Metalloid Clusters

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$[Al(Al_3R_3)_2]$: Prototype of a Metalloid Al Cluster or a Sandwich-Stabilized Al Atom?**

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Dedicated to Professor Heiko Lueken on the occasion of his 65th birthday

Some years ago we established the developing area of metalloid Al clusters with the cluster ion $[Al_7R_6]^-$ (**1**, R = $N(SiMe_3)_2$).[1–4] The topology of the seven Al atoms in the form of two vertex-sharing tetrahedral $\{Al_4\}$ moieties is unique for metal atom clusters and has raised the still unanswered question: Can the central "naked" Al atom with its six directly bound neighbors be regarded as a section of the face-centered cubic (fcc) structure of solid aluminum, that is, the basic form of metalloid clusters, or is it better understood as an Al^{3+} ion stabilized by two aromatic $\{Al_3R_3\}^{2-}$ moieties in a sandwich-type arrangement as in the aluminocenium cation $[AlCp^*{}_2]^+$, prepared by us for the first time ($Cp^* = C_5Me_5$)?[5] In the meantime, we could demonstrate for further substituted $[Al_7R_6]^-$ clusters (R = $N(SiMe_2R')$, R′ = hexyl, Bu, *i*Pr)[6] that these $\{Al_7\}$ clusters are evidently energetically favored in their monoanion form. In an attempt to answer the question concerning the bond situation, we varied the synthesis with the aim of isolating neutral $[Al_7R_6]$ species and obtained the cluster radical $[Al_7R_6]$ (**2**, R = $N(SiMe_2Ph)_2$). The experimentally determined changes in structure between **1** and **2** and additional DFT calculations allow a first approach towards understanding the complicated bonding situation for clusters with such a prototypical $\{Al_7\}$ framework.

When a metastable solution of AlCl in toluene/diethyl ether (1:3), obtained by the simultaneous condensation of the high-temperature species AlCl with the solvent mixture,[3,7] is added to an equimolar amount of solid $Li(NSiMe_2Ph)_2$ at −78 °C,[6] a dark brown pentane extract is obtained after repeated filtration and warming of the solution to 60 °C. From this fraction crystals of $[Al_7\{N(SiMe_2Ph)_2\}_6]$ (**2**), which appear dark crimson in transmitted light, grew over several days. The molecular structure of **2** as determined by X-ray structure analysis is depicted in Figure 1.[8]

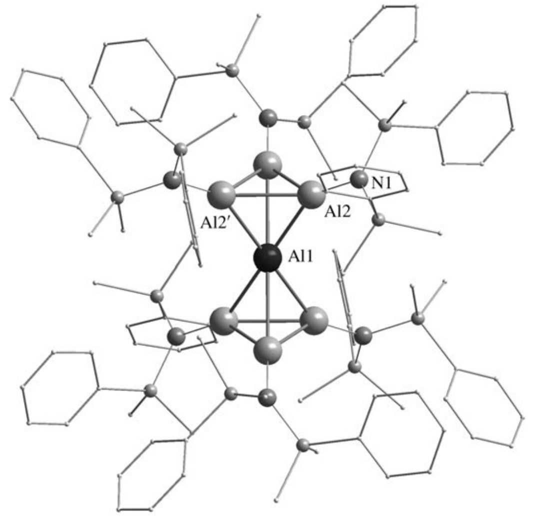

Figure 1. Molecular crystal structure of **2**. Because the topology of the framework of **2** and **1** is the same, relevant bond lengths are listed for **2** as well as for **1** (in brackets). The Al1–Al2 bond length (the distance between the central and each of the six symmetry-equivalent Al atoms) is 2.73 (2.73) Å. The Al–Al bond lengths in the $\{Al_3\}$ rings (Al2–Al2′) is 2.61 (2.53) Å. All Al–N bond lengths are 1.81 (1.84) Å. The environment of each N atom is planar (sum of angles = 360°). The N–Si bond lengths are 1.75 (1.73) Å.

Analogous to **1**, **2** has a D_{3d} structure of the $\{Al_7\}$ framework with one "naked" central atom (i.e., only coordinated by the other six Al atoms), although a significant elongation of the Al–Al bonds in the $\{Al_3\}$ rings relative to **1** is observed (2.61 compared with 2.53 Å), whereas the Al–Al bond lengths to the central Al atom are nearly identical in **1** and **2** (Table 1).

Figure 2 shows the large distances between the clusters in the crystal: The 8 + 6 coordination of each cluster molecule leads to the distances between the centers of the clusters listed

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Table 1: Selected structural parameters for the crystalline cluster species **1** and **2** and calculated structural data for the model compounds **1a** and **2a**, as well as for **3**, $\mathbf{3}^+$, and $\mathbf{3}^-$.[a]

	d(Al1–Al2)	d(Al2–Al2′)	d(AlN)	ΔE (rel.)	HOMO–LUMO
1, exptl	2.73	2.53	1.84		
1, calcd	2.777	2.550	1.878		1.68
2, exptl	2.73	2.61	1.81		
1a, $[Al_7(NH_2)_6]^-$	2.758	2.545	1.837	0	1.64
2a, $[Al_7(NH_2)_6]$	2.714	2.607	1.809	+170	0.42
$\mathbf{3}^-$, $[Al_7H_6]^-$	2.694	2.547	1.636	0	1.65
3, $[Al_7H_6]$	2.638	2.630	1.616	+300	0.50
$\mathbf{3}^+$, $[Al_7H_6]^+$	2.597	2.767	1.604	+660	0.64

[a] The numbering of the atoms corresponds to that in Figure 1. Distances in Å; relative energies in $kJ\,mol^{-1}$; HOMO–LUMO gaps in eV.

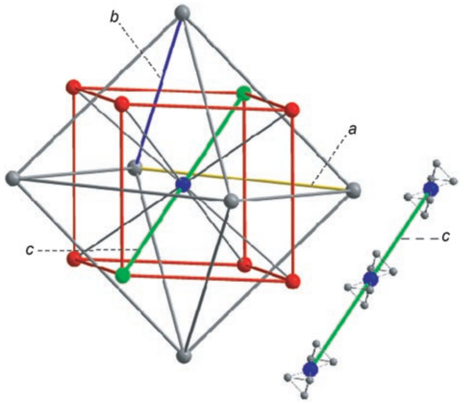

Figure 2. Coordination sphere of cluster **2** in the crystal. The alignment along the *c* axis (green, *c* = 13.997 Å) is emphasized; *a* (yellow) = *b* (blue) = 25.715 Å. The central cluster (blue) is surrounded by a cube (red) with 12 identical distances of 17.535 Å. In the enclosing octahedron (gray) the 12 edges are: 6×25.715 and 6×23.847 Å. The direct coordination sphere of the central cluster (blue) is: 8 (cube) + 6 (octahedron): 8 (2×13.997 Å (green lines) + 6×15.562 Å (thin gray lines)) + 6×17.535 Å (not shown).

in the caption of Figure 2, which vary between 14 and 26 Å.[9] The preferred direction in the crystal is the *c* axis, as the threefold axes of the cluster molecules are arranged in this direction.

The EPR spectrum (Figure 3) of crystals of **2** with a *g* value of about 2 confirms the radical electron structure of the cluster. The expected anisotropy stemming from the arrangement of the clusters in the crystal could be confirmed by rotating the sample (Figure 3). To account for the absence of observable hyperfine structure in the EPR spectrum of the crystalline sample,[10] quantum-chemical calculations[11] were carried out. Simulated spectra of cluster molecules of the model compound **2a** (see below) in various arrangements have a similar line shape without hyperfine structure (see the Supporting Information). Whereas the steep flanks of the EPR resonances indicate Gaussian line shape and therefore good separation of the single clusters in the collective, other results hint at interactions between the clusters of **2**, which lead to stabilization in the crystal (see below).

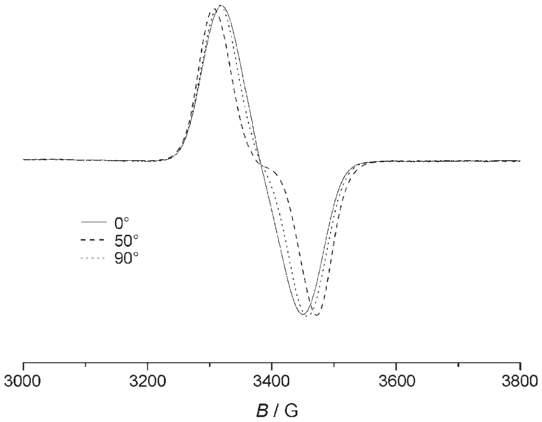

Figure 3. EPR spectrum of crystalline **2**. Rotation of the EPR tube in three positions (0°, 50°, and 90°) leads to the following splitting: 0°: 131 G; 50°: 167 G; 90°: 140 G.

To explain the variation of the bonding situation between cluster species **1** and **2** and to answer the question raised in the introduction regarding the interpretation of bonding in these compounds, we performed DFT calculations[11] on the very simple model compound $[Al_7H_6]$ and the corresponding cationic and anionic species $[Al_7H_6]^+$ ($\mathbf{3}^+$) and $[Al_7H_6]^-$ ($\mathbf{3}^-$). A population analysis for these systems provides explicit contributions for each MO. The essential results of the calculations are shown in Figure 4 and Table 1. The six Al–Al bonds from the central Al atom to the Al atoms of the $\{Al_3\}$ rings are elongated from $\mathbf{3}^+$ to **3** with a maximum value for $\mathbf{3}^-$, whereas the six Al–Al bond lengths in the $\{Al_3\}$ rings show the opposite trend with the shortest bond lengths for $\mathbf{3}^-$. In the neutral species **3** all twelve Al–Al bond lengths are identical. The p_z and the s orbitals of the central Al atom, which are mainly responsible for the variation of distances in the $\{Al_7\}$ framework through their interaction with the symmetry-equivalent combinations of p orbitals in the $\{Al_3\}$ rings (a_{2u}

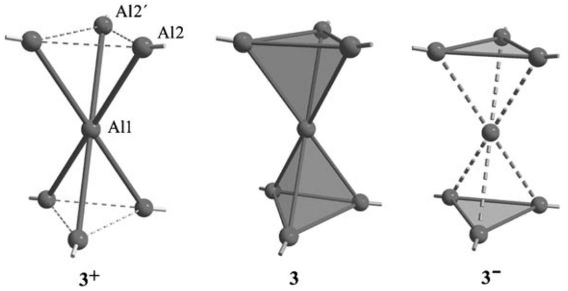

Figure 4. Calculated structural data (Å) and results of the population analysis (SEN, Q) for the $[Al(AlH)_6]$ frameworks in $\mathbf{3}^+$, **3**, and $\mathbf{3}^-$; data for **3** and $\mathbf{3}^-$ in parentheses. d(Al1–Al2) = 2.597 (2.638; 2.694); d(Al2–Al2′) = 2.767 (2.630; 2.547); d(Al–H) = 1.604 (1.616; 1.636); SEN: Al1Al2 = 1.18 (1.14; 1.16): Al2Al2′ = 1.0 (1.4; 1.67); $\{Al_3\}$ ring = 0.07 (0.25; 0.38), Q: Al1 = −0.45 (−0.48; −0.22); Al2 = 0.35 (0.06; −0.07); H = −0.11 (0.02; −0.06).

and a_{1g}), influence the bonds to the central atom and in the $\{Al_3\}$ rings differently for 3^+, 3, and 3^-. This effect is mirrored in the shared electron numbers (SEN)[11] determined by population analyses, which match the bond strengths expected from the distances (Figure 4).[13]

The energetic relationship of 3^+, 3, and 3^- is clarified in Table 1: For example, the addition of one electron to 3 results in a gain of 300 kJ mol^{-1}. The shortening of bond lengths and the increase of the SEN in the $\{Al_3\}$ rings of 3^- indicate that the additional electron is primarily localized in the $\{Al_3\}$ rings.

The model compounds $[Al(AlNH_2)_6]^-$ (**1a**) and $[Al(AlNH_2)_6]$ (**2a**) were studied by DFT calculations to determine whether the energetic and geometrical relations between 3^+, 3, and 3^- can also be applied to 1 and 2. The trend of the distance variations is in accordance with the experimentally determined values for 1 and 2 (Table 1). The calculations also show that the anion **1a** is about 170 kJ mol^{-1} more stable than **2a**. The great stability of **1a** relative to **2a** also shows in the very different HOMO–LUMO gap values: 1.64 eV compared with 0.42 eV. Almost the same values were determined for 3^- and 3 (1.65 eV and 0.50 eV). The very good agreement in trends of stabilities and distance variations in the $\{Al_7\}$ frameworks of $3/3^-$ with **1a**/**2a** (Table 1) justifies the use of 3 and 3^- as model systems for the clarification of the bonding situation in 1 and 2.[14]

Besides the energetic[15] and structural situation of 1 and 2, calculation of the NMR shifts (self-consistent field level with DFT-optimized geometry) of the Al atoms proves helpful in the interpretation of the bonding situation. The following ^{27}Al NMR shifts (ppm) for **1a** and **2a** result: **1a**: $\delta(Al1) = 798$; $\delta(Al2) = 236$; **2a**: $\delta(Al1) = 269$; $\delta(Al2) = 222$. Changes in the method of calculation lead to only small variations in these shifts. The most prominent result is the low-field shift ($\delta = +798$ ppm) of the central Al atom in the anion **1a**,[17] which we related to the Knight shift of Al nuclei in Al metal in earlier studies.[2,18] A high-field shift also would have been plausible for **1a** because of the discussed ring-current effect of the $\{Al_3R_3\}^{2-}$ rings as found in the sandwich compound $[AlCp^*_2]^+$: $\delta = -114$ ppm (see below).[5]

The sum of the results presented for the isolated clusters 1 and 2 shows that the question raised in the title is formulated too simply. Therefore, it cannot be answered definitely, as the bond situations in 1 and 2 are of a very different and partly contradicting nature with respect to conventional classification attempts: According to the results determined for $[Al_7H_6]$ (3), the cluster 2—and not 1, as presumed in the introduction—should be regarded as the prototype of an $\{Al_7\}$ cluster with 12 identical Al–Al bond lengths and thus the simplest metalloid cluster. The description of 2 as a ligand-protected central Al atom ("tamed" Al atom), in analogy to Al atoms in solid noble gas matrices,[19,20] is obviously not adequate: The interactions with the $\{Al_3R_3\}$ rings in 2 through the a_{1g} and a_{2u} MOs already have to be interpreted as Al–Al bonds (see above); that is, these interactions span the whole $\{Al_7\}$ framework (Figure 5).

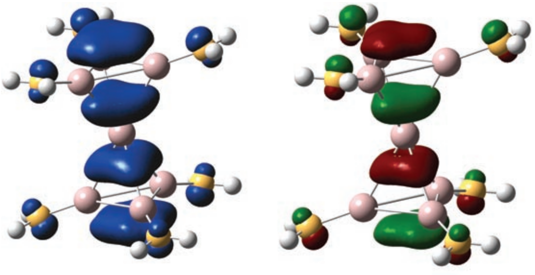
a) b)

Figure 5. a) Spin density and b) SOMO (a_{2u}) of $[Al(AlNH_2)_6]$ (**2a**); Al pink, N yellow, H white.

Since bonding interactions within the $\{Al_3\}$ rings are significantly weaker than those involving the central Al atom, 2 should not be regarded as a sandwich compound. In contrast, this term seems at first to be justified for the monoanion 1, as the Al–Al bonds in the $\{Al_3\}$ rings are considerably stronger and the bonding situation is comparable to that in the $[Al_3R_3]Na_2$ compounds[21] described recently by Power and co-workers. Despite the shortening of the bonds and the higher SEN, these "$\{Al_3R_3\}^{2-}$ fragments" should in our opinion not be described as aromatic systems[3] because of the lack of a ring-current-induced high-field shift for the central atom as is the case in "real" sandwich compounds (e.g., $[AlCp^*_2]^{+[5]}$). Instead, calculations for 1 result in a surprising low-field shift ($\delta = +798$ ppm), which is unique for such molecular species: the central Al atom in 1 is affected by a Knight shift as found for Al nuclei in solid metal, which are deshielded by a delocalized electron gas.[22] Therefore, 1 should actually be regarded as a possible molecular model for the metallic bond. Thus, both cluster species 1 and 2 have to be described as "metalloid" systems: 1 because of its ^{27}Al NMR shift[24] (metalloid in an electronic sense) and 2 because of its topology (nearly equal bond lengths in the $\{Al_7\}$ framework).

It is especially surprising that 2 as a neutral $[Al_7R_6]$ system could actually be observed and structurally characterized. An explanation for this may be found in the collective behavior of 1 and 2 in the crystal: As 1 is additionally stabilized in crystalline form by about 284 kJ (empirically determined according to the unit-cell volume increment method described by Jenkins et al.[25]), an $[Al_7R_6^-]$ cluster should actually be preferred to a comparable neutral cluster without lattice stabilization by $284 + 170 = 454$ kJ.

This metastability of 2 can be experimentally verified: 2 cannot be dissolved in organic solvents without decomposition and precipitation of Al. So, a special challenge for solid-state physical studies will be the explanation of the apparent stabilization of 2 in crystalline form. An answer to this—in our opinion—fundamental question may be reached by applying detailed band-structure calculations to 1 and 2.[26] The results presented herein could initialize further experimental and theoretical studies on the question of to what extent magnetic and electrical interactions can lead to a drastic gain in stability for such separated individual clusters in a lattice.[27] Such fundamental, though hitherto not understood, effects[28] are also indicated by our recent results on the electrical conductivity and superconductivity of a crystalline metalloid $[Ga_{84}R_{20}]$ cluster compound.[29–31]

Experimental Section

Synthesis of **2**: Gaseous AlCl formed at around 1200 K by flowing HCl over liquid aluminum under high-vacuum conditions was condensed at 77 K together with a toluene/diethyl ether mixture (3:1) to give a metastable AlCl solution. This solution (20 mL; 7.1 mmol) was added to $LiN(SiPhMe_2)_2$ in toluene (2.36 g, 8.1 mmol) at −78 °C and the mixture was slowly warmed to ambient temperature to give a dark brown solution and a colorless precipitate. The solution was repeatedly separated from the precipitate and warmed to 60 °C (for 2 days at a time). The solvent was completely removed in vacuum after each filtration. The oily residue was extracted with pentane to give a dark brown solution, from which crystals of **2** were isolated at ambient temperature. Crystals of **2** could also be obtained from the pentane extraction residue by using a toluene/pentane mixture (5:1). The total yield for **2** could therefore be raised to about 15 %; therefore, the major portion of Al-containing species and thus larger metalloid clusters remains in the dark solution.

Measurements of the electron paramagnetic resonance (EPR) at a frequency of 9.45 GHz were performed on an ensemble of approximately three conjoined, unoriented single crystals (total volume of about 1 mm^3) with a Bruker ESP300E spectrometer equipped with an Oxford ESR900 cryostat.

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[1] In accordance with the greek ειδος (ideal, prototype), we have chosen the suffix -oid in the term "metalloid" to demonstrate that the topology of the metal atoms in such clusters is prototypical for that in the metals (elements).

[2] A. Purath, R. Köppe, H. Schnöckel, *Angew. Chem.* **1999**, *111*, 3114; *Angew. Chem. Int. Ed.* **1999**, *38*, 2926.

[3] a) A. Schnepf, H. Schnöckel, *Angew. Chem.* **2002**, *114*, 3683; *Angew. Chem. Int. Ed.* **2002**, *41*, 3533; b) "Clusters of the Heavier Group 13 Elements": G. Linti, H. Schnöckel W. Uhl, N. Wiberg in *Molecular Clusters of the Main Group Elements*, Wiley-VCH, Weinheim, **2004**.

[4] H. Schnöckel, *Dalton Trans.* **2005**, 3131.

[5] C. Dohmeier, H. Schnöckel, C. Robl, U. Schneider, R. Ahlrichs, *Angew. Chem.* **1993**, *105*, 1124; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1655.

[6] G. Hadiprono, *Dissertation*, Univ. Karlsruhe, **2005**.

[7] C. Dohmeier, D. Loos, H. Schnöckel, *Angew. Chem.* **1996**, *108*, 141; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 129.

[8] $[Al_7\{N(SiMe_2Ph)_2\}_6]$: $M_r = 1896.02\ g\,mol^{-1}$, crystal dimensions: $0.5 \times 0.5 \times 0.5\ mm^3$, trigonal, space group $R\bar{3}$, $a = 25.715(4)$, $c = 13.997(3)$ Å, $V = 8015(2)$ Å^3, $Z = 3$, $\rho_{calcd} = 1.178\ g\,cm^{-3}$, $F(000) = 3027.0$, $T = 153(2)$ K, $\mu(Mo_{K\alpha}) = 0.71073\ nm^{-1}$, 11572 reflections, 3490 independent ($R_{int} = 0.0680$), refined for F^2 ($\theta_{max} = 26.02°$), 271 parameters, 0 restraints, $R_1(I > 2\sigma(I)) = 0.0466$, wR_2 (all data) = 0.0973, GoF (F^2) = 1.012, ρ(min./max.) = −0.269/0.271 e Å^{-3}; unit cell determination: 3490 reflections. Diffractometer: $\lambda = 0.7103$ Å, Stoe-IPDS-II; Software: SHELXS-97, SHELXL-97, Stoe-IPDS-Software; structure refinement with direct methods, H atoms at calculated positions. CCDC-624700 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[9] In fullerides such as $[C_{60}]^{2-}$, despite having large cations (e.g. $[Ni(NH_3)_6]^{2+}$),[12] the distances between the $[C_{60}]^{2-}$-ions are only about 10 Å in all directions (compared with 14 Å (2 ×), 15.6 Å (6 ×), and 17.5 Å (6 ×) for **2**, see Figure 2). In fullerides, the HOMOs of individual C_{60} anions (diameter of about 7 Å) are nearly in close contact (i.e. the shortest intermolecular C–C distances of 3.36 Å are of the same length as those in graphite), whereas, for example, the SOMOs of **2**, by analogy to **2a**, are to a large extent localized in the $\{Al_7\}$ moieties and therefore separated from the electronic system of other clusters by the dielectric of the organic ligands. Consequently, the electronic interactions in **2** are expected to be significantly smaller than those in the fullerides.

[10] As **2** cannot be dissolved (e.g. in organic solvents) without decomposition, no EPR spectrum of the individual clusters could be obtained.

[11] Calculations were carried out with the TURBOMOLE program package. a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165; b) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346. DFT methods with the RI approximation and the BP-86 functional were applied; c) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283; d) A. D. Becke, *Phys. Rev. B* **1988**, *38*, 3098; e) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200; f) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822. A split-valence-plus-polarization(SV(P)) basis set was used for all atoms; g) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571. Partial charges were calculated according to the method by Roby and Davidson; h) R. Heinzmann, R. Ahlrichs, *Theor. Chim. Acta* **1976**, *42*, 33; i) R. Ahlrichs, C. Ehrhardt, *Chem. Unserer Zeit* **1985**, *19*, 120. NMR shifts and hyperfine coupling constants for the simulation of the EPR spectrum were calculated with the GAUSSIAN03 program package; j) Gaussian03 (Revision C.02): M. J. Frisch et al., see the Supporting Information.

[12] a) K. Himmel, M. Jansen, *Chem. Commun.* **1998**, 1205; b) H. Brumm, M. Jansen, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1433.

[13] The changes of bonds in the $\{Al_7\}$ framework can be ascribed to the following MOs: In $\mathbf{3}^+$ binding contributions exist only for bonds to the central Al atom in the highest a_{1g} and a_{2u} orbitals. In contrast, for equivalent MOs of **3** a strengthening of bonds is expected for bonds to the central Al atom as well as inside the $\{Al_3\}$ rings. In $\mathbf{3}^-$ the HOMO (a_{2u}) together with binding contributions of a high a_{1g} MO is strongly binding concerning the $\{Al_3\}$ units.

[14] No significant differences result from a control calculation for the complete cluster ion **1** in comparison with **1a** (Table 1).

[15] In the discussion of the bonding situation in **1** and **2** the energetic relation to solid aluminum should be mentioned as a further aspect. Whereas the atomization of Al metal requires 326 kJ mol^{-1},[16] that is, the breaking of each of the 12 Al–Al bonds requires 55 kJ mol^{-1}, the sandwich stabilization of an Al atom by two $\{Al_3R_3\}$ residues in the formation of **2a** provides 447 kJ mol^{-1}, that is, 75 kJ mol^{-1} for each of the six Al–Al bonds to the central Al atom. This strengthening of Al–Al bonds in **2a** relative to the metal was expected because the higher coordination number of 12 in the metal results in a weakening of bonds. Moreover, the bond energy of 75 kJ mol^{-1} in **2a** has to be corrected to smaller values, as the bonds in the $\{Al_3\}$ rings are also enhanced in the formation of **2a** from an Al atom and $\{Al_3R_3\}$ moieties, thus the bond energy of the Al–Al bonds of **1** and **2** and that of Al metal are very similar in view of the factors mentioned.

[16] "NIST-JANAF Thermochemical Tables, Fourth Edition": a) M. W. Chase, Jr., *J. Phys. Chem. Ref. Data Monogr.* **1989**, 9; b) National Institute of Standards Web Based Chemical Data, http://webbook.nist.gov/chemistry/.

[17] a) All other ^{27}Al resonances determined for **1a** and **2a** are in the same region at about 250 ppm and do not indicate an unusual bonding behavior of these atoms; b) The calculation of the ^{27}Al

NMR shifts for the complete cluster ion **1** tends to result in similar values (δ(Al1) = 554 ppm; δ(Al2) = 231 ppm). Furthermore, these results show that the choice of **1a** as a model compound is justified.

[18] P. L. Sagalyn, J. A. Hofmann, *Phys. Rev.* **1962**, *127*, 68.

[19] J. H. Ammeter, D. C. Schlosnagle, *J. Chem. Phys.* **1973**, *59*, 4784; R. Köppe, P. H. Kasai, *J. Am. Chem. Soc.* **1996**, *118*, 135.

[20] In this case, the distances between isolated Al atoms are of the same order of magnitude as those between the central Al atoms of individual clusters in the crystalline compound **2**.

[21] R. J. Wright, M. Brynda, P. P. Power, *Angew. Chem.* **2006**, *118*, 6099.

[22] This is also indicated by the charge of −0.2 determined for the central Al atom in **3**$^-$ (see Figure 4). The corresponding charges for **3**$^+$ and **3** are significantly more negative (−0.45 and −0.48, respectively). Negative charges in neutral metalloid clusters (e.g., [$SiAl_{14}Cp^*_6$])[23] are not atypical.

[23] A. Purath, C. Dohmeier, A. Ecker, R. Köppe, H. Krautscheid, H. Schnöckel, R. Ahlrichs, C. Stoermer, J. Friedrich, P. Jutzi, *J. Am. Chem. Soc.* **2000**, *122*, 6955.

[24] Despite numerous attempts, the calculated ^{27}Al NMR signal could not be experimentally verified. This negative result is, however, not unexpected, as only very rarely can ^{27}Al NMR signals be detected for metalloid clusters.

[25] a) H. D. B. Jenkins, J. F. Liebmann, *Inorg. Chem.* **2005**, *44*, 6359; b) L. Glasser, H. D. B. Jenkins, *Chem. Soc. Rev.* **2005**, *34*, 866.

[26] Comparing these results should be simplified by the fact that both compounds crystallize in the same space group.

[27] The following theoretical (a) and spectroscopic (b) studies are planned or underway: a) As orientating band-structure calculations could not supply any indication for the presumed stronger interactions between cluster molecules of **2**, detailed studies in cooperation with Prof. G. Seifert, TU Dresden, are currently being carried out, the results of which will be the topic of a future publication; b) Further EPR spectroscopic studies (also with pulsed methods) on single, preferably well-orientated, crystals are the aim of current experiments, which are, however, very time-consuming and experimentally difficult because crystals of **2** (like almost all metalloid Al and Ga clusters) are extremely air and moisture sensitive and can even ignite when exposed to air. Therefore, these crystals cannot easily be manipulated without contaminating or destroying them. However, these studies may assist in understanding the possibly unique magnetic interactions of the individual clusters of **2** in the collective.

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