5046 *Inorg. Chem.* **1998,** *37,* 5046−5049

Articles

Preparation, Structure, and Density Functional Calculation of the Solvent-Separated Ion Pair $[(H_5C_2)Al(OC_6H_5)_3{}^{-}\cdots Li^{+}\cdots{}^{-}(H_5C_6O)_3Al(C_4H_9)]^{-}[Li^{+}(DME)_3]$[†]

H. Bock,[*] R. Beck, Z. Havlas,[‡] and H. Schödel

Institute of Inorganic Chemistry, University of Frankfurt, Marie-Curie-Strasse 11,
D-60439 Frankfurt am Main, Germany

Received December 12, 1996

Dimeric aluminum triethyl reacts in dimethoxyethane solution under argon with phenol and lithium *n*-butyl to the crystalline ethylaluminum−lithium−butylaluminum hexaphenolate salt with a solvent-separated tris(dimethoxyethane)lithium cation. Its structure determination at 130 K (monoclinic $P2_1/c$ with $Z = 4$, fw = 968.4, $a = 1275.6(1)$ Å, $b = 1889.0(1)$ Å, $c = 2381.5(1)$ Å, and $\beta = 104.59(1)°$, $wR_2 = 0.177$) proves a linear arrangement of the {Al(O)···Li···(O)Al} centers. Density function calculations based on the structural coordinates provide information on the charge distribution.

Introduction

Lipophilically wrapped polyion aggregates contain a metal salt cluster nucleus $[(Me^{n+}X^{n-}]$, which guarantees thermodynamic stabilization, and are surrounded by a hydrocarbon skin from the ligands $X^{-}(C_nH_m)$, which provides both kinetic shielding and solubility in nonpolar solvents. Within the last year, these aggregates proved to be an advantageous self-organization principle also for main group element compounds.[1,2] On the basis of the structural information collected,[2] the density functional as well as semiempirical calculations that were performed,[2a,b] and the experience gathered in crystallization with small temperature or concentration gradients,[2d] the so far serendipitous self-assembly of suitable compounds to lipophilically wrapped polyion aggregates can now be planned to some extent. For instance, starting from the considerable enthalpy difference between (Al−C) vs (Al−O) bonds, dimeric aluminum triethyl has been reacted under argon in dimethoxyethane solution with stoichiometric amounts of catechol and *n*-butyllithium.[1]

The structure determination shows polymeric strands of dimethoxyethane-bridged and subunits connected via four-membered (Li_2O_2) rings, $\{(DME_{1.5}Li^{+})(H_5C_2Al^{2+}(^{2-}O_2C_6H_4)_2\text{-}(Li^{+}DME)\}$. The formally 2-fold positive $(H_5C_2)Al^{2+}$ fragments are 4-fold coordinated to four oxygen anion centers of two catecholate ligands.[1] The space-filling representation of the structure (Scheme 1) convincingly demonstrates the complete lipophilic wrapping of the oxygen-rich polyion aggregate $[(Al^{2+})_2(Li^{+})_4(O_{18})^{8-11}]$ by its hydrocarbon skin $(C_{38}H_{46})$.[1]

Here we report on the reaction analogous to Scheme 1 with the monodentate phenol, which according to the structure determination of the crystalline product at 130 K in a cooled N_2 flow (Experimental Section), however, yields a different and partly puzzling result. A solvent-separated ion pair has been crystallized, the cation of which is the well-known tris(dimethoxyethane)lithium,[3] and the anion, a triple ion of two alkyl triphenoxyaluminate anions coordinated to a Li^{+} cation (Figure 1). Surprisingly, one aluminum ethyl substituent is replaced by an *n*-butyl group from the lithium *n*-butyl added for the phenol deprotonation. Density functional calculations based on the structural coordinates have been performed (cf. Experimental Section).

It is especially the solvent-separated ion pair (Scheme 2) with six phenolate ligands surrounding its two Al centers which, in analogy to the numerous metal aluminum alkoxides reported,[4] suggests a supplementary sequence of phenyl derivatives with different structures and unexpected molecular properties.[5]

---

[*] To whom correspondence should be addressed.

[†] Interaction in Molecular Crystals 131. For part 130, see ref 1.

[‡] Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Flemingova Nam 2, CS-11610 Prague 6, Czech Republic.

(1) Bock, H.; Beck, R.; Havlas, Z.; Schödel, H. *Chem. Ber.* **1998**, in press.

(2) Recent reports on lipophilically wrapped polyion aggregates include the following. (a) $\{[(Ba^{2+})_6(Li^{-})_3(O^{2-})_2]^{11+}(^{-}O{-}C(CH_3)_3)_{11}\text{-}(OC_4H_8)_3\}$: Bock, H.; Hauck, T.; Näther, C.; Rösch, N.; Staufer, M.; Häberlein, O. D. *Angew. Chem.* **1995**, *107*, 1439; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1353. (b) $\{[OP{-}N^{-}{-}PONa^{+}]_6(C_{144}H_{120}O_{24})\}$: Bock, H.; Schödel, H.; Havlas, Z.; Herrmann, E. *Angew. Chem.* **1995**, *107*, 1441; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1355. (c) $\{[(Li^{+})_6\text{-}(NH_3)_2(O^{-})_6](C_{88}H_{110}O_2)\}$: Bock, H.; John, A.; Näther, C.; Havlas, Z. *J. Am. Chem. Soc.* **1995**, *117*, 9367. (d) $\{[(K^{+})_6(O_{12})^{6-}](C_{102}H_{80}N_6)\}$: Bock, H.; Dienelt, R.; Schödel, H.; Havlas, Z. *Tetrahedron Lett.* **1995**, *36*, 7855. (e) $\{[(Li^{+})_4(O^{-})_4](C_{96}H_{84}O_{10}Si_8)\}$, $\{[(Na^{+})_4(O^{-})_4]\text{-}(C_{96}H_{84}O_6Si_8)\}$, $\{[(K^{+})_4(O^{-})_4(C_{72}H_{60}Si_4)\}$, and $\{[(Li^{+})_4(O^{-})_4]\text{-}(C_{64}H_{76}O_4Si_4)\}$: Bock, H.; Ansari, M.; Nagel, N.; Havlas, Z. *J. Chem. Soc., Chem. Commun.* **1998**, submitted.

(3) Bock, H.; Näther, C.; Havlas, Z.; John, A.; Arad, C. *Angew. Chem.* **1994**, *106*, 931; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 875.

(4) Cf. e.g. Mehrotra, R. C. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 269 and references therein.

(5) A CSD search (version 5.11) for structures containing Li, Al, and O centers yields 17 hits, of which, however, none concerns a lipophilically wrapped polyion aggregate such as that shown in Scheme 1[1], or one of its subunits. The only compound reported, which resembles some facets, however, is monomeric, contains a four-membered ring (AlO_2Li) surrounded by three sterically shielding 2,6-di(*tert*-butyl)-4-methylphenol ligands, and has been prepared from methylaluminum phenolate and diphenyl ketone (Power, M.; Bott, S. G.; Atwood, J. L.; Barron, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 3446.

S0020-1669(96)01484-X CCC: \$15.00

Scheme 1

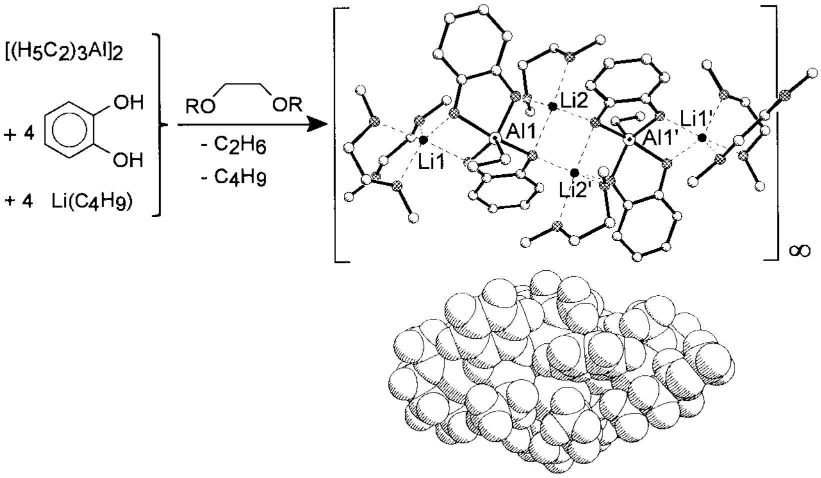

Table 1. Crystallographic Data and Refinement Details for the Solvent-Separated Ion Pair $[(H_5C_2)Al(OC_6H_5)_3{}^{-}\cdots Li^{+}\cdots{}^{-}(H_5C_6O)_3Al(C_4H_9)]^{-}[Li^{+}(H_3CO-CH_2-CH_2-OCH_3)_3]$

formula	$C_{53}H_{71.5}O_{12}Al_2Li_2$	space group	$P2_1/c$ (No. 14)
fw	968.4	T	130 K
a	12.756(1) Å	λ	0.7107 Å
b	18.890(1) Å	d_{calc}	1.158 g cm^{-3}
c	23.815(1) Å	μ(Mo Kα)	4.66 mm^{-1}
Z	4		
no. of unique reflns ($I > 2\sigma(I)$)	5116		
no. of variables	642		
β	104.59(1)	R_1	0.068[a]
V	5553.4(6) Å^3	wR_2	0.177[b]

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

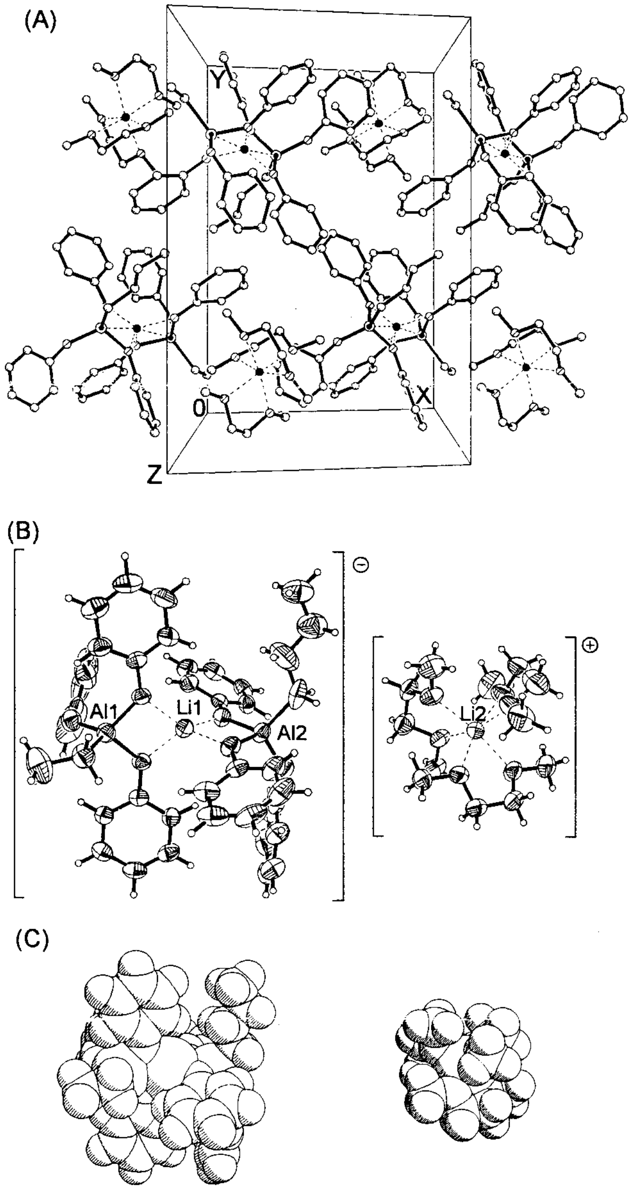

Figure 1. Crystal structure of $[(H_5C_2)Al(OC_6H_5)_3{}^{-}\cdots Li^{+}\cdots{}^{-}(H_5C_6O)_3Al(C_4H_9)]^{-}[Li^{+}(H_3CO-CH_2-CH_2-OCH_3)_3]$ at 130 K. (A) Unit cell (monoclinic $P2_1/c$, $Z = 4$) in Z direction (⊙, Al; ●, Li; ∅, O; ⊙, C; H omitted); (B) solvent-separated ion pair (50% thermal ellipsoids), and (C) space-filling representation.

Experimental Section

Preparation and Single-Crystal Growth of the Solvent-Separated Ion Pair. In a carefully dried Schlenk trap, the solution of 430 mg (4.6 mmol) of phenol in 25 mL of aprotic c_{H^+} (<1 ppm) dimethoxyethane is cooled to −70 °C and 1.5 mL of a 1.6 M *n*-butyllithium solution in *n*-hexane (2.4 mmol) and 1.5 mL of a 1 M hexaethyldialuminum solution in *n*-hexane (1.5 mmol) are injected consecutively in an argon atmosphere. On adding *n*-hexane layers every 3 days, the product crystallizes within 10 days at room temperature in colorless transparent blocks.

Collection and Refinement of X-ray Data. A single crystal of formate, 0.68 × 0.60 × 0.27 mm, was mounted under a continuous nitrogen flow at 130 K on a thin glass fiber. The data collection was carried out using an automated Siemens AED-II four-circle diffractometer employing Mo Kα radiation and a graphite monochromator. Intensity data were collected in the range $3 < 2\theta < 45°$ in the ω scan mode. Of the 7104 reflections measured, 5116 were independent with $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXTL-PLUS) followed by full-matrix least-squares refinement, which converged to final agreement factors of $R = 0.068$ and w$R_2 = 0.177$. After empirical absorption corrections, residuals of +0.59/−0.43 e/Å^3 were found; $S = 1.054$. All Li, C, O, and Al centers were anisotropically refined; the H centers were geometrically idealized, positioned, and refined with fixed isotropic parameters within a riding model. The C-positions, C5 and C6, of the *n*-butyl group (Figure 2A) have been refined assuming 50% population. Crystallographic data are summarized in Table 1, and atomic coordinates and thermal parameters are in Table 2.

Density Functional Calculations. Based on the structural coordinates determined (Table 2), the calculation has been performed at the B3LYP level with 6-31G* basis sets at the NEC SX4 of the Höchstleistungs-Rechenzentrum Stuttgart. For the computation, comprising a total of (1652 + 652) Gaussian functions, (3.7 + 0.5) hours

Scheme 2

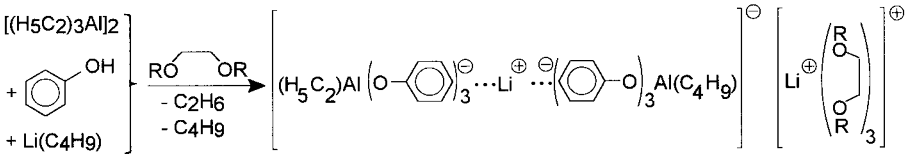

Table 2. Atomic Coordinates ($\times 10^4$) and Isotropic Displacement Parameters [Å^2 × 10^3] for $[(H_5C_2)Al(OC_6H_5)_3{}^{-}\cdots Li^{+}\cdots{}^{-}(H_5C_6O)_3Al(C_4H_9)]^{-}[Li^{+}(H_3CO{-}CH_2{-}CH_2{-}OCH_3)_3]$

	x	y	z	U_{eq}		x	y	z	U_{eq}
Al(1)	9042(1)	2547(1)	−1500(1)	49(1)	C(43)	6305(4)	30(2)	−1256(2)	61(1)
Al(2)	6801(1)	2179(1)	174(1)	49(1)	C(44)	5400(4)	−209(2)	−1104(2)	60(1)
Li(1)	7913(5)	2254(3)	−679(3)	45(2)	C(45)	4967(4)	182(2)	−732(2)	57(1)
C(1)	9987(4)	3399(3)	−1439(2)	65(1)	C(46)	5453(4)	813(2)	−507(2)	50(1)
C(2)	10367(6)	3592(4)	−1956(3)	108(2)	C(51)	8087(3)	3426(2)	225(2)	46(1)
C(3)	7214(5)	1651(3)	886(2)	80(2)	C(52)	8153(4)	3594(3)	794(2)	61(1)
C(4)	8177(7)	1168(5)	985(3)	133(3)	C(53)	8522(4)	4250(3)	1018(3)	76(2)
C(5)	8386(12)	686(8)	1485(6)	104(4)	C(54)	8832(4)	4735(3)	680(3)	74(2)
C(6)	9329(12)	311(6)	1557(6)	100(4)	C(55)	8764(4)	4585(3)	107(3)	70(2)
O(1)	8972(2)	2082(2)	−2124(1)	59(1)	C(56)	8390(3)	3922(2)	−129(2)	57(1)
O(2)	7734(2)	2745(1)	−1417(1)	44(1)	C(61)	4868(4)	3027(3)	−201(2)	54(1)
O(3)	9291(2)	1998(1)	−874(1)	43(1)	C(62)	5021(5)	3743(3)	−143(2)	71(1)
O(4)	6854(2)	1672(1)	−449(1)	47(1)	C(63)	4244(6)	4208(3)	−468(3)	90(2)
O(5)	7746(2)	2778(1)	3(1)	49(1)	C(64)	3313(5)	3934(4)	−844(3)	84(2)
O(6)	5573(3)	2571(2)	137(2)	64(1)	C(65)	3199(5)	3225(4)	−907(3)	86(2)
C(11)	8367(4)	1505(3)	−2322(2)	64(1)	C(66)	3949(4)	2774(3)	−589(2)	72(2)
C(12)	8609(6)	857(3)	−2111(3)	97(2)	Li(2)	2708(6)	3175(3)	1644(3)	45(2)
C(13)	8000(8)	288(4)	−2345(4)	114(3)	O(72)	2199(3)	2268(2)	2012(2)	77(1)
C(14)	7129(8)	317(6)	−2797(5)	133(4)	O(75)	3823(3)	3192(2)	2477(1)	68(1)
C(15)	6830(6)	1018(6)	−3038(4)	139(4)	O(82)	3064(3)	4206(2)	1422(1)	58(1)
C(16)	7448(5)	1576(3)	−2797(3)	86(2)	O(85)	1480(3)	3785(2)	1892(1)	61(1)
C(21)	7000(3)	3217(2)	−1711(2)	41(1)	O(92)	3901(2)	2680(2)	1287(1)	62(1)
C(22)	7094(3)	3511(2)	−2233(2)	44(1)	O(95)	1759(2)	2877(2)	822(1)	58(1)
C(23)	6352(4)	4005(2)	−2520(2)	53(1)	C(71)	1541(6)	1740(3)	1692(3)	111(2)
C(24)	5500(4)	4211(2)	−2292(2)	58(1)	C(73)	2994(6)	2020(4)	2496(3)	104(2)
C(25)	5403(3)	3915(2)	−1780(2)	55(1)	C(74)	3573(7)	2657(4)	2848(3)	115(2)
C(26)	6141(3)	3427(2)	−1489(2)	46(1)	C(76)	4475(6)	3725(4)	2767(3)	87(3)
C(31)	10162(3)	1587(2)	−641(2)	45(1)	C(81)	3612(4)	4369(3)	989(2)	62(1)
C(32)	11051(4)	1561(2)	−880(2)	61(1)	C(83)	2237(4)	4687(2)	1449(2)	64(1)
C(33)	11939(4)	1140(3)	−636(3)	74(2)	C(84)	1743(4)	4503(2)	1921(2)	66(1)
C(34)	11953(5)	744(3)	−146(3)	75(2)	C(86)	858(5)	3578(3)	2281(3)	86(2)
C(35)	11078(5)	761(3)	85(2)	80(2)	C(91)	4903(4)	2414(4)	1579(3)	93(2)
C(36)	10175(4)	1182(3)	−160(2)	65(1)	C(93)	3403(4)	2245(3)	795(2)	64(1)
C(41)	6367(3)	1055(2)	−661(2)	41(1)	C(94)	2443(4)	2656(3)	431(2)	73(2)
C(42)	6786(4)	659(2)	−1040(2)	51(1)	C(96)	859(4)	3218(3)	479(2)	65(2)

of CPU time were required. The total energy calculated for the solvent-separated ion pair amounts to −2571.215 367 6 au for the anion complex and to −934.031 874 3 au for the solvated Li$^+$ cation.

Results and Discussion

Crystal Structure. The ion pairs of the title compound are closely packed in layers with a repeated sequence in the *X* direction and an alternating one in the *Y* direction (Figure 1A). The solvent-separated cations $[Li(H_3CO{-}CH_2{-}CH_2{-}OCH_3)_3]^+$ and anions $[(H_5C_2)Al(OC_6H_5)_3{}^{-}\cdots Li^{+}\cdots{}^{-}(H_5C_6O)_3Al(C_4H_9)]^-$ (Figure 1B) are both lipophilically wrapped by hydrocarbon skins ($C_{12}H_{30}$) and ($C_{42}H_{44}$) (Figure 1C).

The structure refinement (Experimental Section) of the triple ion anion discloses that the Al2 center (Figure 1B) exhibits an approximately 50% *n*-butyl population, whereas for Al1 an exclusive ethyl substitution is confirmed. This surprise structural result can be rationalized by assuming that in the preparation (Experimental Section) an intermediate complex, $[(H_5C_2)Al(OC_6H_5)_3{}^{-}\cdots Li(C_4H_9)]$, is formed, which reacts to the isolated product with partial ethyl/*n*-butyl exchange.

A view of the bis(hexaphenoxyaluminate)lithium anion complex along its triple ion axis $(Al(O)_2{}^{-}\cdots Li^{+}\cdots{}^{-}(O_2)Al)$ (Figure 2A) reveals that the adjacent phenyl rings at the anionic aluminum centers Al1 and Al2 are almost perpendicular to each other. The interplanar angles between the H_5C_6 rings connected to the phenolate centers at 0 2 and 0 6 amount to 87°, and those at 0 1 and 0 4 are twisted 83° relative to each other. Highly correlated wave functions[6] predict substantial $\sigma_H\cdots\pi$ interactions for this herringbone-like arrangement and provide a reasoning for the eclipsed conformation determined for the triple ion anion (Figure 2A).

The triple ion backbone $[RAl(OC_6H_5)_3)^{-}\cdots Li^{+}\cdots{}^{-}(H_5C_6O)_3AlR(O)_3)]$ exhibits average angles ∠O−Al−O of 90° and ∠O−Li−O angles of 80° (Figure 2B), and therefore its ionic axis $(Al(O)_2{}^{-}\cdots Li^{+}\cdots{}^{-}(O)_2Al)$ is close to linear. The Al−O bonds are of standard lengths between 1.71 and 1.78 Å, and the average contact distances Li$^+\cdots$O of 1.94 and 1.97 Å are almost identical. In contrast, the Al−C bond lengths (Figure 2B) vary around an average value of 1.95 Å between 1.92 Å to the ethyl substituent and 1.99 Å pm to the *n*-butyl group. The Al centers with one ∠O−Al−O angle of only 90° and the longer Al−C bond are located in distorted tetrahedra, whereas the coordination geometry around the central Li1 cation with two

---

[6] Hobza, P.; Selzle, H. L.; Schlag, E. W. *J. Am. Chem. Soc.* **1994**, *116*, 3500.

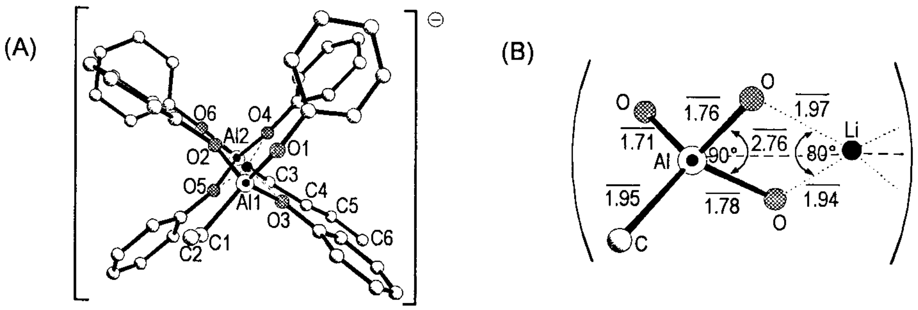

Figure 2. Structural details of the triple ion anion complex $[(H_5C_2)Al(OC_6H_5)_3^-\cdots Li^+\cdots{}^-(H_5C_6O)_3Al(C_4H_9)]^-$ (Figure 1). (A) Axial view with numbering and (B) details of the dialuminate coordination to the Li^+ center (average bond lengths and contact distances [Å]).

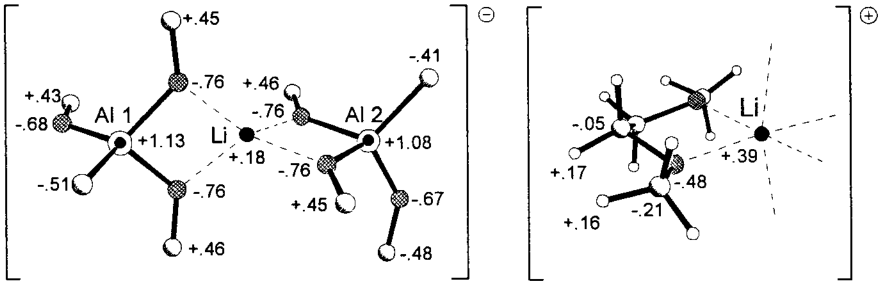

Figure 3. Density functional Mulliken charge orders for the inner part of the triple ion anion and the solvent-separated tris(dimethoxy)lithium cation of the title compound (⊙, Al; ●, Li; ∅, O; ⊙, C; ○, H; cf. text).

∠O−Li−O angles of 80° and four between 120 and 131° is considerably elongated, resulting in rather long contact distances $(Al(O_2)^-\cdots Li^+)$ of 2.76 Å (Figure 2B).

Density Functional Calculations. Based on the structural data and using a 6-31G* basis set at an B3LYP level (Experimental Section), the following charge densities result for the inner part of the triple ion anion complex and for the solvent-separated Li^+ countercation of the title compound with 144 centers altogether (Figure 3).

To begin with the anion complex, nearly equal charges of +1.13 and +1.08 are predicted for the different ethyl- or butyl-substituted Al centers. They are each coordinated to three rather negatively charged phenolate oxygens and one less negative alkyl carbon. Four of the six phenolate O^- centers are also connected to the central lithium, for which a small positive charge of +0.18 results. The total charges for the hydrocarbon substituents amount to an average value of −0.48 for the phenyl rings, −0.51 for the ethyl groups, and −0.26 for the butyl groups. The charges at their connecting carbon centers (Figure 3) are partly compensated especially by the considerably polarized $C^{\delta-}-H^{\delta+}$ bonds within the individual C_nH_m groups.

In the solvent-separated countercation, the tris(dimethoxyethane)-shielded Li^+ center bears a positive charge of only +0.39 and is 6-fold coordinated to dimethoxyethane oxygen centers, for each of which a negative charge of −0.48 is predicted. Again, these are largely compensated by the polarized $C^{\delta-}-H^{\delta+}$ bonds, and for each dimethoxyethane ligand a total charge of about −0.13 is approximated.

Far from considering partial charges, even when obtained from density functional calculations, as real in a molecular crystal, the results (Figure 3) suggest that the formally ionic link $(>Al(O)_2^-)Li^+({}^-(O)_2Al<)$, which represents the effective nuclear charges in the skeletal framework, is kept together by a considerable sharing of electron density between the individual centers.

Conclusions. A search in the Cambridge Structural Database[5] suggests that the solvent-separated ion pair presented, $[Al(OC_6H_5)_3^-\cdots Li^+\cdots{}^-(H_5C_6O)_3Al]^-[Li^+DME_3]$ (Figures 1 and 2), prepared from hexaethyldialuminum, phenol, and lithium *n*-butyl in dimethoxyethane (Scheme 2), as well as the lipophilically wrapped polyion aggregate, $\{[(Al^{2+})_2(Li^+)_4(O_{18})^{8-}](C_{38}H_{46})\}$ (Scheme 1) reported,[1] are the first derivatives of novel classes of aluminum−organic compounds with phenolate ligands.[5] Their formation, based on the tremendous difference in bond enthalpies (AlC) → (AlO), obviously represents another thermodynamically advantageous principle for the self-assembly of main group element molecules and, therefore, is recommended for further use.

Acknowledgment. The project on interactions in molecular crystals is generously supported by the Hoechst Corporation, the Fonds of the Chemical Industry, the German National Science Foundation, and the State of Hesse.

IC961484W