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A Novel Receptor for Ditopic Binding of Alkali Metal Halides

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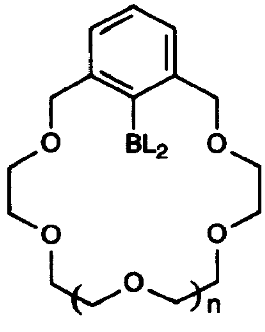
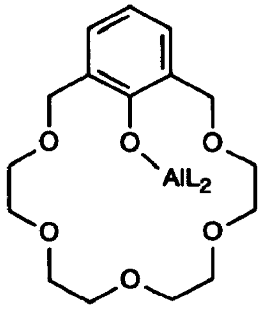
Abstract: *The aluminum phenolate* 2 *having a crown ether ribbon is a selective ditopic host for lithium and potassium salts LiX and KX (X = Cl, Br, I), whereas LiF and KF show no interaction.*

Synthetic receptors capable of binding anions selectively constitute an area of growing interest.[1] Although polyammonium macrocycles have been used most often,[1] preorganized Lewis acid hosts are beginning to show promise.[2] Generally, the host molecules which have been prepared for this purpose behave monotopically, i.e. there is little or no interaction with the cationic counterion. Ditopic binding in which both anion and cation participate in molecular recognition is quite rare.[1-4] We have previously shown that arylboronic acid esters containing crown ether moieties (**1**) bind potassium salts KF, KCN and $KOCH_3$ ditopically in organic solvents, whereas KI undergoes simple classical monotopic K^+-binding and KCl/KBr show no interaction at all.[4] In the ditopic cases the anion interacts with the boron center in the form of reversible dative bond formation, and the K^+ ion binds classically to the crown ether portion. Such selectivity within a particular metal salt series has not been found in any other host molecules. We now describe the synthesis and anion/cation binding properties of a ditopic receptor molecule (**2**) composed of an aluminum-phenolate[5] moiety surrounded by a crown ether ribbon which displays selectivities different from **1**.

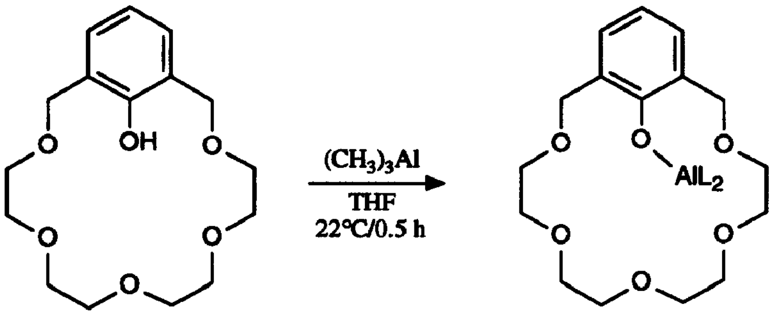


1 (n = 0, 1; L_2 = glycolate, catecholate)



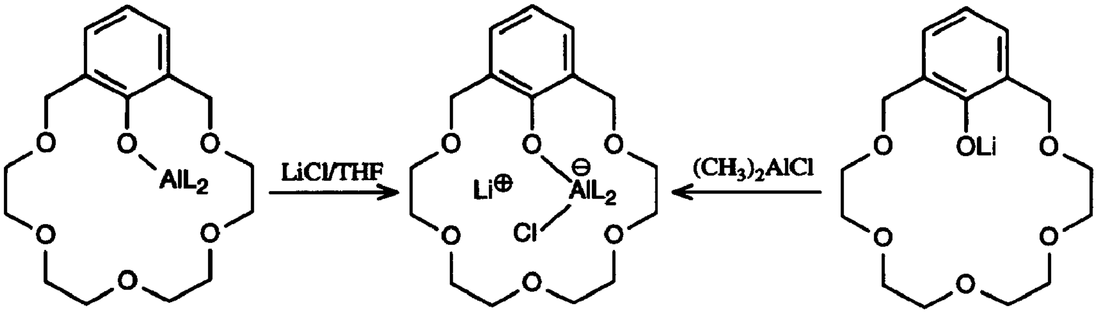
2 ($L = CH_3$)

Upon adding $(CH_3)_3Al$ to a solution of the known crown ether **3**[6] in THF, the phenolic function was metalated with concomitant generation of methane. The ^1H-NMR signal of the phenolic hydrogen in **3** disappeared completely. Compound **2** turned out to be a rather sensitive substance which has to be handled in an inert gas atmosphere. Its ^1H- and ^{13}C-NMR spectra are in accord with the structure shown. For example, the ^1H-NMR signal at 0.4 ppm integrating to 6 protons is readily assigned to the two methyl groups. In the ^{27}Al-NMR spectrum a singlet at 185 ppm (relative to $[Al(H_2O)_6]^{3+}$ as the external standard) speaks for a tri-coordinated aluminum nucleus,[7] although some degree of complexation by THF or crown ether oxygen function cannot be rigorously excluded.



3 **2** (L = CH_3)

Upon treating the host **2** with an equimolar amount of LiCl in THF-d_8, downfield ^{13}C-NMR shifts in the crown ether portion of the molecule are observed, in line with Li^+-binding. Significantly, the ^{27}Al-NMR signal shifts upfield from 185 to 148 ppm. This is strong evidence for chloride being bonded to aluminum as shown in the host/guest species **4**:



2 (L = CH_3) **4** (L = CH_3) **5**

In order to confirm the gross structure of **4**, an independent synthesis involving the reaction of the lithium phenolate **5** derived from **3** with $(CH_3)_2AlCl$ was performed. The product was identical in all respects with the previously prepared species **4**. A solution of the host/guest compound **4** was concentrated and cooled, which led to the formation of crystals. The X-ray structural analysis shows unambiguously the assumed ditopic binding of LiCl, i.e., Cl^- is attached to aluminum and Li^+ is encapsulated in the crown ether ribbon. Additional stabilization of Li^+ occurs by THF-complexation (Fig. 1).[8] It is also interesting to note that there is some interaction between Li^+ and the phenolate oxygen atom. The non-complexed portion of the crown ether ribbon itself and the coordinated THF turned out to be disordered (in two different attempts using different samples). Thus, the X-ray structural analysis has an overall poor quality. However, for the identification of the important structural features it is illuminating.

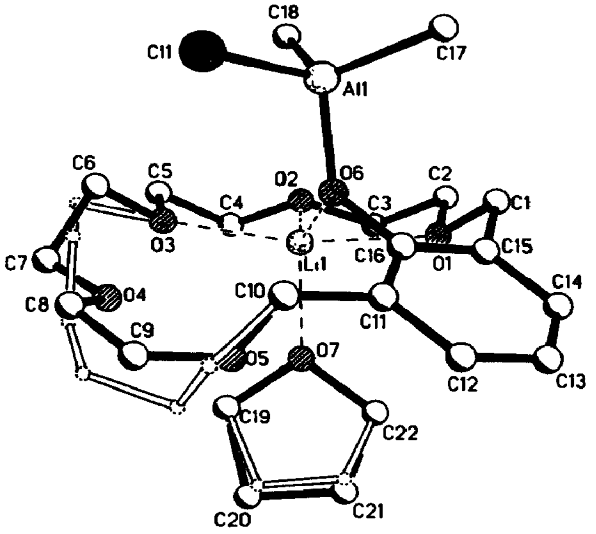


Fig. 1. Crystal structure of 4/THF (disorder indicated by the non-numbered positions)
Selected bond lengths in pm: Al(1) - O(6) = 180.4; Al(1) - C(18) = 205.5; Al(1) - C(17) = 201.7; Al(1) - Cl(1) = 217.6; O(6) - C(16) = 138.7; Angle C(16) - O(6) - Al(1) = 123.2°

In order to test potential binding selectivity with respect to different lithium salts, reactions of LiF, LiBr and LiI with the host **2** were studied. Whereas the suspension of LiF in THF showed no interaction with **2**, the salts LiBr and LiI behaved much like LiCl as evidenced by ^{1}H-, ^{13}C- and ^{27}Al-NMR studies. In these cases the salt suspensions dissolved rapidly and completely with formation of ditopic adducts. For example, the ^{27}Al-NMR signals for 2/LiBr and 2/LiI appear at 148 and 110 ppm, respectively, proving tetra-coordination at aluminum. The observed recognition pattern in the series LiX (X = F, Cl, Br, I) is the result of several factors, including differences in lattice energies of the salts, bond strengths of Al-X entities and solvation energies. Sorting these out on a quantitative basis is currently not possible. The potassium salts KF, KCl, KBr and KI showed qualitatively the same behavior. However, a significant kinetic effect was observed. Whereas the Li-salts bind rapidly within two hours quantitatively, the K-salts require about two weeks, during which partial decomposition of the complexes begins.

In summary, the host **2** displays unique binding selectivity within the series LiX and KX [X = F (no interaction), Cl/Br/I (all ditopic binding)]. Proof of heterotopic binding is derived from NMR experiments and an X-ray structure analysis.

Acknowledgement

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References and Notes

1. *Reviews*: Dietrich, B. *Pure Appl. Chem.* **1993**, *65*, 1457; Vögtle, F. *Supramolecular Chemistry*, Wiley, Chichester, England 1991; Lehn, J.-M. *Angew. Chem.* **1990**, *102*, 1347-1362; *Angew. Chem. Int. Engl.* **1990**, *29*, 1304.
2. Molecular recognition of anionic guests by preorganized Lewis acid hosts: Newcomb, M.; Horner, J. H.; Blanda, M. T.; Squattrito, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 6294-6301; Jurkschat, K.; Rühlemann, A.; Tzschach, A. *J. Organomet. Chem.* **1990**, *381*, C53-C56; Nadeau, F.; Simard, M.; Wuest, J. D. *Organometallics* **1990**, *9*, 1311-1314; Katz, H. E. *J. Org. Chem.* **1989**, *54*, 2179-2183; Yang, X.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem.* **1991**, *103*, 1519-1521; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1507; Jung, M. E.; Xia, H. *Tetrahedron Lett.* **1988**, *29*, 297-300; see also Reinhoudt's interesting work on metalloclefts: Van Doorn, A. R.; Bos, M.; Harkema, S.; van Eerden, J.; Verboom, W.; Reinhoudt, N. D. *J. Org. Chem.* **1991**, *56*, 2371-2380.
3. Schmidtchen has described a ditopic receptor in which a polyammonium macrocycle is connected to a crown ether moiety via a spacer; this interesting host binds the dipolar form of such amino acids as γ-amino butyric acid (GABA) selectively: Schmidtchen, F. P. *J. Org. Chem.* **1986**, *51*, 5161-5168.
4. Reetz, M. T.; Niemeyer, C. M.; Harms, K. *Angew. Chem.* **1991**, *103*, 1515-1517; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1472-1474.
5. Sterically hindered Al-phenolates have been used to bind ethers selectively: Maruoka, K.; Nagahara, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1990**, *112*, 6115-6117.
6. Browne, C. M.; Ferguson, G.; McKervey, M. A.; Mulholland, D. L.; O'Connor, T.; Parvez, M. *J. Am. Chem. Soc.* **1985**, *107*, 2703-2712; Skowronska-Ptasinska, M.; J.; Aarts, V. M. L. J.; Egberink, R. J. M.; van Eerden, J.; Harkema, S.; Reinhoudt, D. N. *J. Org. Chem.* **1988**, *53*, 5484-5491.
7. Akitt, J. W. in *Progress in Nuclear Magnetic Resonance Spectroscopy*; Emsly, J. W.; Feeney, J.; Sutcliffe, L. H. Eds.; Pergamon Press, Vol. 21, 1989, pp 1-149.
8. Crystal data for **4**, $C_{22}H_{27}AlClLiO_7$: Monoclinic space group $P2_1/n$, a = 9.631(2), b = 17.544(1), c = 15.187(4) Å, Z = 4, 6963 collected reflections (Enraf-Nonius CAD4-diffractometer, Cu-Kα-radiation, T = 173 K), 3223 independent reflections. Empirical absorption correction and structure solution with the Siemens-SHELXTL-PLUS-package, refinement on F^2 with all reflections with SHELXL-93, non hydrogen atoms anisotropic, hydrogens riding with fixed isotropic temperature factors. The macrocyclic ring and the THF-ligand are disordered and have been refined with restraints. Due to the poor data quality (R_{int} = 0.105, R_{sigma} = 0.09) and the disorder of a big part of the structure the refinement converged to wR2 = 0.34 (all data) and the conventional R-factor R1 = 0.135 ($I > 2\sigma(I)$) for 366 parameters and 101 restraints, Goodness-of-fit (on F^2) = 1.142. Further details of the crystal structure are available from the Cambridge Crystallographic Data Centre, University Chemical Lab., Lensfield Road, Cambridge CB2 1EW, U. K. Requests should be accompanied by a full literature citation for this communication.

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