Lipophilically Wrapped Polyion Aggregates, 130[◇]

Tetralithium Bis(ethylaluminum) Tetrakis(catecholate) Pentakis(dimethoxyethane): An Oxygen-Rich Cluster $[(Al^{++}{}_2(Li^+)_4(O_{18})^{-8}]$ in a $C_{36}H_{44}$ Hydrocarbon Shell

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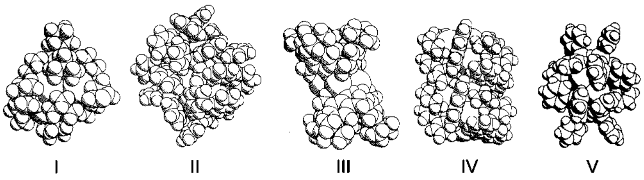
The structure determination of the lipophilically wrapped cluster $\{[Al_2Li_4O_{18}](C_{36}H_{44})\}_\infty$, a novel material crystallized from a mixture of $[(C_2H_5)_3Al]_2$, *n*BuLi, and catechol in DME solution, reveals five-coordinate Al^{++} and Li^+ centers. According to density functional theory calculations, the eight negative charges are well-delocalized over the oxygen-rich framework.

Recent Results on Main-Group Ion Clusters

Lipophilically wrapped polyion aggregates, in which a cluster ion nucleus guarantees thermodynamic stability, and where a surrounding hydrocarbon skin offers both kinetic shielding as well as solubility in non-polar solvents, are representative of a rather favourable self-organization principle,[2][3][4][5][6][7][8] for main-group element compounds (Table 1).

Table 1. Examples of novel lipophilically wrapped main-group element clusters with space-filling structure representation and specification of their components



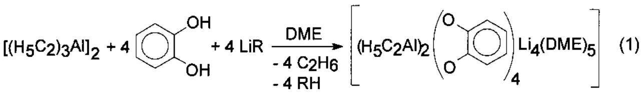
Component	[Lit.]	Cluster	Structure	Lipophilic Skin
I. $[Ba]_x + (H_3C)_3COH$	[4]	$[Ba_6Li_2O_2]^{\oplus 11}$	Octahedron + Prismane	$(^{\ominus}OC(CH_3)_{11})$
II. $Na^{\oplus}(RO)_2\overset{O}{P}\text{-}\overset{\ominus}{N}\text{-}\overset{O}{P}(OR)_2$	[5]	$[Na(OPNPO)]_6$	Ellipsoid	$(C_{144}H_{120}O_{24})$
III. $LiNH_2$ + Calix[4]aren	[6]	$[Li_6(NH_3)_2O_6]$	Double tetrahedron	$(C_{88}H_{110}O_2)$
IV. $K^{\oplus}$(aci-nitrofluorene)	[7]	$[K_6O_{12}]$	Octahedron	$(C_{102}H_{80}N_6)$
V. Silanoles + LiR $[Na]_x$ KH	[8]	$[Li_4O_4]$ $[Na_4O_4]$ $[K_4O_4]$	Cubes	$(C_{96}H_{84}O_{10}Si_8)$ $(C_{96}H_{84}O_6Si_8)$ $(C_{72}H_{60}Si_4)$

Density functional calculations[4] based on structural data confirm the ionic compositions of the aggregates (e.g.[4] Ba^{++}, Li^+, and O^{--}) and their considerable cluster stability (e.g.[5] $\Delta H_f > 5000$ kJ mol^{-1}). In contrast, the energy contributions of the hydrocarbon shells, as estimated from a statistical evaluation of phenyl ring centroid interactions, are only small (e.g.[5] $\Delta H_f \approx 50$ kJ mol^{-1}).

Based on the general principles outlined above, numerous and multifaceted supramolecular compounds can be anticipated.[9] In view of the considerable bond enthalpy difference, $\Delta H_b(Al-C) - \Delta H_b(Al-O) = (274 - 500) = -226$ kJ mol^{-1},[9] alumoxane clusters are expected to be especially favorable candidates.

Preparation and Structure Determination

A mixture of flammable triethylaluminum dimer and a stoichiometric amount of *n*-butyllithium[4] reacts vigorously with catechol in aprotic dimethoxyethane (DME) solution under argon (1) (see Experimental Section).



(1)

A crystalline reaction product can be isolated, provided that exposure to air and/or moisture is carefully avoided. Its structure determination (Figure 1), performed on a sample cooled to 150 K in a flow of nitrogen (see Experimental Section), reveals the formation of $\{[(DME_{1.5}Li^+)\text{-}(H_5C_2Al^{+++--}O_2C_6H_4)_2{}^{--}(Li^+DME)]_2\}_\infty$ (DME = $H_3COCH_2CH_2OCH_3$). The product contains a total of 18 oxygen centers in its polymer chain and is thus the most oxygen-rich polyion aggregate isolated to date (Table 1).

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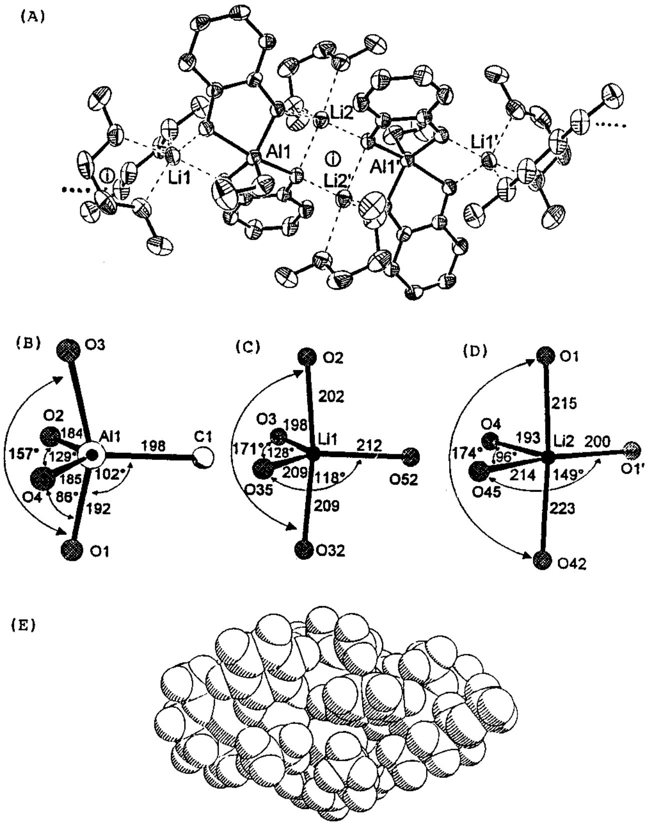
Figure 1. (A) Dimeric subunit of the lithium/aluminum organic polymer with thermal ellipsoids drawn at the 50% probability level and metal center notation; (B) to (D) Al^{++} and Li^+ coordination spheres, and (E) space-filling side view

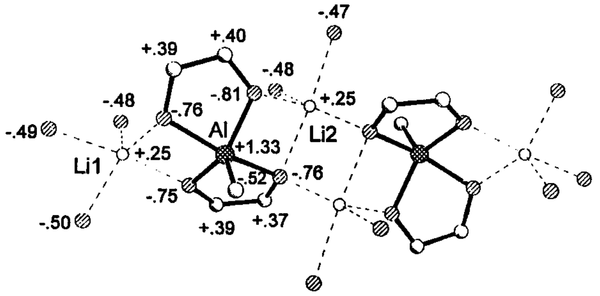


The crystal is seen to contain polymeric strands of dimethoxyethane-bridged subunits, the four-membered central (Li_2O_2) rings of which contain centers of inversion (Figure 1/A: ⓘ). The formally dipositive $(C_2H_5)Al^{++}$ center is fourfold coordinated to the four catecholate O^- centers and forms a distorted trigonal bipyramid with longer axial Al−O distances of 191 pm and the C center of lower effective nuclear charge in the expected equatorial position (Figure 1: B). The Li^+ countercations are also fivefold coordinated: Li1 to two catecholate and three DME oxygen centers, and Li2 to three catecholate and two DME oxygen centers (Figure 1: C and D). Due to the four-membered (Li_2O_2) ring formation, the trigonal bipyramids around the symmetry-equivalent countercations Li2 and Li2′ are more strongly distorted with O−Li2−O angles of up to 149° (Figure 1: D). The space-filling representation (Figure 1: E) illustrates how the hydrocarbon ($C_{36}H_{44}$) shell shields the oxygen-rich $[(Al^{++})_2(Li^+)_4(O_{18})^{-8}]$ cluster and renders it completely soluble in apolar solvents (see Experimental Section).

A search of the Cambridge Structural Database for cluster structures predominantly composed of Al, Li, and O atoms revealed only one monomer[10] bearing no relation to our polyion aggregate. In the meantime, we have been able to isolate crystals from an analogous mixture (1) with the parent molecule phenol.[11] According to their structure determination, these crystals contain a quadruple ion $\{[(H_5C_6O)_3(H_5C_2)Al]^- \cdots Li^+ \cdots {}^-[Al(C_4H_9)(OC_6H_5)_3]\}^-[Li^+(DME)_3]^+$, consisting of a complex triple-ion anion and a DME solvent-separated countercation.[12] Despite the fact that this system is also wrapped by a hydrocarbon skin ($C_{40}H_{40}$), there is no real analogy with the catechol-substituted $[Al_mLi_nO_x]$ polyion aggregate presented (Figure 1), since Al−O−Li connections are in this case completely absent.

Density Functional Calculations

For the polyion aggregate, with its molecular size exceeding 100 atoms, density functional calculations at the B3LYP level using 6-31G* basis sets (see Experimental Section) have been performed, based on the determined structural coordinates (Figure 1). Despite some uncertainty concerning the polarity within the ($Li_4Al_2O_{18}$) cluster, the following calculated Mulliken-type charge distribution (2) will be discussed.



(2)

For the ethyl-substituted and four-fold catecholate oxygen-coordinated Al centers, Mulliken charge densities of +1.33 are calculated, indicating covalent contributions to the ionic interactions $Al^{++} \cdots {}^-O$ as well. Furthermore, the catecholate anion charges are partially delocalized towards the Li^+ countercations, which are strongly solvated (Figure 1: C and D) by a total of six oxygen centers of three sterically unhindered dimethoxyethane chelate ligands. The total charges of the essential cluster components amount to approximately −1.0 for the catecholate ligands, −0.3 for the ethyl substituents, and about +0.2 for the DME solvent molecules. Considering the 18 differently charged oxygen centers, each transfers an average of about 0.7 of a negative charge to the six metal cations, decreasing the polyion aggregate character by metal−oxygen bonding contributions.

Conclusion and Perspectives

A vigorous reaction between triethylaluminum dimer, *n*-butyllithium, and catechol (1) yielded the title compound, which according to its structure determination is an unprecedented oxygen-rich polyion aggregate [$Li_4Al_2O_{18}$] wrapped by a lipophilic hydrocarbon skin ($C_{36}H_{44}$). The predominantly ionic interactions assumed are supported by density functional calculations.

This result encourages us to attempt further crystallizations of main-group element clusters, of which only the simplest examples are as yet known. It also suggests further exploration of (alkylaluminum + phenol) reaction mixtures, especially by those interested in novel ceramic materials, which are presumably accessible by firing hydrocarbon-wrapped clusters [$Li_nAl_mO_x$].

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Experimental Section

Preparation and Crystallization: In a rigorously dried Schlenk trap, 352 mg (3.2 mmol) of catechol was dissolved in 40 ml of anhydrous dimethoxyethane (DME). At −70°C, 1.6 ml (1.6 mmol) of a 1 M solution of triethylaluminum dimer in *n*-hexane followed by 1.5 ml (2.4 mmol) of a 1.6 M solution of *n*-butyllithium in *n*-hexane were quickly injected under argon. The mixture was shaken repeatedly during warming to room temperature. The surface of the solution was then covered with a layer of *n*-hexane and crystallization began after about 2 h. After 1 d, large transparent prisms had grown.

Crystal Structure Determination: $C_{24}H_{38}AlLi_2O_9$ (511.4), colourless prisms, crystal dimensions: $0.82 \times 0.48 \times 0.46$ mm, temperature 150 ± 2 K, $a = 1863.6(1)$, $b = 1486.6(1)$, $c = 2080.6(2)$ pm, $\beta = 1104.93(1)°$, $V = 5569.6(7)$ Å^3, $Z = 8$, $\rho_{\text{calcd.}} = 1.220$ gcm^{-3}, $\mu(\text{Mo-}K_\alpha) = 0.711$ Å, monoclinic, space group $C2/c$ (No. 15), Siemens P4 four-circle diffractometer, 5598 measured reflections in the range $3° \leq 2\theta \leq 52°$, of which 5410 were independent and 4188 had $I > 2\sigma(I)$. Structure solution by direct methods (SHELXS), 331 parameters refined against F^2 (SHELXL-93), $R = 0.041$, $wR_2 = 0.096$, residual electron density $+0.28/-0.26$ eÅ^{-3}, $S = 1.035$. The positions of Li, C, O, and Al were refined anisotropically; H centers were ideally geometrically positioned and refined using fixed displacement parameters within a riding model. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number CCDC-103178.

Density functional calculations were performed using the Gaussian-94 program. For the 104 cluster atoms, a total of 2576 Gaussian functions within 6-31G* basis sets were applied. The NEC SX4 computer system at the high performance computing center, Stuttgart, Germany, required 14.8 h of CPU time to calculate the total energy as −4053, 414614 a.u.

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