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Hemispherand-Strapped Calix[4]pyrrole: An Ion-pair Receptor for the Recognition and Extraction of Lithium Nitrite

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Supporting Information

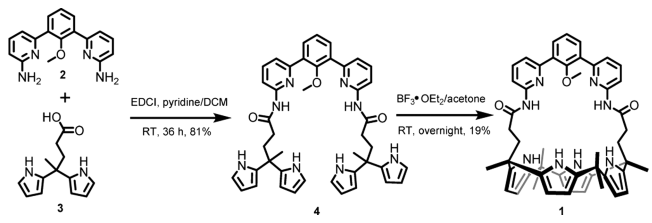
ABSTRACT: The hemispherand-strapped calix[4]pyrrole (**1**) acts as an ion pair receptor that exhibits selectivity for lithium salts. In organic media (CD_2Cl_2 and CD_3OD, v/v, 9:1), receptor **1** binds LiCl with high preference relative to NaCl, KCl, and RbCl. DFT calculations provided support for the observed selectivity. Single crystal structures of five different lithium ion-pair complexes of **1** were obtained. In the case of LiCl, a single bridging water molecule between the lithium cation and chloride anion was observed, while tight contact ion pairs were observed in the case of the LiBr, LiI, $LiNO_3$, and $LiNO_2$ salts. Receptor **1** proved effective as an extractant for $LiNO_2$ under both model solid–liquid and liquid–liquid extraction conditions.

The lithium cation is of considerable commercial interest. It plays a central role in modern battery technology, is important in lubricants, and is used therapeutically for the treatment of depression.[1] Salt flats in Bolivia provide much of the lithium currently in use, although other more limited reserves remain throughout the world.[2] Although not representing an imminent crisis, there are growing concerns regarding the dwindling supply of available lithium.[3] An ability to recognize and purify this cation, e.g., through solid–liquid extraction (SLE) or liquid–liquid extraction (LLE) protocols, may help alleviate these concerns.

So-called ion-pair receptors, species containing disparate binding sites for cations and anions, offer considerable advantages in terms of affinity and selectivity as compared to analogous single ion receptors.[4] In recent years, they have attracted attention in areas as diverse as ion extraction, recognition, through-membrane transport, salt solubilization, ion sensing, and logic gate design, among other applications.[4c,5] Our own interest has centered around calix[4]arene-strapped calix[4]pyrroles.[6] These polytopic receptors were found to be effective for cesium salt recognition, extraction, and ion-triggered release.[4c] However, lithium selective salt recognition could not be achieved. In fact, more broadly, receptors capable of recognizing the Li^+ cation[7] or lithium ion pairs[8] are rare. Those capable of extracting simple lithium salts are all but unknown. In classic early work, Cram and coworkers demonstrated that his spherands could be used to extract the lithium cation from an aqueous phase into an organic phase. This extraction was not affected in the form of an ion pair; rather, it was achieved by using the rather hydrophobic picrate anion as the counterion.[9] In 2004 Smith and coworkers disclosed a metal-free ditopic receptor that bound lithium chloride in the form of a water-bridged complex and showed that it could be used to affect the solid–liquid (chloroform) extraction of LiCl and LiBr.[10] These seminal reports not withstanding, to our knowledge, no system has been reported that is capable of promoting the extraction of simple lithium salts under aqueous–organic LLE or transport conditions. We thought that by using a lithium coordinating subunit to strap a calix[4]pyrrole anion recognizing core we would be able to create ion pair receptors capable of recognizing and extracting lithium salts under both solid–liquid and liquid–liquid conditions. Of particular interest would be systems capable of extracting lithium nitrite because of the importance of the nitrite anion in the environment, its use in the construction industry, and its presence at high levels in U.S. radioactive tank waste. Such considerations led to the design of receptor **1**.

The synthesis of compound **1** is shown in Scheme 1. Precursor **2** was prepared in 63% yield via a tetrakis(triphenylphosphine)-palladium(0)-catalyzed Suzuki–Miyaura cross-coupling reaction using 1,3-di-pinacolboronate-2-methoxybenzene (S4) and 6-bromopyridin-2-amine as the starting materials. Dipyrromethane **3** was prepared in 19% yield by condensing levulinic acid with pyrrole in the presence of excess methanesulfonic acid (see Supporting Information (SI)). Condensation of **2** and **3** in the presence of *N*-ethyl-*N*′-(3-(dimethylamino)propyl)carbo-dii-

Scheme 1. Synthesis of receptor 1



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mide hydrochloride (EDCI) and pyridine in CH_2Cl_2 yielded the key intermediate **4** in 81% yield. The resulting species was condensed with acetone in the presence of excess $BF_3{\cdot}OEt_2$ to give **1** in 19% yield. Compound **1** was characterized by NMR spectroscopy and mass spectrometry (see SI) as well as via X-ray diffraction analyses of single crystals grown under three different conditions (cf. Figure S1)

Initial evidence that compound **1** could act as an ion pair receptor for lithium salts came from a single-crystal X-ray diffraction analysis of the LiCl complex. Suitable crystals were obtained via the slow evaporation of a $CHCl_3/CH_3CN/CH_3OH$ solution of receptor **1** in the presence of excess lithium chloride. The resulting structure revealed a 1:1 LiCl complex (Figure 1).

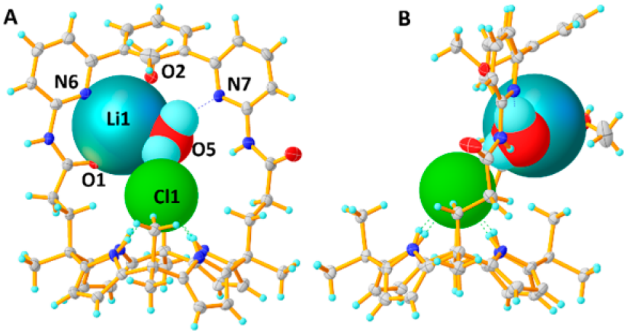

Figure 1. (A) Front view and (B) side view of the single crystal X-ray diffraction structure of the lithium complex [**1**·LiCl·H_2O·MeOH].

The Li^+ ion resides on one side of the cavity in a cleft formed by the hemispherand and the amido group. In addition to the receptor, Li^+ is bound to a methanol and water molecule. Key distances observed in this structure include: 1.89 Å ($Li^+{\cdots}O1$), 2.12 Å ($Li^+{\cdots}N6$) 3.22 Å ($Li^+{\cdots}O2$), and 4.30 Å ($Li^+{\cdots}N7$). The Cl^- ion is hydrogen-bonded to the NH groups of the calix[4]pyrrole subunit (with $N{\cdots}Cl^-$ distances in the range of 3.34−3.40 Å), as well as to the water molecule bound to the Li^+ cation. The distance between the Li^+ cation and the Cl^- anion was 4.34 Å, as would be expected for a solvent-bridged ion pair complex. A similar single-crystal structure was also obtained with the Li^+ cation included in the other side of the pocket formed by the hemispherand and the amido groups (Figure S2). This finding led us to consider that in solution the Li^+ cation might possibly shuttle rapidly between the two subcavities defined by the central methoxy group.

The ability of **1** to bind lithium chloride in solution was probed via ^1H NMR spectroscopy using a mixture of CD_2Cl_2 and CD_3OD (9:1, v/v) as the solvent (Figure 2). Spectroscopic analysis of compound **1** revealed only one set of resonances. Upon exposure to excess LiCl, the singlet associated with the NH proton seen at 8.48 ppm in free **1** underwent a shift to 10.50 ppm, a change attributed to interactions between the bound Cl^- and the NH protons of the calix[4]pyrrole subunit. Significant downfield shifts were also observed for the aromatic hydrogen atom signals, except proton ***e***. The upfield shift for proton ***e*** is ascribed to the loss of an intramolecular hydrogen bond (highlighted in light red in Figure 2) resulting from the conformational changes associated with Li^+ complexation. The signals for the methoxy protons attached to the benzene ring (***h***) and the methylene groups (***f***) connected to the amide subunits underwent considerable downfield shifts in the presence of LiCl. These changes are rationalized in terms of the deshielding that results from the lithium cation−oxygen atom interactions and

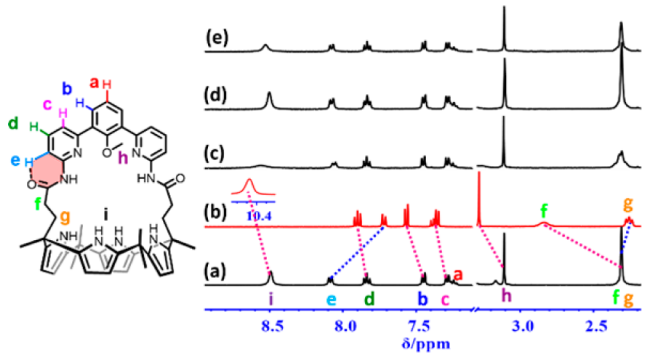

Figure 2. Partial ^1H NMR spectra of a 5.0 mM solution of (a) **1** only and **1** with (b) excess LiCl, (c) excess NaCl, (d) excess KCl, and (e) excess RbCl in CD_2Cl_2 and CD_3OD (9:1, v/v).

the structural changes induced upon lithium cation complexation. Taken together, these findings are consistent with the expectation that Li^+ and Cl^- are cobound by receptor **1**. Moreover, the observation of only one set of signals in the complex supports the proposal that the Li^+ cation moves rapidly within the large hemispherand cavity on the NMR time scale and is not constrained to one binding site.

Under the same ^1H NMR spectroscopic conditions as employed above, no appreciable changes in any of the receptor-based proton signals were seen when receptor **1** was treated with excess NaCl, KCl, and RbCl as compared to the free receptor (Figure 2). Exposure to $LiClO_4$ was found to induce changes in the aromatic proton signals of the hemispherand moiety analogous to those seen with LiCl (Figure S3). In contrast, treatment with $NaClO_4$ (up to 20 equiv) failed to induce any significant change in these signals (Figure S4). On this basis we conclude that the lithium cation is selectively bound to the hemispherand subunit and that the high selectivity of receptor **1** for LiCl over other alkali metal salts originates at least in part from the cation binding site. Further evidence of this selectivity came from the finding, confirmed by a single crystal diffraction analysis, that a 1:1 complex of **1**·LiCl was obtained when a solution of receptor **1** in $CH_3Cl/CH_3OH/CH_3CN$ containing an excess of LiCl, NaCl, KCl, and RbCl was subject to slow evaporation (Figure S2).

Theoretical support for the conclusion that receptor **1** was highly selective for LiCl over NaCl and KCl came from density functional theory (DFT) calculations carried out in the gas phase at the B3LYP/6-31g*//B3LYP/6-31g* level (Figures S5−S7). Two possible limiting complexation modes for **1**·MCl (M = Li, Na, K), namely without and with hydration, were considered (Table S1). In the absence of water, the calculated binding energies of complexes, **1**·MCl, were −220.49, −198.06, and −174.65 kcal mol^{-1} for LiCl, NaCl, and KCl, respectively. In contrast, for the putative hydrates, the energies for the corresponding complexes, **1**·MCl·H_2O, were −244.27, −217.44, and −188.65 kcal mol^{-1} for LiCl, NaCl, and KCl, respectively. We thus conclude that formation of the lithium chloride complexes is favored independent of the model used.

To obtain further insights into ion-pair complexation of **1**, several lithium salts with larger anions, e.g., Br^-, I^-, NO_2^-, and NO_3^-, were screened. Evidence for ion-pair recognition and following 1:1 ion-pair complexation of **1** in the solid state came from the single crystal X-ray structures of the LiBr, LiI, $LiNO_2$, and $LiNO_3$ complexes (Figure 3). The resulting crystal structures revealed that these four lithium salts were encapsulated by

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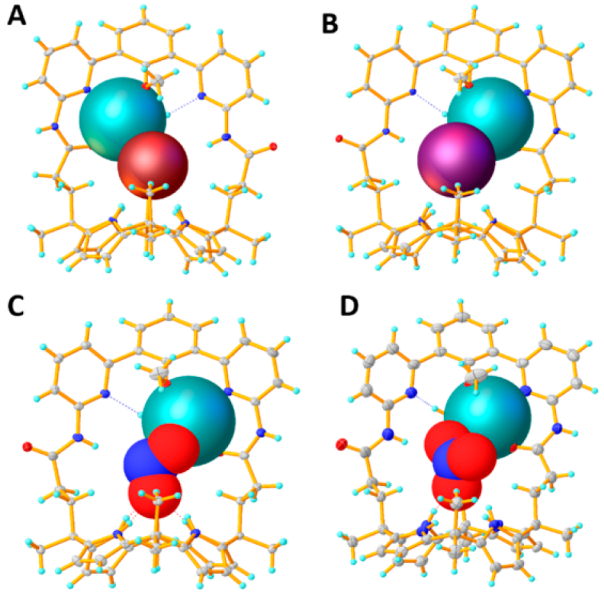

Figure 3. Single crystal structures of complexes of receptor **1** with (A) LiBr, (B) LiI, (C) $LiNO_2$, and (D) $LiNO_3$.

receptor **1** as tight contact ion pairs (as opposed to hydrated species) with $Li^+\cdots A^-$ distances of 3.040, 3.064, 2.077, and 2.609 Å for the LiBr, LiI, $LiNO_2$, and $LiNO_3$ complexes, respectively. In all four structures, the lithium cation is bound to one side of the hemispherand strap with contact distances ranging from 1.863 to 2.219 Å. All counteranions were hydrogen-bonded to the NH groups of the calix[4]pyrrole subunits with average $N\cdots A^-$ distances of 3.59, 3.80, 3.05, and 3.05 Å for LiBr, LiI, $LiNO_2$, and $LiNO_3$, respectively.

DFT calculations were also carried out in an effort to estimate the selectivity of receptor **1** for LiCl, LiBr, $LiNO_2$, and $LiNO_3$ (Figures S5B and S8, Table S2). The initial input coordinates were obtained from the crystal structures discussed above. The resulting binding energies for the complexes were calculated to be −244.27 kcal mol^{-1} for $LiCl\cdot H_2O$, −236.72 kcal mol^{-1} for LiBr, −237.91 kcal mol^{-1} for $LiNO_2$, and −230.24 kcal mol^{-1} for $LiNO_3$, leading us to infer no appreciable selectivity between these lithium salts. Experimental analyses of intralithium salt selectivity came from ^{1}H NMR spectroscopic titrations (Figures S9−S13) and fitting the data to a 1:1 binding mode. The resulting binding constants were found to be 45 ± 1, 74 ± 8, 108 ± 7, and 263 ± 13 M^{-1} for LiBr, LiI, $LiNO_2$, and $LiNO_3$, respectively.

Due to the relatively low hydration energy of the nitrite anion (−330 kJ mol^{-1} for NO_2^- vs −475 kJ mol^{-1} for Li^+),[11] which should favor liquid−liquid extraction, and its presence at high levels in U.S. radioactive tank waste (2−4 M in many instances),[12] additional efforts were devoted toward understanding the determinants of lithium nitrite recognition in the case of **1**. As a first step in this effort, ^{1}H NMR spectroscopic titration studies were carried out using $TBANO_2$. Even after the addition of 20 equiv, no appreciable chemical shifts in the signals for receptor **1** were observed (Figure S15), leading us to infer that **1** does not bind the NO_2^- anion effectively in the absence of the lithium cation. However, upon addition of either lithium tetraphenylborate or $LiClO_4$ to a solution of **1** in a mixture of CD_2Cl_2 and CD_3OD (9:1, v/v) in the absence of a nitrite anion source, the aromatic protons corresponding to the benzene and pyridine rings underwent shifts analogous to those seen in the case of **1**·LiCl above (cf. Figure S16). Subsequent addition of $TBANO_2$ resulted in a significant shift of both the NH and aromatic protons. Taken in concert, these findings lead us to suggest that the recognition of nitrite by receptor **1** is facilitated when the lithium cation is prebound as illustrated in Figure S17.

While a number of receptors capable of complexing other nitrite anion salts are known,[13] to the best of our knowledge, the hemispherand-strapped calix[4]pyrrole **1** is the first system capable of recognizing $LiNO_2$ as an ion pair. Its ability to act as an extractant was thus probed in detail.

As a first test, solid−liquid extraction studies were carried out using ^{1}H NMR spectroscopy (Figure 4). Exposing receptor **1** in

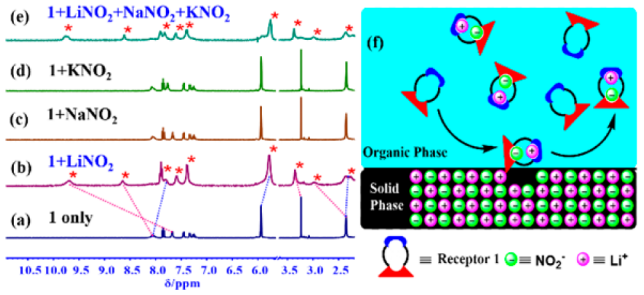

Figure 4. Partial ^{1}H NMR spectra of a 5.0 mM solution of (a) **1** only and **1** with (b) excess $LiNO_2$, (c) excess $NaNO_2$, (d) excess KNO_2, and (e) excess $LiNO_2$ + $NaNO_2$ + KNO_2 in CD_2Cl_2. (f) Cartoon illustration of the solid−liquid extraction of $LiNO_2$.

CD_2Cl_2 to an excess of microcrystalline $LiNO_2$ engendered distinctive changes in the ^{1}H NMR spectrum (Figure 4b). In contrast, no appreciable changes were observed in the ^{1}H NMR spectrum of an analogous CD_2Cl_2 solution receptor **1** after exposure to excess $NaNO_2$ and KNO_2, even after 20 min under sonication (Figure 4c,d). Competition experiments, involving the use of $LiNO_2$, $NaNO_2$, and KNO_2, produced spectral changes identical to those seen in the presence of $LiNO_2$ alone (cf. Figure 4e,b). We thus conclude that receptor **1** is able to extract $LiNO_2$ efficiently and with high selectivity over $NaNO_2$ and KNO_2 under solid−liquid extraction conditions as illustrated schematically in Figure 4f.

In order to test whether receptor **1** could extract $LiNO_2$ from an aqueous phase to an organic phase, model liquid−liquid extraction studies were carried out using a 10 mM solution of **1** in $CDCl_3$ and various saturated D_2O salt solutions. A comparison of the ^{1}H NMR spectrum of free **1** in D_2O saturated $CDCl_3$ revealed considerable changes in the resonance signals after contacting with a saturated D_2O solution of $LiNO_2$ (Figure 5a,b). In contrast, almost no appreciable chemical shift changes were observed in the ^{1}H NMR spectrum of the $CDCl_3$ layer containing receptor **1** after it was washed thoroughly with saturated D_2O solutions of either $NaNO_2$ or KNO_2. We thus conclude that receptor **1** is able to bind and extract $LiNO_2$ from D_2O phase into a $CDCl_3$ phase and do so selectively under these initial test conditions.

In summary, a new ion-pair receptor, the hemispherand-strapped calix[4]pyrrole **1**, was synthesized and characterized by standard spectroscopic protocols as well as by single X-ray crystal diffraction analysis. Receptor **1** was shown to form 1:1 ion-pair complexes with several lithium salts (e.g., LiCl, LiBr, LiI, $LiNO_2$, and $LiNO_3$) with high selectivity over the corresponding sodium and potassium salts both in the solid state and in organic media. These experimental findings were supported by DFT calcu-

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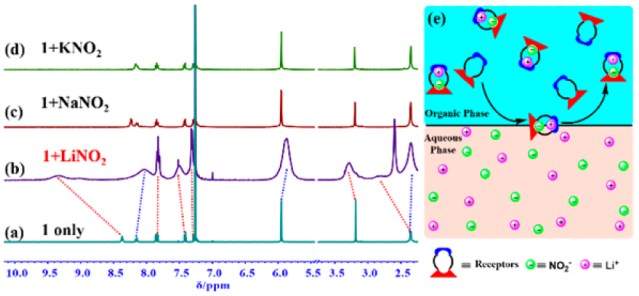

Figure 5. Partial ^{1}H NMR spectra of a 10 mM solution of **1** in $CDCl_3$ exposed to (a) D_2O, (b) saturated $LiNO_2$ in D_2O, (c) saturated $NaNO_2$ in D_2O, and (d) saturated KNO_2 in D_2O. (e) Cartoon illustration of the liquid–liquid extraction of $LiNO_2$ inferred on the basis of these studies.

lations. To the best of our knowledge, compound **1** is the first ion-pair receptor capable of recognizing and extracting lithium nitrite under both solid–liquid and liquid–liquid conditions and to do so with high selectivity relative to sodium nitrite and potassium nitrite.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05713.

Synthetic details, NMR and procedure and additional data for extraction, calculation data for optimized geometry of the complexes with receptor **1**, and X-ray structural data for free **1** and complexes (PDF)
X-ray crystallographic data for **1**-LiBr (CIF)
X-ray crystallographic data for **1**-LiI (CIF)
X-ray crystallographic data for **1**-$LiNO_2$ (CIF)
X-ray crystallographic data for **1**-$LiNO_3$ (CIF)
X-ray crystallographic data for **1**-LiCl-right (CIF)
X-ray crystallographic data for **1**-LiCl-left (CIF)
X-ray crystallographic data for **1**-CH_3CN (CIF)
X-ray crystallographic data for **1**-$2H_2O$ (CIF)
X-ray crystallographic data for **1**-$2CH_3H$ (CIF)

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Notes

The authors declare no competing financial interest.

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