# $[Al_7\{N(SiMe_3)_2\}_6]^-$: A First Step towards Aluminum Metal Formation by Disproportionation[**]

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*Dedicated to Professor Arndt Simon
on the occasion of his 60th birthday*

The formation of an $Al_{77}$ cluster, the largest metal atom cluster yet characterized by X-ray structure analysis, shows that metastable aluminum monohalide solutions can be the key to the synthesis of such clusters.[1] Thus they open the way to a current area of research at the borders to nanochemistry. It is not known at this point to what extent the formation mechanism of the $[Al_{77}\{N(SiMe_3)_2\}_{20}]$ dianion is a model for the formation of the solid metal. One of our aims has therefore been to capture at low temperatures primary products of the disproportionation of $AlNR_2$ to $Al(NR_2)_3$ ($R = N(SiMe_3)_2$), products in which small sections of metal structure occur. The $Al_{77}$ compound was the only main group cluster known up to now that showed such a structure centered around a metal atom.[2] Herein we present a further metal atom centered cluster, which as far as we are aware represents the first example of an especially small but characteristically close-packed section of metal atoms.

Co-condensation of the high-temperature molecule AlCl with a xylene/diethyl ether mixture at −196 °C and subsequent warming to −78 °C yields a metastable AlCl solution. Reaction occurs on addition of this solution to solid $LiN(SiMe_3)_2$ at −78 °C; subsequent slow warming to room temperature gives solid lithium chloride within one day, which is separated from the dark colored solution. After a few weeks at −30 °C, black crystals of the composition $[Al_7\{N(SiMe_3)_2\}_6]^-$ $[Li(OEt_2)_3]^+$ (**1**) precipitate from this solution; the X-ray crystal structure of **1** is shown in Figure 1.[3]

The central Al atom in **1** is surrounded by a distorted octahedron of six further Al atoms, each of which is saturated with one $NR_2$ ligand. The distance from the six-coordinate central atom to its neighbors is 273 pm, a distance which is intermediate between that of typical Al–Al bonds (266 pm)[4] and that of Al metal (286 pm). This therefore represents relatively weak Al–Al bonding, as in the $[Al_4Cp^*_4]$ molecule[5] (277 pm; $Cp^* = C_5Me_5$). On the other hand, the Al–Al bonds of the two $Al_3R_3$ groups are surprisingly short (254 pm), indicating that these are as strong as the "bond order 1½" Al–Al bonds of radical anions of the type $R_4Al_2^-$ (253 pm).[6]

The Al–N and N–Si distances correspond to expectations, as do the observed angles. The cation, needed for overall charge neutrality, is so far from the $Al_7R_6^-$ ion that interactions having any effect on structure can be ruled out.

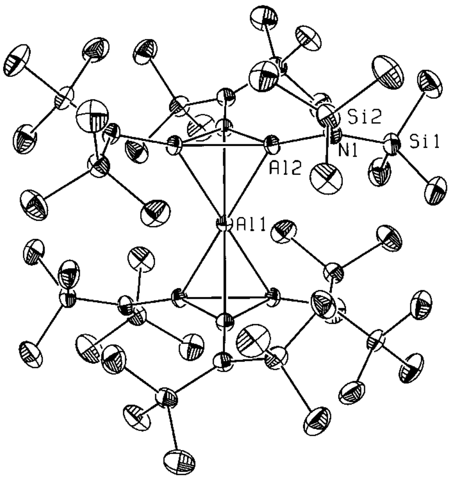

Figure 1. Structure of $[Al_7\{N(SiMe_3)_2\}_6]^-$ in the crystal (ORTEP; thermal vibrational ellipsoids 50%, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Al1–Al2 2.7370(4), Al2–Al2′ 2.5395(7), Al2–N1 1.8439(12), N1–Si1 1.7306(12); Al2-Al1-Al2 124.717(14), Al1-Al2-N1 138.00(4), Si1-N1-Si2 122.50(7)

The arrangment of the seven Al atoms is unusual; we are not aware of any other instance of two metal atom tetrahedra that are vertex-connected through a mutual "naked" metal atom. Such an arrangement of atoms can be viewed as a primary configuration on the way to close packing, since adding only six further Al atoms, arranged around the central atom in the plane between the three-membered rings, would give a cuboctahedral coordination sphere (Figure 2).[7]

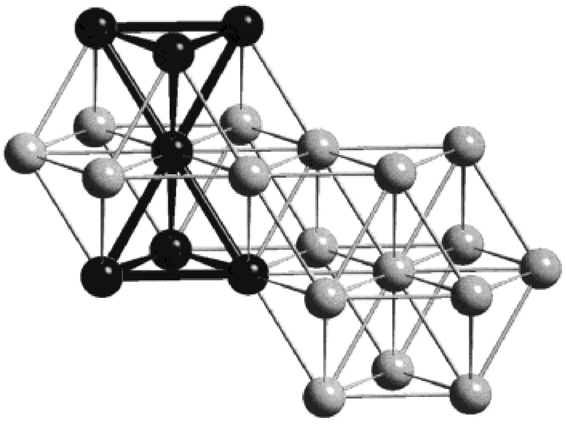

Figure 2. Section of the solid-state structure of aluminum (ccp). The $Al_7$ fragment is shaded darkly.

For the interpretation of bonding, it seemed reasonable to account for the conspicuously short Al–C bonds in the $Al_3R_3$ groups by aromatic stabilization, as formulated for $Ga_3R_3^{2-}$ species. The same fractional bond shortening with respect to normal two-electron, two-center (2e2c) Ga–Ga bonds is observed in the latter as in **1**.[8] This interpretation means that the $Al_3R_3$ groups have to be assigned a double negative charge, so that the central atom must be considered as $Al^{3+}$, that is a comparable relationship to that in the aluminocenium cation $[Cp^*_2Al]^+$.[9] Based on the measured and calculated high-field shifts of the $^{27}Al$ NMR signal of $[AlCp^*_2]^+$, a

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description of this cation as a ferrocene-like sandwich compound was justified. This interpretation could not be made to fit compound **1**, since the calculated $^{27}$Al NMR signal—a measurement of the resonance was not yet possible—is not high-field shifted, but rather shifted extremely to low field.[10] The value of $\delta = +801.6$ lies in a region reached by no other molecular Al compound until now. Since such frequencies are already halfway to the shift of aluminum metal ($\delta = +1640$[11]), it is plausible to consider the central Al atom, with its special coordination sphere, to be of similar character to atoms in solid aluminum. A comparison with small anionic Al clusters (e.g. an $Al_{13}^-$ species[12a]), in which high-field shifts are calculated to be $\delta = -195.2$, is not fruitful. Such clusters present no contradiction to the above hypothesis, since the potential at the central Al atom is obviously completely different to that of the central atom in the $Al_7R_6^-$ group, in which the negative charge is localized primarily on the ligands and a slight positive charge on the six outer Al atoms. Evidently, in **1** the environment of the central Al atom comes closer electronically to that of the metal than in small naked $Al_n$ clusters.[13] It is therefore conceivable that such compounds with well-defined environments about naked Al atoms could provide models for the physical characterization of single metal atoms with the methods of nanotechnology (Figure 3). All sensational measurements of this type to date were carried out on samples in which the contact between single Al atoms and the atoms of the bulk was not precisely defined.[14]

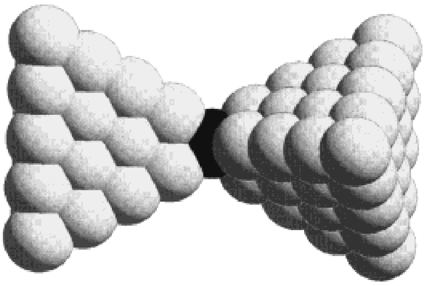

Figure 3. Model geometry for an atomic aluminum contact.[14]

The isolation and characterization of an $Al_7R_6^-$ cluster as the primary step towards formation of the metal provides encouragement to look for further examples of such metalloid clusters[15] using this reaction path, and thereby achieve better understanding of this type of complex but elementary reaction. Our chosen synthetic method – the mild disproportionation of $Al^I$ compounds – shows promise in pushing back the boundaries of an area of chemistry where only a few structures have been securely characterized such as $[Ga_9\{Si(SiMe_3)_3\}_6]^-$[16] or $[Au_{39}(PPh_3)_{14}Cl_6]^{2+}$.[17]

### *Experimental Section*

All work was carried out either in a nitrogen atmosphere on a Schlenk line or in a glove-box (MBRAUN 150) under argon with dried degassed solvents.

**1**: Cold AlCl solution (−78 °C; 8.0 mL, 0.15 M, *m*-xylene/$Et_2O$, 1.2 mmol) was added to solid $LiN(SiMe_3)_2$ (200 mg, 1.2 mmol) at −78 °C. The reaction mixture was allowed to warm slowly to 20 °C (several hours). After 24 h at +20 °C the LiCl precipitate was separated and the dark solution was stored at −30 °C. After several weeks at −30 °C black crystals of **1** formed in an oily precipitate. Compound **1** is insoluble in pentane and benzene and decomposed in THF. Yield in crystalline form: ca. 10 mg (4 %), X-ray structure analysis: see Figure 1.

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[1] A. Ecker, E. Weckert, H. Schnöckel, *Nature* **1997**, *387*, 379.

[2] The $In_{12}$ compound of a recent publication likewise represents a section of close-packed In atoms: N. Wiberg, T. Blank, H. Nöth, W. Ponikwar, *Angew. Chem.* **1999**, *111*, 887; *Angew. Chem. Int. Ed.* **1999**, *38*, 839.

[3] Crystal structure analysis of **1**: STOE IPDS diffractometer, $Mo_{K\alpha}$ radiation, measurement temperature 200(2) K, crystal mounted in perfluoropolyether, crystal dimensions: $0.5 \times 0.4 \times 0.2$ mm$^3$, hexagonal, space group $R\bar{3}$, $a = b = 20.6709(15)$, $c = 17.9876(14)$ Å, $V = 6656.1(9)$ Å$^3$, $Z = 3$, $\rho = 1.033$ g cm$^{-3}$, $\mu(Mo_{K\alpha}) = 0.28$ mm$^{-1}$, $5.06 \leq 2\theta \leq 51.78$ in $-25 \leq h \leq 25$, $-25 \leq k \leq 25$, $-22 \leq l \leq 22$, measured reflections 21826, 2870 independent, $2484 > 2\sigma(I)$, 138 parameters, numerical absorption correction ($T_{max} = 0.8396$, $T_{min} = 0.9122$), $R1 = 0.0351$, $wR2 = 0.0939$ (all data), GOOF = 1.171, 0 "restraints", residual electron density: max./min. 0.425/−0.256 e Å$^{-3}$. The structure was solved with direct methods and refined against $F^2$ for all observed reflections. Software used: SHELXS 94, 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-120842. 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).

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[5] a) C. Dohmeier, C. Robl, M. Tacke, H. Schnöckel, *Angew. Chem.* **1991**, *103*, 594; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 564; b) Q. Yu, A. Purath, A. Donchev, H. Schnöckel, *J. Organomet. Chem.* **1999**, *584*, 94.

[6] C. Pluta, K. R. Pörschke, C. Krüger, K. Hildenbrand, *Angew. Chem.* **1993**, *105*, 451; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 388.

[7] This substance, a metastable intermediate on the path towards larger aggregates (e.g. $Al_{77}$ cluster) or even aluminum metal, could not yet be isolated, because the synthesis of, for example, $Al_{77}$ involves work at room temperature and briefly at higher temperatures.

[8] Whereas Ga−Ga distances of 251.5 pm are found in neutral digallanes $[\{(i\text{Pr}_3C_6H_2)Ga\}_2]$,[8a] this distance is shortened to 244 pm in the trimeric compound $K_2[Mes_2C_6H_3Ga]_3$ (Mes = 2,4,6-$Me_3C_6H_2$).[8b] a) X. He, R. A. Bartlett, M. O. Olmstead, K. Ruhlandt-Senge, B. E. Sturgeon, P. P. Power, *Angew. Chem.* **1993**, *105*, 761; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 717; b) X. W. Li, W. T. Pennington, G. H. Robinson, *J. Am. Chem. Soc.* **1995**, *117*, 7578.

[9] C. Dohmeier, H. Schnöckel, C. Robl, U. Schneider, R. Ahlrichs, *Angew. Chem.* **1993**, *105*, 1714; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1655.

[10] The following programs were used for the quantum chemical calculations of the model compound $[Al_7(NH_2)_6]^-$: a) Turbomole: O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346; b) Funktional BP86: A. D. Becke, *Phys. Rev. A* **1998**, *38*, 3098; J. P. Perdew, *Phys. Rev. B* **1996**, *33*, 8822; c) RIDFT: K. Eichhorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652; K. Eichhorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119. The $^{27}$Al NMR shifts were calculated using SCF orbitals at a molecular geometry optimized with the denstity functional theory (DFT) method.

[11] Measurements of nanometer Al particles (ca. 3 nm) also produced $^{27}$Al NMR shifts in this region ($\delta = 1650$): S. Faber, Dissertation, Saarbrücken, **1996**.

[12] a) The central Al atom is surrounded by an icosahedron of 12 further Al atoms: R. Ahlrichs, S. D. Elliott, *Phys. Chem. Chem. Phys.* **1999**, *1*, 12; b) calculated Mulliken charges for $Al_{13}^-$ were $Al_{central} = -1.86$; $Al_{icos} = +0.07$.

[13] For $[Al_7(NH_2)_6]^-$ the Mulliken charge at the central Al atom is $-0.18$, at the other Al atoms $+0.11$. By contrast, all N atoms are strongly negative ($-0.66$) and every H atom positively ($+0.20$) polarized. The calculation was carried out in $S_6$ symmetry with the orientation of $NH_2$ groups corresponding to that in **1**. The calculated Al–Al lengths are $d(Al2{-}Al2') = 254.5$ pm and $d(Al1{-}Al2) = 275.0$ pm. The HOMO-$(13a_u)$ – LUMO$(25e_u)$ gap is 1.64 eV.

[14] E. Scheer, N. Agrait, J. C. Cuevas, L. A. Yeyati, B. Ludoph, A. Martin-Rodero, G. R. Bollinger, J. M. van Ruitenbeek, C. Urbina, *Nature* **1998**, *394*, 154

[15] The definition chosen by Cotton for a metal cluster[18] is so general that it includes many compounds which bear little resemblance to species such as $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$ or the subject of this paper, $[Al_7\{N(SiMe_3)_2\}_6]^-$. By designating these metal-rich molecular species as metalloid clusters, we would like to distinguish them from such compounds. Metalloid (metal-like) clusters should be epitomized by the property that the number of metal–metal contacts exceeds the number of metal–ligand contacts and by the presence of metal atoms which participate exclusively in metal–metal interactions.

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[18] F. A. Cotton, *Q. Rev. Chem. Soc.* **1966**, 389.

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# Hyperbranched Polyether Polyols with Liquid Crystalline Properties

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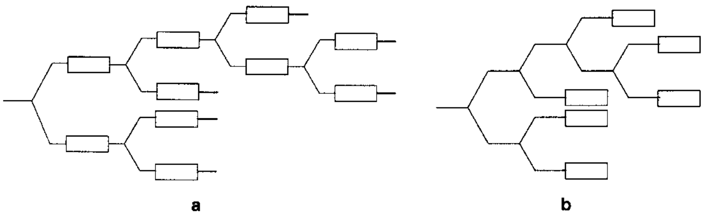
In general, highly branched molecules do not crystallize, but in combination with mesogenic units they can exhibit liquid crystalline (LC) phases.[1] In this context, particularly cascade-branched molecules have been investigated, that is flexible dendrimers[2] and their structurally less perfect analogues, the hyperbranched polymers.[3] In principle, two different strategies have been employed for the incorporation of mesogenic structural elements into cascade-branched architectures (Scheme 1). Either the mesogen can be part of each branching monomer (**a**) or it can be coupled to the end groups of the scaffold (**b**). Structures of type **a** have been prepared by Percec et al. and Ringsdorf et al. for liquid crystal dendrimers as well as hyperbranched polymers.[4] Structures of type **b** with mesogenic end groups attached to flexible dendrimer scaffolds have been the subject of numerous recent publications both of our group as well as others. In almost all cases the formation of smectic phases was observed.[5] To date, no hyperbranched thermotropic liquid crystal polymers with mesogenic end groups are known, since a fundamental problem is the choice of a suitable flexible and well-defined hyperbranched scaffold.



Scheme 1. Structural types of branched LC architectures; rods symbolize rigid structural elements (mesogens); connecting lines indicate flexible parts of the scaffold, for example alkyl chains. **a**: Mesogens are part of every monomer unit of the scaffold, **b**: Structurally isotropic hyperbranched scaffold with mesogenic end groups.

Recently, we have developed a synthetic strategy based on the ring-opening multibranching polymerization (ROMBP) of glycidol (2,3-epoxy-1-propanol), leading to hyperbranched polyglycerols with narrow polydispersity ($M_w/M_n < 1.5$, mostly $< 1.3$).[6] By using this approach it was possible to achieve molecular weights of up to 8000 g mol$^{-1}$, that is 100 hydroxy end groups per molecule. Herein we use these highly flexible aliphatic polyether polyols ($T_g \approx -25\,°C$) to attach mesogenic end groups in order to prepare hyperbranched LC polymers of structural type **b**.[7] We study the effect of molecular weight of the scaffold and the influence of spacer length between mesogen and scaffold on the LC properties.

For the attachment of the mesogenic acids **1** and **2** to the OH end groups of two polyglycerol samples (**PG1**: $M_n = 1500$ g mol$^{-1}$ and **PG2**: $M_n = 3500$ g mol$^{-1}$)[8] we employed a modified esterification with diisopropylcarbodiimide (Scheme 2).[9] In order to obtain a high degree of functionalization of the polyglycerols with mesogens despite the strong difference in polarity between substrate and product, it was necessary to change the solvent in the course of the reaction. However, even after reaction times of several days it was not possible to achieve higher degrees of functionalization than 88 % of all hydroxy groups of the lower molecular weight sample **PG1** ($^1$H NMR, Table 1). For the higher molecular weight sample **PG2** the degree of functionalization ranged between 73 and 79 %. The incomplete reaction of the end groups is most probably explained by the bulkiness of the mesogenic units and the difference in reactivity of the primary and secondary hydroxy groups of polyglycerol.

Gel permeation chromatography (GPC) measurements showed narrow, monomodal molecular weight distributions for all three samples ($M_w/M_n < 1.2$) in agreement with the polydispersities observed for the polyglycerols used (Table 1). The apparent molecular weights determined from GPC (PS standards) correspond to the values calculated from NMR spectra in their order of magnitude.

The LC properties of the three samples prepared were investigated by differential scanning calorimetry (DSC), polarizing microscopy, and wide-angle X-ray scattering (WAXS). In general, all polyglycerols functionalized with mesogenic end groups showed similar phase behavior. In comparison with the unmodified polyglycerol samples, a

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