Solid-State Structures

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$Al_{12}K_8[OC(CH_3)_3]_{18}$: A Wade, Zintl, or Metalloid Cluster, or a Hybrid of All Three?**

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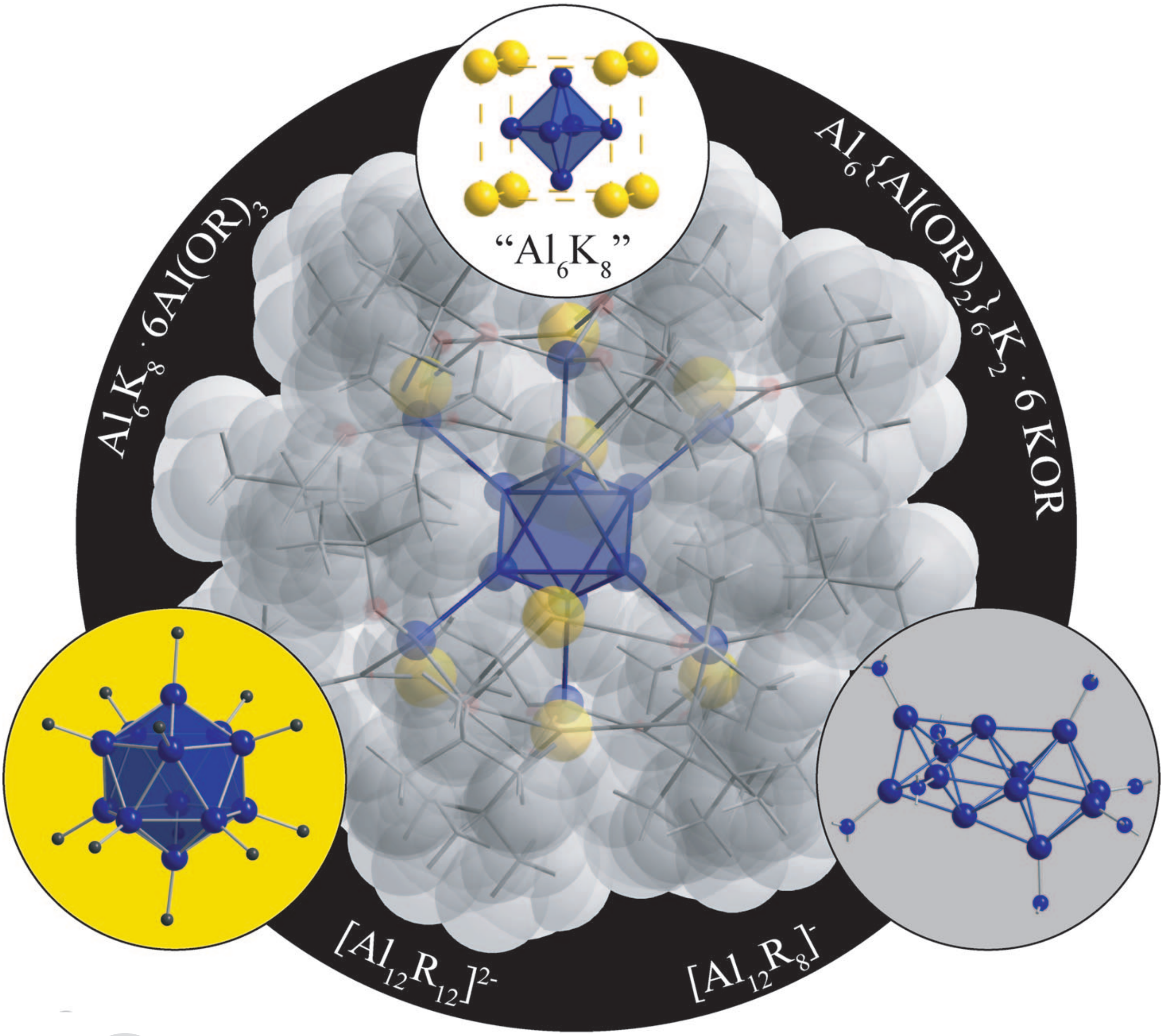
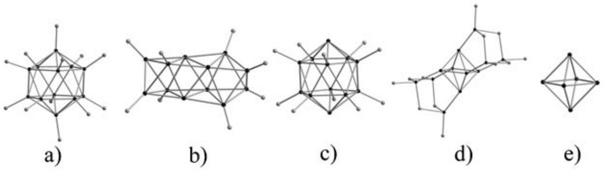
Dedicated to Professor Arndt Simon on the occasion of his 70th birthday





Scheme 1. Structures of Al/Ga clusters containing twelve and six metal atoms (see text): a) $[Al_{12}R_{12}]^{2-}$, b) $[Al_{12}R_8]^{-}$, c) $[Ga_{12}R_{10}]^{2-}$, d) $[Ga_6(GaX_2)_6]^{2-}$, e) $[Al_6]^{8-}$.

The icosahedral $[Al_{12}R_{12}]^{2-}$ cluster (R = *i*Bu; Scheme 1) of W. Uhl[1] was one starting point for a recent renaissance of Group 13 chemistry.[2,3] This Wade-type *closo* cluster,[4] with bonding similar to the corresponding boron clusters, is in contrast to the $[Al_{12}R_8]^{-}$ cluster (R = N(SiMe$_3$)$_2$; Scheme 1)[5] with a mixed-valent bonding situation (average oxidation number $n_{av} = 0.58$) that belongs to the class of metalloid clusters.[6–12] In the M_{12} cluster chemistry of gallium, the $[Ga_{12}R_{10}]^{2-}$ species (R = fluorenyl; Scheme 1)[13] has been interpreted as being a cluster between the metalloid and Wade-type. For the halide-substituted $[Ga_{12}X_{12}]^{2-}$ species, a metalloid isomer $[Ga_6(GaX_2)_6]^{2-}$ is preferred to the Wade-type structure (Scheme 1).[14,15] The central bare Ga$_6$ octahedron is reminiscent of the Ga_6^{8-} unit (Scheme 1) in the $Ba_5Ga_6H_2$ Zintl phase.[16–18] Though there are some similarities between Zintl cluster ions and metalloid clusters, there are also essential differences:[19,20] the positive oxidation numbers of metalloid clusters, which are intermediates between the normal valent metal salts and the metals, and the usually highly negatively charged Zintl anions (e.g. Ga_6^{8-}),[25] which are only stabilized in a sea of strongly electropositive cations within an ionic lattice.[26] However, to our knowledge, the difference between both types of cluster compounds (ionic solids and molecular solids) has never been investigated, for example, with respect to the thermodynamic stabilities. The missing link between the two types of clusters makes both experimental (e.g. thermodynamic) and theoretical investigations highly challenging.

Herein we present a crystalline, molecular Al$_{12}$ cluster compound that may help solve this fundamental problem, and which may be called a hybrid between a metalloid cluster and a hypothetical molecular Zintl phase. DFT calculations based on experimentally determined thermodynamic and structural data support this idea.

A metastable AlBr solution obtained by the simultaneous condensation of the high-temperature molecule AlBr and a solvent mixture of toluene/THF (3:1)[30] was treated with a solution of KO*t*Bu in toluene at −78°C. After periodic heating to room temperature, 60°C, and 80°C, the reaction mixture was cooled to room temperature and the solvent removed. From a red pentane solution of the solid residue, orange-colored crystals of $[Al_6K_8\{Al(OtBu)_3\}_6]$ **1** were isolated (Supporting Information, S1).

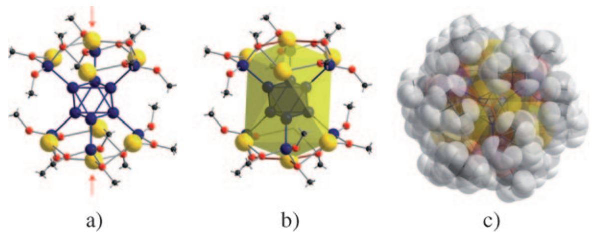


Figure 1. Three different presentations of **1** (see text): a) emphasizing the central Al$_6$ unit with six direct bonds to further six Al atoms, b) showing the bicapped trigonal-antiprismatic arrangement of the eight K atoms, and c) a space-filling model of the whole molecule surrounded by 54 CH$_3$ moieties (transparent gray and white) viewed along the threefold axis. Al blue, K yellow, O red, *tert*-butyl groups gray.

The results of the X-ray diffraction experiments[31] and DFT calculations (Supporting Information, S1) are shown in Figure 1. The central distorted-octahedral (slightly trigonally compressed antiprismatic) Al$_6$ core and the six surrounding aluminum atoms are shown together with the eight potassium atoms, two of which are situated on the threefold axis (red arrows). Figure 1b shows the arrangement of the eight potassium atoms surrounding the central Al$_6$ core. All of the potassium atoms form Coulomb interactions to the 18 oxygen atoms of the O*t*Bu moieties; the two potassium atoms on the threefold axis are each three-coordinate, whilst the other six are each two-coordinate. There are three types of O*t*Bu groups present: terminally bonded to aluminum, μ_2-bridging between aluminum and potassium, and μ_3-bridging between aluminum and two potassium atoms. Each of the six outer aluminum atoms is ligated by three oxygen atoms, one of each type.

The structure can be considered as a central Al$_6$ "superatom" surrounded by two capping $\{K_4Al_3(OtBu)_9\}$ "ligands" (Figure 1b). These ligands each have C_3 symmetry, and under the $\bar{3}$ site symmetry, the two units will be of opposite handedness to prevent unfavorable contacts between the terminal O*t*Bu groups from the two caps. However, changing the handedness of a cap has very little effect on its external shape (Supporting Information, S3), and in the crystal structure, such a twofold disorder of the caps is indeed found. Attempts to either allow for possible merohedral

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twinning in the space group $R\bar{3}$ or to refine the structure in R3 or $P\bar{1}$ (as a racemic or *pseudo*-merohedral twin, respectively) did not improve the structure, and this statistical orientation disorder about the threefold axis, involving all atoms apart from the central aluminum atoms and the two potassium atoms on the threefold axis, is considered real. These disorder problems are consistent, appearing in each of several synchrotron crystal structure measurements, and prevent satisfactory refinement of the structure, with concomitant high *R* factors.

As only the central six aluminum atoms and two of the potassium atoms are largely unaffected by the disorder, bond lengths involving any of the other atoms suffer from a lack of precision, and therefore the bonding discussion of **1** has to be supported by DFT calculations on the model compound $Al_{12}K_8(OMe)_{18}$ **1a** (Supporting Information, S2). As expected (see above), only the experimentally obtained distances within the Al_6K_2 unit confirm the DFT calculations: Al_3 triangle 270.1 (exp.)/270.6 (DFT) and six connecting Al–Al distances 262.6 (exp.)/263.1 pm (DFT). One potassium atom caps each of the Al_3 triangles with distances of 361 (exp.)/370.7 pm (DFT).[32] The structural data of all other atoms (apart from Al_6K_2) are consequently only discussed on the basis of DFT results. As expected, the Al–Al distances from the Al_6 core to the terminal aluminum atoms are shorter (261 pm) than the central atoms[33] having a stronger covalent character, which is in line with the trend of the calculated SEN values (shared electron number; Supporting Information, S2). The Al–O distances are in the expected range: 177.9, 181.6, and 185.5 pm, depending on whether or not there is a further coordination of the oxygen atoms to one of the potassium atoms; that is, the Al–O distances increase with increasing coordination number of the oxygen atoms from two to three to four (Supporting Information, S2, S3). The angle sum of the six outer AlO_3 moieties (324.2°) is in accordance with sp^3 bonding. The K–O bond lengths from the bicoordinate potassium atoms are 275.9 and 260.6 pm to the μ3-bridging and μ2-bridging alkoxo oxygen atoms, respectively, whilst there are longer K–O bonds to the two tricoordinate potassium atoms (282.9 pm; Supporting Information, S1, S3). The K–Al distances between the six terminal aluminum atoms and the two potassium atoms on the threefold axis (367.9 pm) are in the same range as the above-mentioned distances to the central Al_6 moiety. As the distances between the Al_6 moiety and the distances between the six terminal aluminum atoms and all other potassium atoms are even shorter (355.1, 360.2), **1** could be called an $Al_{12}K_8$ cluster. This conclusion is in line with the experimentally detected larger AlK distances of 400.5 pm within the above-mentioned $[Al_{12}R_{12}]^{2-}$ cluster.[1] The O–C distances of **1a** are 138.7, 141.3, and 141.7 pm, depending on the coordination of the oxygen atoms.

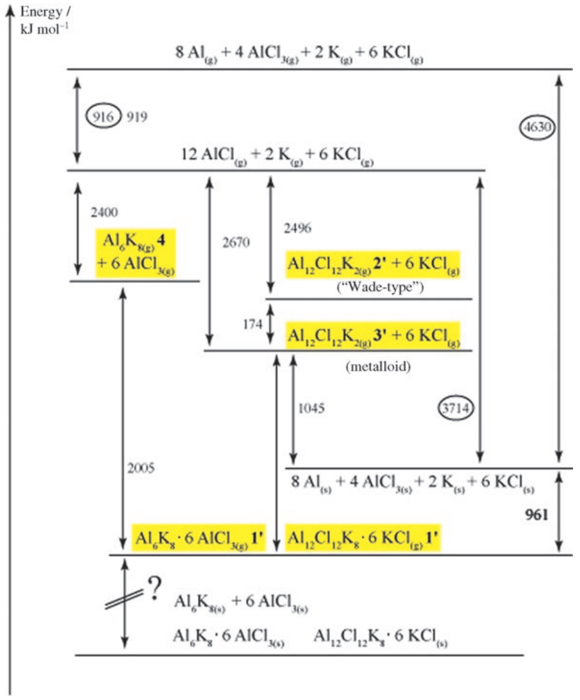
Although all the atoms affected by the above-mentioned orientation disorder could be split and refined, the thermal parameters of the partial atoms remained high and anisotropic, indicating either high thermal motion or possibly full dynamic disorder between the two conformations. The latter would exchange the μ_2- and μ_3-bridging O*t*Bu groups (Supporting Information, Figure S3), and such dynamic behavior can indeed be observed by ^{1}H NMR measurements in [D$_8$]toluene solution,[36] with three different *t*Bu signals at −40 °C and only two (intensity 2:1) at 60 °C. However, on dissolving **1** in a donor solvent, such as THF, in an attempt to measure its mass spectrum (electron spray ionization, ESI), no characteristic fragment could be observed; such solvents destroy the cluster and especially the Al–K interactions.

The bonding in **1** becomes clearer when the following model clusters (with OR groups substituted by chloro ligands)[37] are discussed with the help of DFT calculations: $[Al_{12}Cl_{12}]^{2-}$ **2**, $[Al_{12}Cl_{12}K_2]$ **2′**, $[Al_6Cl_6]^{2-}$,[39] $[Al_6]^{8-}$, $[Al_6(AlCl_2)_6]^{2-}$ **3**, $[Al_6(AlCl_2)_6K_2]$ **3′**, and Al^6K_8 **4** (for structural data, ^{27}Al NMR spectra, and a diagram, see the Supporting Information, S4, S6). Although the structural data of the clusters under discussion (and even the Al–K distances) are more or less similar, there is a drastic electronic difference between the icosahedral $K_2[Al_{12}Cl_{12}]$ cluster **2′** and the Al_6K_8 species **4** and all the other clusters; only these two clusters have calculated ^{27}Al NMR values that are shifted heavily to low-field in the direction of the Knight shift: **2′** 458 ppm, **4** 482 ppm.[11,41–44] On the basis of these NMR data, it is evident that the Zintl-type and Wade-type bonding in **2** and **4** is different from the bonding in metalloid clusters. Therefore, the molecular compound **1′** (^{27}Al NMR: 168, 148 ppm) may be described more adequately as a metalloid cluster $[Al_6(AlCl_2)_6]K_2{\cdot}6\,KCl$ than a Zintl phase-like cluster $[Al_6K_8{\cdot}6\,AlCl_3]$, with the Wade/Zintl-type typical bonding properties of molecular moiety Al_6K_8 **4** suppressed by the complexation of the six $AlCl_3$ units.

To confirm our interpretation, thermodynamic calculations were carried out (Scheme 2). The starting point corresponds to the experimental chemistry with $12\,AlCl_{(g)} + 2\,K_{(g)} + 6\,KCl_{(g)}$.[45] The disproportionation reaction to the gaseous species $8\,Al + 4\,AlCl_3 + 2\,K + 6\,KCl$ experimentally is endothermic (916 kJ) and in accordance with the calculated value (919 kJ). The formation from the AlCl level of both $[Al_{12}Cl_{12}]K_2$ clusters (**2′** and **3′**) is strongly exothermic: metalloid cluster **3′** 2670 kJ, icosahedral Wade-type cluster **2′** 2496 kJ. The metalloid isomer **3′** is thus favored by 174 kJ, and the metalloid cluster **3′** is favored in comparison to the molecular Zintl phase **4** by 270 kJ; that is, **3′** is exothermically formed by a comproportionation reaction from **4** and $AlCl_3$ (compare with the stoichiometry given in Scheme 2 and the comments below).

The clusters **2′** and **3′** react in a strongly exothermic fashion upon addition of six KCl molecules to the gaseous model compound $[Al_6(AlCl_2)_6]K_2{\cdot}6\,KCl$ (**1′**). On the other hand, there is a stronger exothermic reaction ($-2005\ \text{kJ mol}^{-1}$) from the molecular Zintl phase Al_6K_8 **4** to the gaseous model compound $[Al_6K_8{\cdot}6\,AlCl_3]$ (**1′**). This gaseous species **1′** should finally exothermically condense to solid **1′** according to $Al_6K_{8(s)} + 6\,AlCl_{3(s)}$; that is, by their comproportionation reaction as in the gas phase (see above).

The thermodynamic data presented herein thus show that there is a fluent energetic change between both types of clusters (Zintl/Wade and metalloid). However, even before the complexation by six $AlCl_3$ or six KCl molecules, the metalloid cluster **3′** is preferred in comparison to **2′** and **4**. Therefore it is not surprising that also after the complexation



Scheme 2. The energetic relationship between the hypothetical Al_6/Al_{12} clusters (marked in yellow): $Al_{12}Cl_{12}K_2$ (**2'**), $Al_6(AlCl_2)_6K_2$ (**3'**), Al_6K_8 (**4**), and $[Al_6(AlCl_2)_6]K_2{\cdot}6\,KCl/[Al_6K_8{\cdot}6\,AlCl_3]$ (**1'**). The experimentally derived energy values are marked by circles.

the metalloid character in gaseous **1'** is still present. This bonding type is also expected in solid **1'**; however, on the way to solid **1'**, the solid Zintl phase Al_6K_8 **4** with a non-metalloid (Wade-type) bonding has to be addressed as an intermediate.

Furthermore, all results presented herein show that the oxidation number of the aluminum atoms n provides an impressive though formal description of the different cluster types: $n = -1.3$ for **4**, $n = +0.3/+3$ for **1'**, and $n = 0.83$ for **2** (Supporting Information, S5).

Apart from these first results on the fundamental bonding situation,[46] there are some synthetic points which should be addressed briefly. The essential role of $AlCl_3$ as a Lewis acid for the stabilization and dissolution of the molecular Zintl phase Al_8K_8 by six lone-pair interactions seems very plausible, because Zintl cations can be stabilized by $AlCl_4^-$ as Lewis bases.[48,49] Furthermore, many solid transition metal halides can be solvated by $AlCl_3$ in the gas phase to increase their tendency for the gaseous state; that is, many solid MX_n salts can be purified and recrystallized by the gaseous $AlCl_3$ complexes with the help of a chemical transport procedure.[50–52] Therefore, the role of $AlCl_3$ may be important for a novel preparation method of Zintl phases as they should be easily solvated by $AlCl_3$ by equilibrium reactions; that is, liquid $AlCl_3$ may be a solvent with a high synthetic potential for the chemistry of Zintl phases. A similar synthetic route in direction to metalloid clusters should also be possible in principle; however it should be restricted to thermodynamically stable clusters.

Compound **1** is key to understanding of bonding in the field of two important kinds of metal–metal clusters: metalloid and Zintl/Wade species. The bonding description for **1** as a metalloid cluster is favored over a solvated Zintl phase by thermodynamic and by structural and spectroscopic properties of some model compounds. Therefore, from a solid Zintl phase and $AlCl_3$ by a comproportionation reaction, a solid compound $[Al_6(AlCl_2)_6]K_2{\cdot}6\,KCl$ should be favored as a KCl-complexed metalloid cluster. Possibly both cluster species (Zintl phase, for example $[Al_6K_8]$, and metalloid cluster **1'**) may be detectable within an equilibrium reaction between all clusters **4**, **2'**, **3'**, and **1'** together with $AlCl_3$/KCl (Scheme 2). This expectation seems to be plausible, as **1'** cannot only be described as an $AlCl_3$-solvated Zintl phase $[Al_6K_8{\cdot}6\,AlCl_3]$, and in experiments it should be possible to dissolve Zintl phases with several solvation steps in liquid $AlCl_3$. On the other hand, it seems to be possible that Al/Ga subhalide clusters, such as $Ga_{24}Br_{22}$,[53] can react with KBr to a hybrid cluster such as **1'**: $Ga_{24}Br_{22} + 14\,KBr \rightarrow Ga_{12}K_{14}{\cdot}12\,GaBr_3$.[54] Therefore, the experimentally based considerations presented herein may initiate activities for the development of a novel unified metal atom cluster concept.

As the formation of the model cluster **1'** in the gaseous state is exothermic even when starting from the solid educts 8 Al, 4 $AlCl_3$, 2 K, and 6 KCl (−691 kJ; Scheme 2; perhaps this is one of the most important practical aspects of this contribution), the formation of the solid model compound **1'** from the same starting materials should be highly exothermic; that is, this reaction should provide a novel strategy for the synthesis of Zintl phases, thermodynamically stable metalloid cluster compounds, or a new class of hybrid clusters of both.

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[31] Crystal data for **1**: $C_{72}H_{162}Al_{12}K_8O_{18}$, $M_r = 1952.58$, trigonal, $R\bar{3}$ (rhombohedral axes) $a = 15.0168(11)$ Å, $\alpha = 107.910(1)°$, $Z = 1$, $V = 2747.2(3)$ Å^3, $T = 150$ K, $\rho_{calc} = 1.180\,g\,cm^{-3}$, $F(000) = 1046$, $\mu = 0.474\,mm^{-1}$; $\lambda = 0.8000$ Å, $2\Theta_{max} = 55.24°$, 13304 data, 2968 unique ($R_{int} = 0.0513$), 169 parameters, final $wR_2 = 0.3631$, $S = 1.033$ (all data), R_1 (2491 data with $I > 2\sigma(I)) = 0.1374$, largest final difference peak/hole $+0.99/-0.97\,e\,Å^{-3}$. See The Supporting Information (S3) for refinement details. CCDC 757644 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.

[32] This discrepancy is not caused by the orientation disorder; it simply seems to be a consequence of the repulsion interaction of the O*t*Bu moieties in direction to the Al_6 core. In contrast, the calculated values are based on the sterically less demanding OCH_3 groups causing less repulsion and therefore longer KAl distances.

[33] A similar bonding situation is observed for molecular $Al_{12}(AlCl_2)_{10}$ species in which the Al–Al bonds from the icosahedral center to the $AlCl_2$ moieties are significantly shorter (252.9 pm) than the bonds within the Al_{12} icosahedron (276.5 pm).[34,35]

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[54] This disproportionation reaction should proceed by the following step: $Ga_{24}Br_{22} + 14\,KBr \rightleftharpoons 16\,2/3\,Ga + 7\,1/3\,GaBr_3 + 14\,KBr$.