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Targeted preparation of highly efficient lithium extractants based on 14-membered crown ethers

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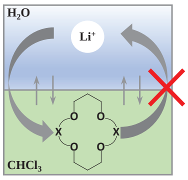
Modification of benzene rings in dibenzo-14-crown-4 by hydrogenation of a cyclohexane moiety or introduction of *tert*-butyl substituents leads to macrocycles superior to benzo-15-crown-5 in extraction of lithium salts from aqueous solutions and in resistance to leaching into the aqueous phase.



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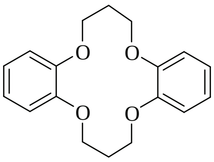
Since the end of the last century, the world consumption of lithium compounds has increased sharply. Lithium is used, for example, in rechargeable batteries,[1] additives regulating the acidity of coolants in modern pressurized-water nuclear power plants,[2] main components of coolants in thorium-type nuclear reactors under development[3] or pharmaceuticals for the treatment of mood disorders.[4] The world recoverable reserves of lithium are small and mainly localized in Latin America and Australia. This leads to the search for alternative sources and development of cost-effective methods for the extraction of Li^+ ion from industrial waste and dilute aqueous solutions like seawater. One of the approaches to the recovery of lithium salts employs crown ethers (CEs) as extractants.[5] In the development of lithium-selective extraction systems a serious challenge originates from the small size of Li^+ ion and its high positive charge density resulting in a strong hydrate shell surrounding the cation. Macrocyclic ligands of small size can compete with water molecules for Li^+ ions, ensuring their effective extraction from an aqueous phase into the organic one. Thus, currently benzo-15-crown-5 **1**[6,7] as well as 14-membered aromatic[5] and aliphatic[8] CEs are considered the main lithium-selective polyether ligands. The 14-membered macrocycles, in particular the aliphatic ones, demonstrate unique selectivity for the Li^+ extraction from aqueous solutions,[8] the main problem being related to their complicated synthesis. Disadvantages of CE **1** are more critical and consist in low extraction ability and selectivity for Li^+ ions[9] as well as noticeable solubility of this ligand and its lithium complexes in water and especially concentrated aqueous solutions of lithium salts.[9–11] This stimulates extensive experimental[5] and theoretical[12] investigations to create fundamental principles for the design of lithium-selective macrocycles. An additional incentive for this search represents the need for macrocyclic systems capable of separating lithium isotopes in addition to the ones just selective for Li^+ ions.[6,7,9,10]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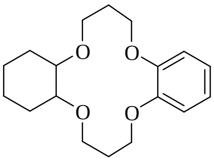
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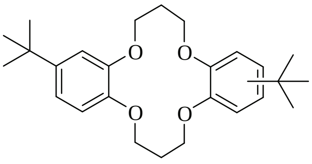
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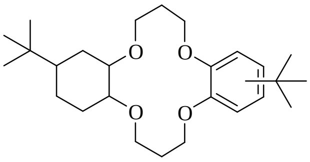
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As a rule, modern theoretical modeling of the lithium-selective macrocyclic ligand structure is limited to optimization of geometric parameters of the macrocycle in its Li^+ complex as well as calculation of the Li^+ binding energy in gas phase or after hydration by water molecules.[12] Other key factors for the Li^+ extraction, such as the effect of anion on the structure of the complex and the effect of macrocycle solvation by solvent molecules, are typically ignored. This reduces to some extent the prognostic value of the developed theoretical models and indicates the importance of an empirical approach based on the fundamental principles of macrocyclic chemistry, which links the structure of polyether ligands to their complexing ability in a solution.

Taking into account the above considerations, in our approach to the design of an effective lithium extractant we chose 14-membered dibenzo-14-crown-4 **2** as a structural block for further modification to increase the macrocycle solubility in an organic phase and reduce its solubility in an aqueous phase by introducing branched alkyl substituents as well as enhance the extraction ability for Li^+ ions by elevating the basicity of polyether oxygen atoms. In light of this, we synthesized the following 14-membered CEs using known techniques:[13,14] benzocyclohexano-14-crown-4 **3**, di-*tert*-butylbenzo-14-crown-4 **4** and di-*tert*-butylbenzocyclohexano-14-crown-4 **5** as well as characterized them (for details, see Online Supplementary Materials). Their efficiency was evaluated using two key parameters, namely (i) extractability for Li^+ ions and (ii) resistance to CE leaching into an aqueous phase, employing the system composed of 0.1 M solution of CE in $CHCl_3$ as an organic phase and 2.0 M solution of LiBr in H_2O as the aqueous one (for details, see Online Supplementary Materials).

In a simplified form, the process of Li^+ extraction from the aqueous solution into the organic phase can be described as the following:

$$CE_{org} + Li^+_{aq} + Br^-_{aq} \rightleftharpoons CE{\cdot}LiBr_{org}. \qquad (1)$$

Stability of the extraction system to ligand loss (leaching) was evaluated using the constant of CE distribution $K_{d(CE)}$:

$$K_{d(CE)} = [CE]_{org}/[CE]_{aq}, \qquad (2)$$

where $[CE]_{org}$ and $[CE]_{aq}$ represented equilibrium concentrations of macrocycle in the organic and aqueous phases, respectively. The latter was determined by the known[11,15] techniques (for details, see Online Supplementary Materials). Efficiency of the Li^+ extraction was estimated using the distribution coefficient D_{Li} as a criterion:

$$D_{Li} = [Li]_{org} /[Li]_{aq}, \qquad (3)$$

where $[Li]_{org}$ was the equilibrium concentration of Li^+ ions in the organic phase and $[Li]_{aq}$ represented the one in the aqueous phase (for details, see Online Supplementary Materials).

In accordance with the strategy chosen for the modification of the 14-membered macrocycles, the introduction of *tert*-butyl groups into the benzene and cyclohexyl moieties resulted in (i) a significant increase in solubility of the ligand in $CHCl_3$, in particular, fourfold for CE **4** compared with unmodified structure **2** (1.2 and 0.3 mol l^{-1}, respectively), and (ii) a sharp growth of the $K_{d(CE)}$ value for CEs **4** and **5** (Figure 1, violet bars). In other words, the transfer of macrocycles bearing *tert*-butyl groups from their solutions in $CHCl_3$ to the aqueous phase was almost completely suppressed. The $K_{d(CE)}$ value for benzo-15-crown-5 **1** obtained under the same experimental conditions is given in Figure 1 as a reference. The $K_{d(CE)}$ value for compound **3** is between those for ligands **1** and **2**.

Unmodified structure **2** and reference macrocycle **1** demonstrate approximately the same extraction ability for Li^+ ions (see Figure 1, olive bars). The introduction of *tert*-butyl substituents into the aromatic groups of CE **2**, resulting in ligand **4**, led to a twofold growth of D_{Li}. In this case, the electron donating properties of the alkyl group may promote the extractability of Li^+. Hydrogenation of aromatic groups in CE **2** appeared a significantly more effective tool for improving D_{Li}. Thus, fivefold and 30-fold increase in the D_{Li} value is revealed for compounds **3** and **5** compared with that of initial structure **2**. The observed trend correlates well with the pioneering work of Pedersen,[13] where higher basicity of polyether donor atoms led to better stability of the macrocyclic complexes of the general formula $Met^{n+}{\cdot}CE{\cdot}A_n^-$.

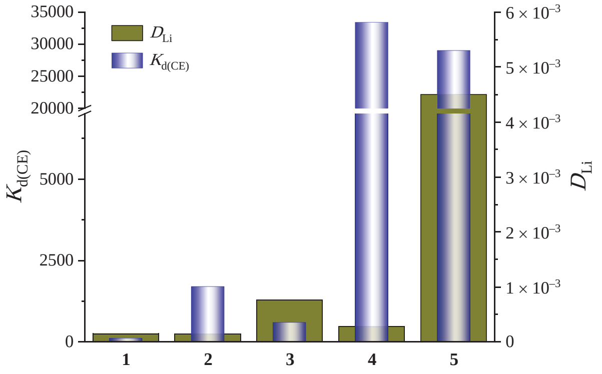

Figure 1 Macrocycle distribution constants $K_{d(CE)}$ (violet bars) and extractability of Li^+ D_{Li} (olive bars) in the system composed of 0.1 M solution of CE in $CHCl_3$ and 2.0 M solution of LiBr in H_2O. Data for benzo-15-crown-5 **1** are given for comparison.

The results obtained demonstrate the superiority of 14-membered ligands not only over traditionally used benzo-15-crown-5 **1**,[9,10] but also over the systems based on alkyl and carboxyl derivatives of dibenzo-14-crown-4 **2** considered as promising ones in combination with molecular solvents and ionic liquids.[5] Solutions of compounds **3**–**5** in $CHCl_3$ possess an exceptional resistance to leaching of the ligand to an aqueous phase as well as high extractability of Li^+ ions. Thus, the empirical approach proposed in this work allows one to create new compounds capable of an efficient Li^+ extraction from aqueous media.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.09.034.

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