Crystallization and Structure of $\{(H_{53}C_{44}O_4{}^{3-})[Li^+{}_6(NH_3)_2]({}^{3-}O_4C_{44}H_{53})\}$, an Edge-Shared $Li^+{}_6$ Double Tetrahedron between Calix[4]arenetrianion Half-Shells: Another Self-Organized and Lipophilically-Wrapped Polyion Aggregate

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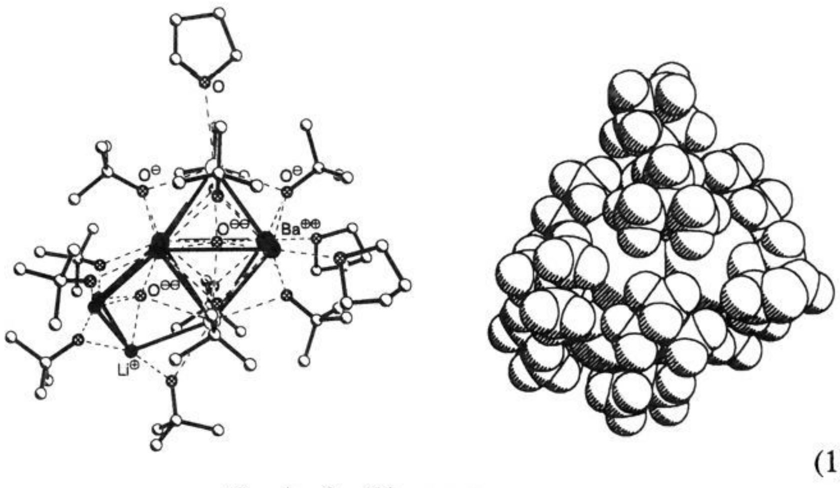
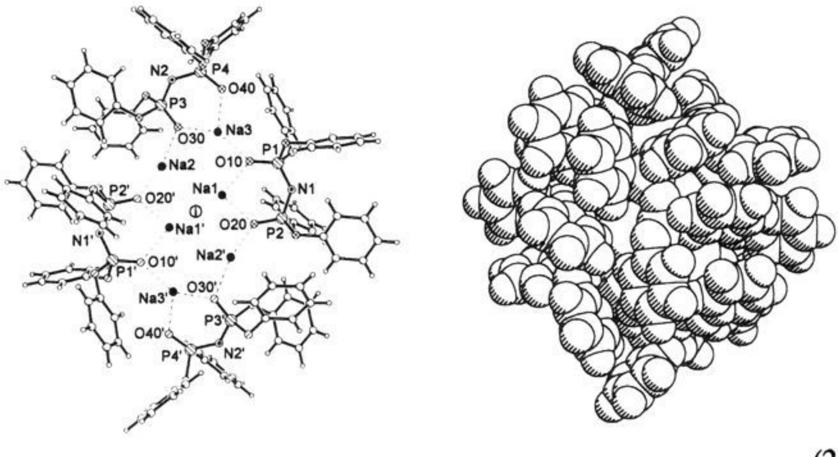
The first two examples[1a] of novel lipophilically-wrapped polyion aggregates,[2] in which a cluster of cations and anions provides thermodynamical stability and a kinetically persistent impenetrable hydrocarbon skin, have both been discovered serendipitously: the (octahedron + prismane) polyhedron (1) crystallized after addition of *n*-butyllithium to the solution obtained from dissolving barium metal in *tert*-butyl alcohol (1), and the hexameric sodium imido diphosphonate was prepared by reacting the tetraphenoxydiphosphonate imine with NaH in benzene (2):



(1)

$\{[Ba^{2+}{}_6Li^+{}_3O^{2-}{}_2]^{11+}({}^-OC(CH_3)_3)_{11}(OC_4H_8)_3\}$

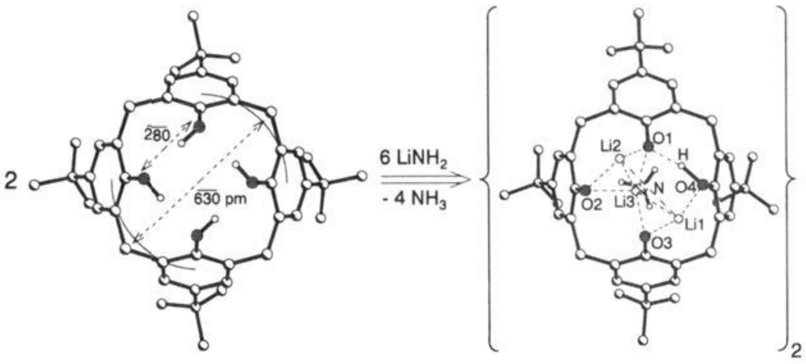


(2)

$\{(H_5C_6O)_{24}[OPN^-PONa^+]_6\}$

For the hexabarium−trilithium−dioxide−undecacation (1), a relativistic density functional calculation comprising 33 centers with 460 electrons substantiated the polyion cluster $[Ba^{2+}{}_6Li^+{}_3O^{2-}{}_2]$ and predicted a force constant $f_{12} \sim 0.1$ mdyn/Å for the O(1)−O(2) coupling.[1a] The interactions in the hydrocarbon skin have been analyzed statistically for the 24 phenoxy groups in the hexameric sodium phosphate (2) using centroid distances as well as interplanar angles and enthalpy contributions of about −50 kJ mol^{-1}, i.e. about one-hundredth of the Coulombic stabilization in the $(Na^+O^{\delta-}{}_2)_6$ core.[1a]

In the meantime we have learned how to design further examples of polyionic self-organization[3] limited by the van der Waals interactions[4] in the space-filling and slightly bonding[4] hydrocarbon skin and to crystallize them under aprotic conditions. A prototype example is *tert*-butylcalix[4]arene, the "C_{16}" perimeter of which shows an average diameter of 630 pm and holds four "HO" cation-docking sites with O•••O distances of about 280 pm:[5]



(3)

Reaction with lithium amide in aprotic toluene[6] yields ammonia and colorless prisms of the title compound. Its structure, determined at 150 K (Figure 1), shows an edge-shared $(Li^+{}_6)$ double tetrahedron fixed to each three O's in both of the calix[4]arene ligands and to an additional ammonia, which covers the open space between their four $(H_3C)_3CH_2C_6$ subunits. The view from the center of inversion between the two half-shells (3) shows the hydrogen bond $(1)O^{\delta-}\cdots H{-}O(4)$ of the unreacted fourth hydroxyl group to an adjacent $O^{\delta-}$ center (Figure 1, 1a•••4a).

The polyion aggregate $[Li^+{}_6O^-{}_6(HO)_2(NH_3)_2]$ in between the calix[4]arene hydrocarbon $(C_{44}H_{53})$ half-shells (Figure 1) contains twice three different Li^+ and O^- centers, two hydrogen bonds $O^-\cdots H{-}O$ and two NH_3 ligands (3). Altogether 35 short contact distances can be recognized, of which 11 are $Li^+\cdots Li^+$,

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(1) (a) Preceding examples are the *tert*-butanolate-wrapped cluster $[Ba_6Li_3O_2]^{+11}$ (Bock, H.; Hauck, T.; Näther, C.; Rösch, N.; Staufer, M.; Häberlen, O. D. *Angew. Chem.* **1995**, *107*, 1439; *Int. Ed. Engl.* **1995**, *34*, 1353) and the phenoxy-covered sodium imidodiphosphonate hexamer (Bock, H.; Schödel, H.; Havlas, Z.; Herrmann, E. *Angew. Chem.* **1995**, *107*, 1441; *Int. Ed. Engl.* **1995**, *34*, 1355). (b) Part of Ph.D. thesis: Näther, C. University of Frankfurt, 1994. (c) On leave from Czech Academy of Sciences, Flemingovo Nam, CZ, 16610 Prague.

(2) Despite considerable effort, a global search for analogous lipophilically-wrapped polyion aggregates in the Cambridge Structural Database provided no evidence for selected classes of compounds. The following reports are pointed out: (a) S- and Se-containing transition metal clusters are reviewed: Fenske, D.; Longini, G.; Schmid, G. In *Clusters and Colloids—From Theory to Applications* Schmid, G., Ed.; VCH Verlag: Weinheim, Germany, 1994; p 89−298. (b) Alkali metal oxides such as Rb_9O_2 or $Cs_{12}O_3$ with O-filled metal octahedrons are known since 1971 (cf. Simon, A. *Struct. Bonding* **1979**, *36*, 81. (c) Individual compounds comprise lithium 3,3-dimethyl-1-buten-2-olate−tetrahydrofuran $[(H_3C)_3C{-}C({=}CH_2)O^-Li^+(OC_4H_8)]_4$ (Amstutz, R.; Schweizer, W. B.; Seebach, D.; Dunitz, J. D. *Helv. Chim. Acta* **1981**, *64*, 2617) or nonameric sodium *tert*-butanolate $[(H_3C)_3CO^-Na^+]_9$ (Davies, J. E.; Kopf, J.; Weiss, E. *Acta Crystallogr., Sect. B* **1982**, *38*, 2251), of which the $(Li^+O^-)_4$ cubane is more lipophilically covered than the $(Na^+O^-)_9$, a double hexagon.

(3) Examples quoted are hexameric *aci*-9-nitrofluorene potassium, $\{(H_8(C_{12}C{=}N[O^-{}_2K^+]_6(OC_4H_8)_2(O_2C_4H_8)\}$, with a $K^+{}_6O^{\delta-}{}_{12}$ nucleus (Bock, H.; Dienelt, R.; Schödel, H.; Havlas, Z. *Tetrahedron Lett.*, submitted) or lithium−aluminium−bis(catecholate)−pentakis(dimethoxyethane), $\{(H_{76}C_{48})[Li^+{}_4Al^{2+}{}_2O^-{}_8O_{10}]\}$, containing a "$Li_4Al_2O_{18}$" string (Bock, H.; Beck, R.; Schödel, H.; Havlas, Z. Unpublished results. Cf. Beck, R. Master Thesis, University of Frankfurt, 1995.

(4) (a) Reviews: Bock, H. *Mol. Cryst. Liq. Cryst.* **1994**, *240*, 155. Or *Acta Nova Leopoldina* **1994**, *38*, 221 and references within. (b) Bock, H.; Meuret, J.; Ruppert, K. *Angew. Chem.* **1993**, *105*, 413; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 414. (c) Bock, H.; Meuret, J.; Ruppert, K. *J. Organomet. Chem.* **1993**, *445*, 19. (d) Bock, H.; Meuret, J.; Schödel, H. *Chem. Ber.* **1993**, *126*, 2227.

(5) Reviews on calixarenes containing structural details: Böhmer, V.; Mckervey, M. A. *Chem.—Ztg.* **1991**, *25*, 195−207 or Gutsche, D.; Igbal, M.; Nam. K. S.; See, K. A.; Alam, I. *Pure Appl. Chem.* **1988**, *60*, 483−488. For known metal complexes, cf. e.g.: Harrowfield J. M.; Ogden M. I.; White. A. H. *J. Chem. Soc., Dalton Trans.* **1991**, 2625 and (together with Richmond, W. R.) *J. Chem. Soc., Chem. Commun.* **1991**, 1159 or Atwood, J. L.; Bott, S. G.; Jones, C.; Raston C. L. *Ibid.* **1992**, 1344 and references within.

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20 $Li^+\cdots O^-$, two $Li^+\cdots N$, and two extremely short hydrogen bridges with distances $O\cdots(H)O$ of only 250(1) pm (!).[7] Based on the structural coordinates determined at 150 K[6] (Figure 1), MNDO calculations[8] have been performed to gather more detailed information. The MNDO charges for the individual centers, which range from +0.16 to +0.24 for $Li^{\delta+}$ and from −0.27 to −0.44 for $O^{\delta-}$, possibly underestimate the ionic character, including the $Li^{+0.16}\cdots N^{-0.11}$ coordination and the $O^{-0.44}\cdots H^{+31}{-}O^{-0.27}$ hydrogen bond. The MNDO enthalpy of formation, $\Delta H^{MNDO} = -63$ kJ mol^{-1}, can be subdivided into three consecutive steps:[8] (i) The formation of the $[Li^{\delta+}]_6$ cluster in its edge-shared double-tetrahedral arrangement which should require $\Delta\Delta H_f^{MNDO} = +9810$ kJ mol^{-1}—including the sum of six ionizations $6Li \rightarrow 6\ Li^+ + 6e^-$, $6\Delta H_f^{MNDO} = 6(656) = 3936$ kJ mol^{-1}, and allowing for all the individual, distance-dependent $Li^{\delta+}/Li^{\delta+}$ Coulomb repulsions. (ii) The fixation of the cluster $[Li^+]_6$ at the O centers of the two calix[4]arene half-shells without the $O^{\delta-}\cdots H{-}O$ bridges, $\{H_{53}C_{44}O_4{}^{3-})\text{-}[Li^+]_6({}^{3-}O_4C_{44}H_{53})\}$, yields the negative enthalpy difference $\Delta\Delta H_f^{MNDO} = -10\,960$ kJ mol^{-1}, or an averaged enthalpy of −550 kJ mol^{-1} for each of the 20 contacts $Li^{\delta+}\cdots O^{\delta-}$, which compares with the experimentally determined[9] value $\Delta H_f(Li_2O) = -591$ kJ mol^{-1}). (iii) For the NH_3 complexation at two of the $[Li^+]_6$ centers, $\Delta\Delta H_f^{MNDO} = -653$ kJ mol^{-1} is estimated.[8]

In the summary, the energetically favorable, largely ionic bonds $Li^{\delta+}\cdots O^{\delta-}$ add considerably to the thermodynamical stability of the title compound—as did the $Ba^{2+}\cdots O^-$ and $Li^+\cdots O^-$ Coulombic interactions in our first, serendipitously discovered lipophilically-wrapped polyion aggregate (1) with its $[Ba^{2+}{}_6Li^+{}_3O^{2-}]$ nucleus.[1a] Other structures are now known,[3] and there will be many more examples in the future to further substantiate the self-organization principle, based on an energetically advantageous ionic core and limited by van der Waals interactions in its lipophilic hydrocarbon skin.

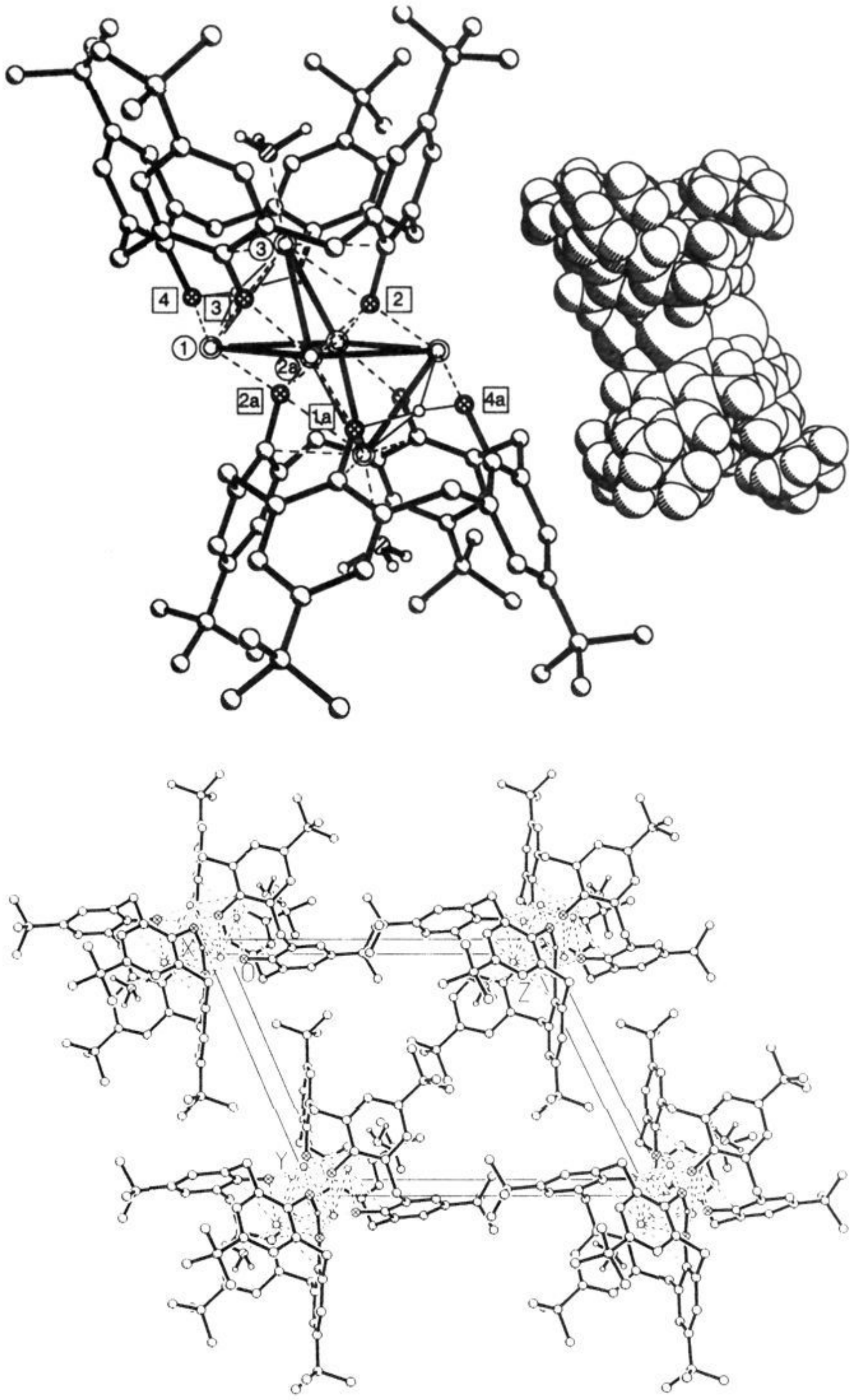

Figure 1. Single crystal structure (150 K)[6] of the polyion aggregate $[Li^+{}_6O^-{}_6(HO)_2(NH_3)_2]$ between two *tert*-butylcalix[4]arene hydrocarbon ($C_{44}H_{52}$) trianion half-shells. Upper left: Side view of the edge-shared double tetrahedron $(Li^+)_2(Li^+)_2(Li^+)_2$ with all Li^+ fixed to three of the four calixarene O centers (with the fourth HO(4) group hydrogen-bonded to (1) $O^{\delta-}$) and to one NH_3 ligand in each of the calix[4]arene cavities (O:Li^+; O:O; O:N, O:C). Selected bond lengths (pm) and angles (deg): Li(1)Li(2a), 257(1); Li(1)Li(2), 309(1); Li(2)Li(2a), 260(1); Li(2)Li(3), 276(1); Li(1)Li(3), 283(1); Li(2a)Li(3), 286(1); Li(1)O(2a), 190(1); Li(1)O(3), 184(1); Li(1)O(4), 185(1); Li(2)O(1), 192(1); Li(2)O(2), 203(1); Li(2)O(2a), 191(1); Li(2a)O(3), 191(1); Li(3)N, 205(1); O(1)(H)O(4), 250(1); Li(2a)Li(1)Li(2), 53.6(2); Li(2a)Li(1)Li(3), 63.6(2); Li(2a)Li(2)Li(1), 52.9(2); Li(2a)Li(2)Li(3), 64.4(2); Li(2a)Li(3)Li(2), 55.0(2); Li(1)O(3)Li(3), 95.2(3); Li(1)O(3)Li(2a), 86.7(3); Li(2a)O(3)Li(3), 93.9(3). Right: space-filling representation of the lipophilically-wrapped lithium plane between the two *tert*-butylcalix[4]arene half-shells. Bottom: Unit cell (monoclinic $P\bar{1}$, $Z = 2$) in *X*-direction. The crystal contains four toluene solvent molecules per formula unit, which fill interlattice positions with contact distances >370 pm to nearest centers.

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Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic thermal parameters, bond lengths and angles, and crystal data (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(6) **Preparation and Crystallization of Trilithium−4-*tert*-Butylcalix[4]arene**: To 0.5 g (0.77 mmol) of 4-*tert*-butylcalix[4]arene suspended in 15 mL of purified toluene at room temperature and under argon are added 0.07 g (3.05 mmol) of lithium amide and 10 mL of purified toluene. After being stirred for 45 min, the mixture is heated to reflux until a clear solution results. The hot solution is filtered under argon over a Schlenk frit, and after 1 week, colorless prisms of the title compound can be harvested. **Single Crystal Structure Analysis:** ($C_{40}H_{53}O_4Li_3{\cdot}NH_3{\cdot}2C_7H_8$) (M.G. = 775.85), $a = 1259.0(3)$ pm, $b = 1333.1(3)$ pm, $c = 1575.5(5)$ pm, $\alpha = 66.60(2)°$, $\beta = 89.95(2)°$, $\gamma = 71.12(1)°$, $V = 2271.3 \times 10^6$ pm^3 ($T = 150$ K), $\varrho_{calcd} = 1.134$ g cm^{-3}, triclinic, $P1$ (No. 2), $Z = 1$, Siemens P4 four-cycle diffractometer, Mo Kα irradiation, $\mu = 0.07$ mm^{-1}, 5773 measured reflections between $3° < 2\theta < 45°$, of which 5456 independent and 5452 used for refinement. Structure solution by direct methods and difference Fourier technique (SHELXS-86), refinement vs F^2(SHELXL-93), 577 parameters, $w = 1/[\sigma^2(F_o{}^2) + (0.0544P)^2 + 1.76P]$, R for 3690 $F_o > 4\sigma(F_o) = 0.0531$, wR^2 for all 5456 data = 0.1403, GOF = 1.042, rest electron density 0.22/−0.23 e/Å^3. The Li, C, N, and O positions are anisotropically refined. The H centers were set in the geometrical ideal positions and refined isotropically within the riding model using individual displacement parameters ($[U(H) = 1.5U_{eq}$ (C-methyl)], $[U(H) = 1.2U_{eq}$(C-methylene). The C centers of the toluene as well as of one *tert*-butyl group are disordered with respect to two orientations and, therefore, have been refined using a split model and isotropic displacement parameters.

(7) Cf.: Elmsley, J. Very Strong Hydrogen Bonding. *Chem. Soc. Rev.* **1980**, *9*, 91 references within.

(8) The MNDO calculations were performed using the program package SCAMP IV/1 (Dr. T. Clark, University of Erlangen) on our work station IBM RISC 6000/320. An additional test of the Li parameters yields a satisfactory reproduction of the first vertical ionization energy $Li \rightarrow Li^+ + e^-$ by 495 kJ mol^{-1} = 5.13 eV vs the experimental value $IE_1{}^v = 5.39$ eV.[8] For a methoxy-substituted cluster model $[Li^+)_6({}^-OCH_3)_6(HOCH_3)_2(NH_3)_2]$, an enthalpy of formation $\Delta H_f^{MNDO} = -1823$ kJ mol^{-1} is calculated for dissociation at the individual Li^+ centers, $(>Li^+\cdots{}^-OCH_3) \rightarrow\ >Li^+ + {}^-OCH_3$. Dissociation enthalpies ΔH_{diss} between −634 and −809 kJ mol^{-1} are approximated, and for methanol split-off, $(>Li^+\cdots O(H)CH_3) \rightarrow\ >Li^+ + HOCH_3$, $\Delta H^{MNDO} = 175$ kJ mol^{-1}. For the compexation $Li^+ \leftarrow NH_3$ at an optimized distance $d(Li^+\cdots N) = 207$ pm, an enthalpy difference $\Delta\Delta H_f^{MNDO} = -145$ kJ mol^{-1} results. For the addition of NH_3 to the complex $(Li^+)_6$(calix[4]arene) based on the structural data determined (Figure 1), surprisingly, a small repulsion is calculated, which indicates some spatial overcrowding.

(9) Wiberg, N. *Hollemann/Wiberg: Lehrbuch der Anorganischen Chemie, 91−100*. de Gruyter: Berlin/New York, 1985; p 954.