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Selective Solid–Liquid Extraction of Lithium Halide Salts Using a Ditopic Macrobicyclic Receptor

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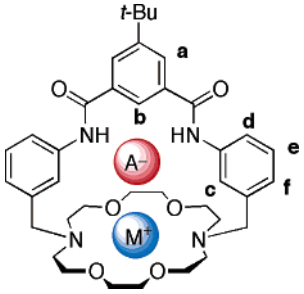
A ditopic salt receptor that is known to bind and extract solid NaCl, KCl, NaBr, and KBr into organic solution as their contact ion pairs is now shown by NMR and X-ray crystallography to bind and extract solid LiCl and LiBr as water-separated ion pairs. The receptor can transport these salts from an aqueous phase through a liquid organic membrane with a cation selectivity of $K^+ > Na^+ > Li^+$. However, the selectivity order is strongly reversed when the receptor extracts solid alkali metal chlorides and bromides into organic solution. For a three-component mixture of solid LiCl, NaCl, and KCl, the ratio of salts extracted and complexed to the receptor in $CDCl_3$ was 94:4:2, respectively. The same strong lithium selectivity was also observed in the case of a three-component mixture of solid LiBr, NaBr, and KBr where the ratio of extracted salts was 92:5:3. This observation is attributed to the unusually high solubility of lithium salts in organic solvents. The study suggests that ditopic receptors with an ability to extract solid salts as associated ion pairs may have application in separation processes.

Introduction

The extraction of salts from aqueous and solid sources is an important industrial topic.[1] Of particular interest is the selective extraction of lithium salts, with potential applications in high technology and medicine.[2] A major effort has been made to develop synthetic receptors that have a high and selective affinity for lithium cations.[3] In terms of liquid extraction and membrane transport, almost all reported efforts have focused on the transfer of lithium salts from an aqueous liquid phase into an organic liquid phase, which means that the supramolecular goal is develop an ionophore that can overcome the Hofmeister bias against lithium cation. In other words, the small lithium cation is strongly solvated in water, and an organic-soluble lithium ionophore has to have an affinity that is high enough to overcome the highly unfavorable Gibbs free energy for transfer from aqueous to organic phase. If an uncharged lithium ionophore is employed, then the efficiency of the extraction process is strongly affected by the properties of the extracted counteranion. For example, a competitive anion with a localized charge is much harder to extract. Two strategies can be envisioned to circumvent the interference of a competitive counteranion. One approach is to use a binary mixture of cation receptor and anion receptor (dual receptor strategy),[4] or alternatively, a single ditopic receptor can be employed that can simultaneously bind a cation and an anion (ditopic ion-pair receptor strategy).[5]

Chart 1. Ditopic Salt Receptor **1**



We are investigating the salt binding properties of ditopic salt receptor **1** (Chart 1). Previously, we have reported that compound **1** has an impressive ability to solubilize monovalent salts in nonpolar organic solvents.[6] The receptor achieves this by binding the salts as contact ion pairs. Receptor **1** can also transport alkali metal halide salts out of an aqueous

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(1) (a) *Principles and Practices of Solvent Extraction*; Rydberg, J., Nusikas, C., Choppin, G. R., Eds.; Marcel Dekker: New York, 1992. (b) *Fundamentals and Applications of Anion Separations*; Moyer, B. A., Singh, R. P., Eds.; Kluwer: Dordrecht, The Netherlands, 2004.
(2) Bartsch, R. A.; Ramesh, V.; Bach, R. O.; Shono, T.; Kimura, K. In *Lithium Chemistry-A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995; Chapter 10.
(3) Severin, K. *Coord. Chem. Rev.* **2003**, *245*, 3−10 and references therein.

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phase and through a phospholipid bilayer[7] or a liquid organic membrane.[8] For a constant anion, the membrane transport selectivity is $K^+ > Na^+ > Li^+$. In this present contribution, we quantify the ability of **1** to extract solid alkali metal chlorides and bromides into organic solution, and we find that the selectivity order is strongly reversed; that is, the process is highly lithium selective.[9] This observation is attributed to the unusually high solubility of lithium ion pairs in organic solvents. The study highlights the strategic advantage that is gained by using a ditopic salt receptor (such as **1**) that has an ability to extract solid salts as associated ion pairs.

Results and Discussion

NMR Studies of Single Salt Extraction. Solid/liquid extraction studies were performed by allowing a solution of **1** in $CDCl_3$ to stand over an excess of a powered alkali metal chloride or bromide salt in an NMR tube. The extractions were monitored by ^1H NMR. Peaks corresponding to a receptor:salt complex appeared over time (exchange between the free receptor and receptor:salt complex was slow on the NMR time scale), and after about 2 weeks the receptor **1** was saturated with salt. The changes in receptor chemical shift, listed in Table 1, are consistent with the formation of a 1:1 receptor:salt complex with the salt bound inside the receptor cavity. Furthermore, previous NMR titration studies have shown that **1** prefers to bind alkali metal halides in organic solution as their associated ion pairs (i.e., **1**:M^+A^-) rather than a mixture of **1**:M^+ and **1**:A^-.[6]

X-ray Structures. X-ray-quality crystals were grown by slow evaporation (over a few weeks) of solutions of [**1**·LiCl] and [**1**·LiBr] in ethyl acetate. The crystallization vessels were loosely capped, and no effort was made to exclude water from the atmosphere. Unlike the previously reported crystal structures of [**1**·NaCl], [**1**·KCl], [**1**·NaBr], and [**1**·KBr], which all have the salt complexed inside the receptor as a contact ion pair,[8] the lithium salt structures have a bridging water molecule between the cation and the anion (Figures 1 and 2).[10] Presumably, the water is derived adventitiously from the atmosphere during the weeks long crystallization process. Incorporation of water within the coordination sphere of Li^+

Table 1. Change in Receptor ^1H NMR Chemical Shifts (ppm) upon Salt Extraction into $CDCl_3$[a]

proton	LiCl	NaCl[b]	KCl[b]	LiBr	NaBr[b]	KBr[b]
NH	+0.79	+0.94	+1.32	+0.58	+0.83	+0.97
H_a	−0.04	+0.02	−0.11	−0.01	+0.17	−0.10
H_b	+0.38	+0.66	+0.44	+0.61	+0.55	+0.23
H_c	+0.67	+0.87	+0.61	+0.89	+0.81	+0.69
H_d	+0.01	+0.07	+0.05	−0.07	−0.02	+0.02
H_e	−0.04	−0.05	0.00	−0.03	−0.02	−0.01
H_f	−0.05	−0.06	−0.01	−0.10	−0.06	−0.05

[a] $T = 295$ K. See Chart 1 for the hydrogen-labeling diagram. Negative value indicates upfield movement toward zero ppm. All spectra referenced to tetramethylsilane (0.00 ppm). [b] Data from ref 8.

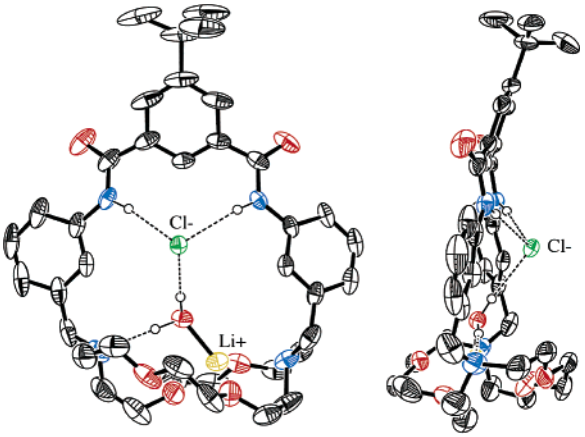

Figure 1. Front and side views of the ORTEP structure of [**1**·Li·H_2O·Cl], showing 50% probability ellipsoids. The solvent in the crystal lattice has been excluded for clarity. Only relevant protons are shown.

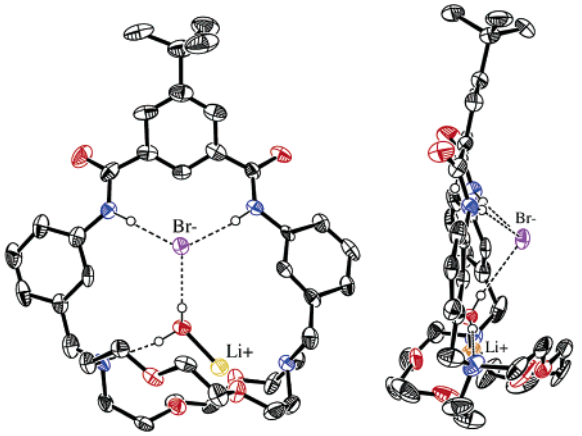

Figure 2. Front and side views of the ORTEP structure of [**1**·Li·H_2O·Br], showing 50% probability ellipsoids. The solvent in the crystal lattice has been excluded for clarity. Only relevant protons are shown.

(4) Recent examples of dual receptor systems that simultaneously complex an anion and a cation: Byriel, K. A.; Gasperov, V.; Gloe, K.; Kennard, C. H. L.; Leong, A. J.; Lindoy, L. F.; Mahinay, M. S.; Pham, H. T.; Tasker, P. A.; Thorp, D.; Turner, P. *Dalton Trans.* **2003**, 3034−3040. Cafeo, G.; Gargiulli, C.; Gattuso, G.; Kohnke, F. H.; Notti, A.; Occhipinti, S.; Pappalardo, S.; Parisi, M. F. *Tetrahedron Lett.* **2002**, *43*, 8103−8106. Cafeo, G.; Gattuso, G.; Kohnke, F. H.; Notti, A.; Occhipinti, S.; Pappalardo, S.; Parisi, M. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 2122−2126. Qian, Q.; Wilson, G. S.; Bowman-James, K.; Girault, H. H. *Anal. Chem.* **2001**, *73*, 497−503. Kavallieratos, K.; Moyer, B. A. *Chem. Comm.* **2001**, 1620−1621. Kavallieratos, K.; Sachleben, R. A.; Van Berkel, G. J.; Moyer, B. A. *Chem. Comm.* **2000**, 187−188.

(5) For recent papers that discuss ditopic salt-binding receptors, see: Turner, D. R.; Spencer, E. C.; Howard, J. A. K.; Tocher, D. A.; Steed, J. W. *Chem. Commun.* **2004**, 1352−1353. Plieger, P. G.; Tasker, P. A.; Galbraith, S. G. *Dalton Trans.* **2004**, 313−318. Pajewski, R.; Ferdani, R.; Schlesinger, P. H.; Gokel, G. W. *Chem. Commun.* **2004**, 160−161. Zhou, L.; Sun, H.; Li, H.; Wang, H.; Zhang, X.; Wu, S.; Lee, S. *Org. Lett.* **2004**, *6*, 1071−1074. Gale, P. A. *Coord. Chem. Rev.* **2003**, *240*, 191−221. Shukla, R.; Kida, T.; Smith, B. D. *Org. Lett.* **2000**, *2*, 3039−3248. Deetz, M. J.; Shang, M.; Smith, B. D. *J. Am. Chem. Soc.* **2000**, *122*, 6201−6207.

(6) Mahoney, J. M.; Beatty, A. M.; Smith, B. D. *J. Am. Chem. Soc.* **2001**, *123*, 5847−5848. Mahoney, J. M.; Marshall, R. A.; Beatty, A. M.; Smith, B. D.; Camiolo, S.; Gale, P. A. *J. Supramol. Chem.* **2001**, *1*, 289−292. Mahoney, J. M.; Davis, J. P.; Smith, B. D. *J. Org. Chem.* **2003**, *68*, 9819−6820.

(7) Koulov, A. V.; Mahoney, J. M.; Beatty, A. M.; Smith, B. D. *Org. Biomol. Chem.* **2003**, *1*, 27−29.

(8) Mahoney, J. M.; Nawaratna, G. U.; Beatty, A. M.; Duggan, P. J.; Smith, B. D. *Inorg. Chem.* **2004**, *43*, 5902−5907.

(9) Examples of solid−liquid extraction of lithium salts with weakly competitive counteranions include the following: Inokuma, S.; Takezawa, M.; Satoh, H.; Nakamura, Y.; Sasaki, T.; Nishimura, J. *J. Org. Chem.* **1998**, *63*, 5791−5796. Inokuma, S.; Yamamoto, T.; Nishimura, J. *J. Org. Chem.* **1990**, *31*, 97−100. Nishizawa, K.; Takano, T.; Ikeda, I.; Okahara, M. *Sep. Sci. Technol.* **1988**, *23*, 333−343.

(10) The unit cell in the [**1**·LiBr] crystal contains four independent but structurally similar complexes.

is fairly common in crystal structures of lithium salts complexed by macrocycles.[11] In both crystal structures, the Li^+ is coordinated by four of the six crown heteroatoms (three oxygens and one nitrogen), with a water oxygen acting as a fifth coordination atom. The average $Li-O_{crown}$ distance in both structures is 2.11 Å for the three coordinating crown oxygens. The average $Li-O_{water}$ distances are 1.90 and 1.91 Å, for LiCl and LiBr, respectively, whereas the Li−N distances for the coordinating crown nitrogen are 2.37 and 2.33 Å, respectively. The Cl^- is hydrogen bonded to the amide NH residues (average N−Cl distance of 3.30 Å and average N−H−Cl angle of 177.5°) and to the bound water (Cl−O distance is 3.10 Å). Similarly, the Br^- has an average $N_{amide}-Br$ distance of 3.41 Å, an average N−H−Br angle of 176.9°, and an average $Br-O_{water}$ distance of 3.29 Å.

Competitive Solid−Liquid Salt Extraction. Recently, we described how ditopic receptor **1** can transport alkali metal halides through a liquid organic membrane.[8] In particular, a competitive transport experiment was conducted with a polymer-supported liquid membrane containing **1** (50 mM) and an aqueous source phase containing a mixture of KCl, NaCl, and LiCl (1 M of each). After 3 h of transport the ratio of metal cations in the aqueous receiving phase was found to be K^+ (81%), Na^+ (19%), and Li^+ (0%). This trend is in general agreement with the Hofmeister series, a solvation-based selectivity bias that is typically observed for liquid/liquid partitioning processes.[12] Transport fluxes decrease with the smaller, more charge-dense ions because they have a more unfavorable Gibbs free energy for aqueous to organic transfer.[13] The data indicates that the Hofmeister bias overwhelms any difference in salt/receptor binding affinities.

In this study we evaluate the ability of **1** to extract solid salts into organic solution. Specifically, competitive solid/liquid salt extraction studies were undertaken using solutions of **1** in $CDCl_3$ layered over mixtures of equal molar amounts of powdered alkali metal chloride or bromide salts. Control experiments showed that exchange between the different receptor/salt complexes is slow on the NMR time scale. Thus, the ^1H NMR signals for each complex could be observed directly and their relative concentrations measured from the signal integration. For a three-component mixture of solid LiCl, NaCl, and KCl, the ratio of salts extracted and complexed to **1** in $CDCl_3$ (i.e., **1**·LiCl:**1**·NaCl:**1**·KCl) was 94:4:2, respectively. The same strong lithium selectivity was also observed in the case of a three-component mixture of solid LiBr, NaBr, and KBr where the ratio of extracted salts was 92:5:3. In other words, solid/organic extraction with salt receptor **1** produces a cation selectivity order that is highly lithium selective and reverse to that observed for aqueous/organic extraction.

Scheme 1. Two-Step Process for Extraction of Salt, M^+A^-, Using a Salt Receptor R[a]

$$M^+_{aq} + A^-_{aq} \overset{K_p}{\rightleftharpoons} (M^+A^-)_{org} \overset{K_a,\ R}{\rightleftharpoons} R\cdot(M^+A^-)_{org} \quad \textbf{(eq 1)}$$

$$(M^+A^-)_{solid} \overset{K_p}{\rightleftharpoons} (M^+A^-)_{org} \overset{K_a,\ R}{\rightleftharpoons} R\cdot(M^+A^-)_{org} \quad \textbf{(eq 2)}$$

[a] Aqueous/organic extraction is shown in eq 1, and solid/organic extraction is shown in eq 2.

These results can be rationalized in terms of the equilibria that govern aqueous/organic extraction and solid/organic extraction (Scheme 1). Extraction of a salt, M^+A^-, into an organic phase mediated by a salt receptor, R, can be considered as a two step process. The first equilibrium, K_p, involves partitioning of the salt into the organic phase, and the second equilibrium, K_a, concerns association of the partitioned salt with the receptor. The case of aqueous/organic extraction (eq 1) has already been described above, where the equilibrium step controlling liquid membrane transport and determining cation selectivity is K_p (which follows the Hofmeister series).

The notable result reported here is that solid/liquid extraction mediated by **1** (eq 2) is highly lithium selective. This is also due to large differences in the partitioning equilibrium K_p; however, the order of K_p for solid/liquid extraction is opposite to that for aqueous/organic extraction. Solid LiCl and solid LiBr are significantly more soluble in nonpolar solvents than the corresponding sodium or potassium salts.[14] The bonding in alkali metal halides, including lithium halides, is predominantly ionic; however, many lithium salts are known to have unusually low melting points and good solubilities in organic solvents.[15] This is due to the small size of the lithium cation and the molecular nature of its associated ion pairs.[16]

The mechanism for salt transfer from aqueous to organic is not the same as the mechanism for solid/organic partitioning. Aqueous/organic partitioning involves the transfer of individual, hydrated ions that subsequently associate in the organic phase, whereas solid/organic partitioning more likely involves the transfer of associated ion pairs from solid to organic phase.[17] In this latter case, it appears that receptor **1** binds the solubilized ion pairs[18] and retains them in organic solution,[19] which converts the large differences in solid/organic K_p into a potentially useful, lithium-selective extraction process.[20]

(11) Olsher, U.; Izatt, R.; Bradshaw, J. S.; Dalley, N. K. *Chem. Rev.* **1991**, *91*, 137−164. Boulatov, R.; Du, B.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1999**, *38*, 4554−4558. Chivers, T.; Downard, A.; Parvez, M.; Schatte, G. *Inorg. Chem.* **2001**, *40*, 1975−1977.

(12) Levitskaia, T.; Marquez, M.; Sessler, J. L.; Shriver, J. A.; Vercouter, T.; Moyer, B. A. *Chem. Commun.* **2003**, 2248−2249.

(13) Olsher, U.; Kankins, M.; Kim, Y. D.; Bartsch, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 3370−3371.

(14) The solubility of LiBr and LiCl in dry $CDCl_3$ was determined to be 0.9 and 0.1 mg/mL, respectively, whereas the solubilities of NaCl, KCl, NaBr, and KBr in dry $CDCl_3$ are all less than 0.02 mg/mL.

(15) Snaith, R.; Wright, D. S. In *Lithium Chemistry-A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995; Chapter 8.

(16) Excellent lithium salt solubility is often seen when the solvent contains a polar aprotic additive (such as TMEDA or HMPA) that can coordinate to the lithium and produce solvated ion-pair aggregates with an ionic core and an organic periphery.

(17) A property that in many ways is analogous to hydration energy is the salt lattice energy, which in the case of chloride salts is LiCl (834 kJ/mol) > NaCl (769 kJ/mol) > KCl (701 kJ/mol) > CsCl (657 kJ/mol). However, this property does not correlate with solubility of the solid salt in an organic solvent.

The ability of **1** to extract salts as associated ion pairs is likely a major reason it is so effective at solubilizing solid alkali metal halide salts in organic phases. Receptor systems that extract solid salts as separated ions (i.e., a dual receptor system, or a ditopic receptor that simultaneously binds a cation and an anion as spatially separated ions) have to overcome a Coulombic penalty due to ion separation, which should produce two effects: diminished ability to extract solid salts into organic phases; diminished extraction selectivity for lithium salts since they have the highest lattice energies. There is literature evidence for the former,[21] whereas the latter remains to be tested.

Conclusions

The ditopic salt receptor **1** is able to extract solid alkali metal halides into organic solution as associated ion pairs. It appears that NaCl, KCl, NaBr, and KBr are extracted as contact ion pairs, and solid LiCl and LiBr are extracted as water-separated ion pairs (Figures 1 and 2). Receptor **1** can transport these salts from an aqueous phase through a liquid organic membrane with a cation selectivity of $K^+ > Na^+ > Li^+$. However, the selectivity order is strongly reversed when receptor **1** extracts solid alkali metal chlorides and bromides into organic solution; that is, the process is highly lithium selective. This observation is attributed to the unusually high solubility of associated lithium ion pairs in organic solvents. Thus, receptor **1** may have utility as an extractant in lithium salt purification processes. From a more general perspective, solid/liquid extraction may be a strategy that is applicable to other salts. The aim would be to design and construct multitopic receptors with an ability to extract the solid salts as associated ion pairs.

Experimental Section

X-ray Crystallography. X-ray crystal determinations were performed on a Bruker Apex diffractometer, with graphite monochromated Mo Kα (λ = 0.710 73 Å) radiation at 170 K. The structures were solved by direct methods using SHELXS-97 and refined using SHELXL-97 (G. M. Sheldrick, University of Göttingen).

[1·Li·H$_2$O·Cl]. Receptor **1** in $CHCl_3$ was saturated with LiCl by solid−liquid extraction. X-ray-quality crystals were obtained by slow evaporation of a solution of the complex in ethyl acetate. The crystallization vessel was loosely capped, but no effort was made to exclude water from the atmosphere. Crystallographic summary: orthorhombic, *Pbca*; $Z = 8$ in a unit cell of dimensions a = 10.9083(7) Å, b = 12.6401(8) Å, c = 33.139(2) Å, α = 90°, β = 96.319(2)°, γ = 90°, and V = 4541.5(5) Å^3; μ(Mo Kα) = 0.144 mm^{-1}; D_{calcd} = 1.245 Mg/m^3; R1 ($I > 2\sigma(I)$) = 12.46%, wR2 ($I > 2\sigma(I)$) = 30.27% for 11 275 observed independent reflections. Hydrogen atom positions were generated at idealized positions, except for hydrogen atoms bound to nitrogen atoms and water oxygen atoms, which were located from the difference map. A riding model with fixed thermal parameters [$u_{ij} = 1.2U_{ij}$(eq) for the atom to which they are bonded] was used for subsequent refinements. The asymmetric unit contains a macrocycle with associated LiCl ion pair with bound water molecule, one disordered ethyl acetate molecule located in two positions (50% occupancies), and half of a disordered ethanol molecule (located on an inversion center). The source of the ethanol is likely from the initial $CHCl_3$ which contained 0.5−1% ethanol as a stabilizer. The X-ray data can be retrieved from the Cambridge Crystallographic Data Center using deposition no. CCDC 215469.

[1·Li·H$_2$O·Br]. Receptor **1** was saturated with LiBr by solid−liquid extraction. X-ray-quality crystals were obtained by slow evaporation of a solution of the complex in ethyl acetate. The crystallization vessel was loosely capped, but no effort was made to exclude water from the atmosphere. Crystallographic summary: orthorhombic, *Pbca*; $Z = 8$ in a unit cell of dimensions a = 21.7876(9) Å, b = 25.7171(10) Å, c = 33.3343(13) Å, α = 90°, β = 100.7300(10)°, γ = 90°, and V = 18351.1(13) Å^3; μ(Mo Kα) = 0.953 mm^{-1}; D_{calcd} = 1.267 Mg/m^3; R1 ($I > 2\sigma(I)$) = 6.70%, wR2 ($I > 2\sigma(I)$) = 17.83% for 31 895 observed independent reflections. Hydrogen atom positions were generated at idealized positions, except for hydrogen atoms bound to nitrogen atoms and water oxygen atoms, which were located from the difference map. A riding model with fixed thermal parameters [$u_{ij} = 1.2U_{ij}$(eq) for the atom to which they are bonded] was used for subsequent refinements. The asymmetric unit contains four macrocycles with associated LiBr ion pairs and lithium-coordinated water molecules, three water molecules (40% occupancy each), and six ethyl acetate molecules (three with 100% occupancies, the remaining at 60%, 58%, and 50% occupancies). Hydrogen atoms for the low-occupancy water molecules were not included in the refinement. All solvent molecules except the coordinated water molecules were refined isotropically. The structure was refined in the space group *Cc* as a two-component chiral twin (TWIN command) with 51%/49% contributions (BASF parameter). The X-ray data can be retrieved from the Cambridge Crystallographic Data Center using deposition no. CCDC 215470.

Single Salt Extractions. Solutions of receptors in $CDCl_3$ (~10 mM) were prepared in 5 mm NMR tubes. The $CDCl_3$ was dried oven 4 Å molecular sieves prior to use. Salts were oven-dried for 24 h prior to use. An initial ^{1}H NMR spectrum was acquired for each tube, and then excess powdered salt was added. The solution was allowed to stand without stirring, and a ^{1}H NMR spectrum was acquired every 24 h until the signals for the uncomplexed receptor disappeared. The changes in receptor chemical shifts (ppm) were calculated by using the following formula: $\Delta\delta = \delta_{final} - \delta_{initial}$.

Competitive Salt Extractions. The above procedure was followed except that a mixture of equal molar amounts of excess powdered salts was allowed to stand in the bottom of the NMR

(18) Receptor **1** appears to bind the sodium and potassium salts in solution as contact ion pairs and most likely binds the lithium salts as water-separated ion pairs (as illustrated in Figures 1 and 2), where the water is derived adventitiously from the atmosphere. The question arises whether receptor **1** can bind the lithium salts in extremely anhydrous solution as contact ion pairs; however, this is a technically difficult experiment to conduct in an unambiguous manner and was not attempted.

(19) It is possible that receptor **1** accelerates the solubilization process by removing associated ion pairs directly from the solid surface.

(20) An alternative explanation for the lithium extraction selectivity is that **1** has a highly selective K_a for lithium salts. The heterogeneous nature of the extraction system makes it technically very difficult to measure appropriate K_a values; however, the literature data (see ref 2 and references therein) strongly suggest that receptor **1** does not have a selective affinity for lithium salts over sodium or potassium salts.

(21) Several ditopic receptors that likely bind salts as separated ion pairs have been reported to be poor solubilizers of solid alkali metal chlorides: Webber, P. R. A.; Beer, P. D. *Dalton Trans.* **2003**, 2249−2252. Evans, A. J.; Beer, P. D. *Dalton Trans.* **2003**, 4451−4456. Tumcharern, G.; Tuntulani, T.; Coles, S. J.; Hursthouse, M. B.; Kilburn, J. D. *Org. Lett.* **2003**, *5*, 4971−4974.

tube. ^{1}H NMR signals for each complex could be observed directly and their relative concentrations measured from the signal integration.

Salt Solubility in $CDCl_3$. Samples (10 mmol) of solid LiCl, LiBr, NaCl, NaBr, NaI, KCl, KBr, and KI were allowed to stand in contact with 5 mL of dry $CDCl_3$ in separate vials for 14 days. The solutions were physically agitated every 12 h. After 14 days each solution was filtered and evaporated to obtain the mass of the dissolved salt in each vial. The solubility of each salt (mg/mL) was calculated from these data.

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Supporting Information Available: X-ray data files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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