, for the simplified $Al_{14}H_{12}^{2-}$ species) indicated that the 3s electrons of the apical Al atoms are not involved to an appreciable extent in the bonding of the Al_{14} framework; that is, with 28 framework electrons ($12 \times 2 + 2 \times 1 + 2$) a *precloso* structure would be expected.

[14] The MO analysis for **1a** showed that this stabilization with respect to **1b** results from bonding interactions of the 3s electrons of the central and apical Al atoms with the Al_{14} framework.

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