8632 *Inorg. Chem.* **2009**, *48*, 8632–8637
DOI: 10.1021/ic901136b

Inorganic Chemistry
Article

Recognition of Li^+ by a Salophen−UO_2 Homodimeric Complex

Massimo Cametti, Laura Ilander, and Kari Rissanen*

Nanoscience Center, Department of Chemistry, University of Jyväskylä, Jyväskylä, Finland

Received June 12, 2009

Self-assembly via mutual U-coordination of the salophen−UO_2 complex **1** creates a dimeric species which is shown to be useful for metal binding. Indeed, the **1** dimer has affinity for alkali metal cations and, interestingly, a marked selectivity for Li^+, determined by electrospray ionization mass spectrometry and ^1H NMR techniques. X-ray diffraction helped in the elucidation of the dimeric complex structure, which presents a crown-ether-type coordination site, in analogy to the more familiar 12-crown-4, responsible for the metal interaction. Comparison with isomer **2**, and the salen derivative **3**, increases the understanding of the behavior of such systems in solution and in the solid state.

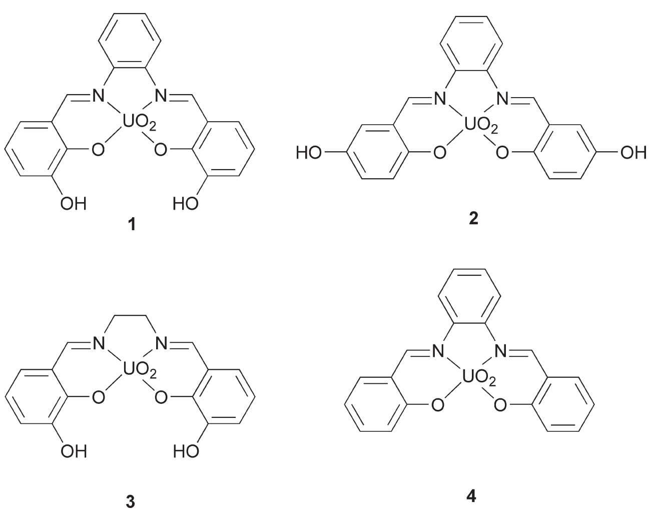
Introduction

Recognition of alkali metal cations by small synthetic molecules has been a central theme of supramolecular chemistry since its early age.[1] Due to their hard acidic nature, electrostatic interactions are most commonly employed to achieve binding with such metal ions in solution. Polyoxa-macrocycles, such as Pedersen's crown ethers, stand on high ground in alkali metal recognition.[2] Their high affinity and selectivity are committed to a set of alternating donor atoms and suitable spacers which provide multiple ion−dipole interactions. Crown-ether moieties, as binding sites in larger and more elaborate (multitopic) receptors, are also common in the recent literature,[3] especially in combination with calix[*n*]arene scaffolds.[3e,3f]

Within the alkali metal ion series, the lithium cation (Li^+) generates additional interest for its pharmacologic relevance, since lithium carbonate is largely used for the treatment of some human pathologies.[4] This explains the interest in obtaining new molecular species able to bind the lithium cation in solution.[5]

Here, we report on the selective recognition of the Li^+ cation over larger alkali metal ions (Na^+ and K^+) by a dimeric species constituted by the assembly of two UO_2-complex units (**1**, see Scheme 1) connected via a double, mutual, coordinative bond to each of the UO_2 centers. This dimeric species, whose structure has been elucidated by X-ray diffraction and ^1H NMR spectroscopy, possesses a site composed of a high number of oxygen atoms, four of which in what resembles a crown-ether-like arrangement. This, we believe, is responsible for the interaction with alkali metal cations and the observed selectivity for Li^+. The properties of complex **1**, and its dimer, were also compared with those of the isomeric **2**, the more flexible salen−UO_2 derivative **3**, and its dimer, and the parent salophen−UO_2 complex **4** (Scheme 1).

Scheme 1. Molecular Formulae of Salophen− and Salen−UO_2 Complexes **1**−**4**



---

*Author to whom correspondence should be addressed. E-mail: kari.t.rissanen@jyu.fi.

(1) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, Germany, 1995.Steed, J. W. *Coord. Chem. Rev.* **2001**, *215*, 171–221.

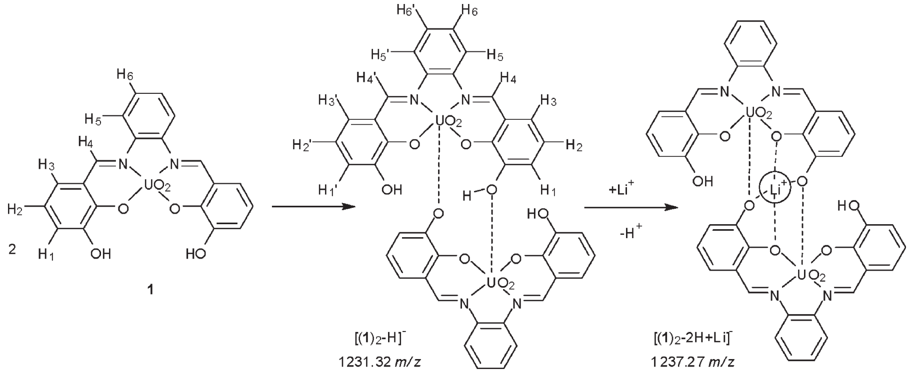
(2) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 2495. Czech, B. P.; Babb, D. A.; Son, B.; Bartsch, R. A. *J. Org. Chem.* **1984**, *49*, 4805–4810.

(3) (a) Chae, M. K.; Lee, J.-I.; Kim, N.-K.; Jeong, K.-S. *Tetrahedron Lett.* **2007**, *48*, 6624–6627. (b) Mahoney, J. M.; Nawaratna, G. U.; Beatty, A. M.; Duggan, P. J.; Smith, B. D. *Inorg. Chem.* **2004**, *43*, 5902–5907. (c) Michel, S. L. J.; Barrett, A. G. M.; Hoffman, B. M. *Inorg. Chem.* **2003**, *42*, 814–820. (d) Even, P.; Boitrel, B. *Coord. Chem. Rev.* **2006**, *250*, 519–541. (e) Gaeta, C.; Martino, M.; Neri, P. *Org. Lett.* **2006**, *8*, 4409–4412. (f) Stoll, I.; Eberhard, J.; Brodbeck, R.; Eisfeld, W.; Mattay, J. *Chem. Eur. J.* **2008**, *14*, 1155–1163.

(4) Winstock, A. R.; Lea, T.; Copeland, J. *J. Psychopharmacol.* **2009**, *23*, 84–93. Carli, M.; Morissette, M.; Hébert, C.; Di Paolo, T.; Reader, T. A. *Biochem. Pharmacol.* **1997**, *54*, 391–397.

(5) Rochat, S.; Grote, Z.; Severin, K. *Org. Biomol. Chem.* **2009**, *7*, 1147–1153. Grote, Z.; Scopelliti, R.; Severin, K. *J. Am. Chem. Soc.* **2004**, *126*, 16959–16972. Hilmey, D. G.; Paquette, L. A. *J. Org. Chem.* **2004**, *69*, 3262−3270 and references therein. Barclay, T. M.; McAuley, A.; Subramanian, S. *Chem. Commun.* **2002**, 170–171. Capó, M.; Saá, J. M.; Alvarez, A. *Chem. Commun.* **2002**, 1982–1983. Scheibitz, M.; Winter, R. F.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 924–926.

Scheme 2. Dimerization and Li^+-Binding Processes, Corresponding Peak Formula As Monitored by ESI-Mass Spectrometry, and ^1H Numbering for the Monomeric and Dimeric Species



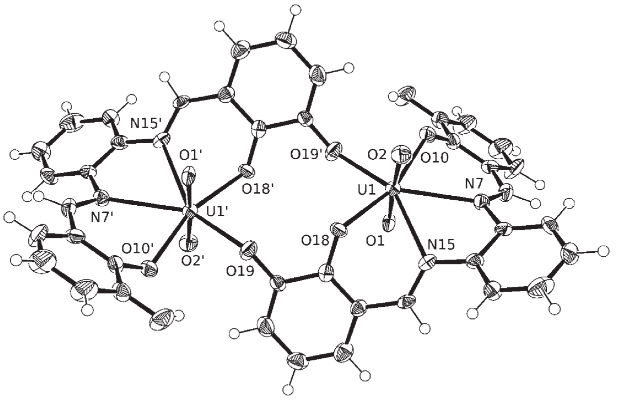


Figure 1. Ortep plot of the $[(Et)_3NH^+)_2(\mathbf{1}_2\text{-}2H)^{2-}]\cdot(acetone)_2$ crystal structure (thermal ellipsoids at 50% probability level). The HTEA cations and the solvent molecules are omitted for clarity.

Results and Discussion

The electrospray ionization (ESI) mass spectrum of a 2 × 10^{-5}M solution of **1** in acetonitrile shows two main peaks at 615.22 and 1231.41 (100/100) *m*/*z*, in the negative ion mode. The first peak belongs to the monodeprotonated species $[\mathbf{1}\text{-}H]^-$, while the second equally intense peak has an *m*/*z* value which corresponds to the $[(\mathbf{1})_2\text{-}H]^-$ formula. We tentatively attributed the latter peak to a dimeric species, formed by mutual coordination of a deprotonated OH group of one UO_2 complex to the UO_2 center of a second molecule, as shown in Scheme 2. This idea remained speculative until we were able to obtain a good quality single crystal of a structurally similar dimeric complex with Et_3NH^+, by the slow evaporation of a 1:1 mixture of $(Et)_3N$ and **1** in acetone.

Figure 1 depicts the X-ray determined structure of this centrosymmetric homodimeric complex of composition $[(Et)_3NH^+)_2(\mathbf{1}_2\text{-}2H)^{2-}]\cdot(acetone)_2$. Its main structural feature consists of an interesting arrangement of four oxygens atoms which are connected via alternating $-UO_2-$ and $-CH_2(sp^2)-CH_2(sp^2)-$ spacers in what resembles a 12-crown-4 ether. The oxygen−oxygen distances are indeed quite similar to those found in uncomplexed 12-crown-4 solid-state structures.[6] Interestingly, not only the distances but also the relative orientation of the oxygen atoms are very similar, with the electron pairs of two oxygen atoms [O18 and O19] pointing above and two [O18′ and O19′] pointing below the plane. This structural feature raised the question of whether such a dimeric complex could possess an affinity toward alkali metal cations, in analogy with the well-known crown ethers.

Dimeric or oligomeric assemblies are known for several transition metal complexes. In particular, the self-assembly of Ni(II) complexes with salicylaldimine ligands have been shown to create a well-defined environment for the binding of Na^+ and Li^+ cations.[7] Mn(II) and Co(II) complexes of this kind are also reported, where alkali metal cation binding is achieved in their dimeric or monomeric form in the solid state.[8] In some cases, Li^+ has been reported to act as a template in the formation of dimeric helicates made of Ti(IV) and MoO_2(VI) complexes in solution and in the solid state.[9] For structurally simple UO_2 complexes, such as **4**, due to the presence of two apical U=O bonds, the dimerizazion can occur only on the equatorial plane of the metal. It is well-known that, in the absence of any specific Lewis basic guest molecule, the fifth equatorial position on the U atom is generally occupied by a solvent molecule.[10] When **4** is dissolved in noncoordinative solvents such as $CHCl_3$, usually a water molecule is found coordinated to the UO_2 center. The need for carefully dried solvent explains why the first salophen−UO_2 dimer $(\mathbf{4})_2$ has been only recently observed.[11] In the case of **1**, however, the two additional OH groups give easier access to the dimeric system, which can be formed in more polar and coordinating solvents, such as MeCN and DMSO.

Intrigued by the oxygens' spatial arrangement in the dimeric complex, we first decided to investigate its binding

---

[6] The distances between the O atoms in $[(Et)_3NH^+)_2(\mathbf{1}_2\text{-}2H)^{2-}]$ (2.68 [O18−O19], 3.00 [O19−O18′], 3.79 [O18−O18′], and 4.26 Å [O19−O19′]) are nearly identical to those in free 12-crown-4 (2.97, 3.01, 4.10, and 4.36 Å, respectively); see: Groth, P. *Acta Chem. Scand.* **1978**, *23*, 279.

[7] Schall, O. F.; Robinson, K.; Atwood, J. L.; Gokel, G. W. *J. Am. Chem. Soc.* **1991**, *113*, 7434–7435. Jones, M. W.; Gupta, N.; Schepartz, A.; Thorp, H. H. *Inorg. Chem.* **1992**, *31*, 1308–1310. Schall, O. F.; Robinson, K.; Atwood, J. L.; Gokel, G. W. *J. Am. Chem. Soc.* **1993**, *115*, 5962–5969.

[8] Fachinetti, G.; Floriani, C.; Zanazzi, P. F.; Zanzari, A. R. *Inorg. Chem.* **1979**, *18*, 3469–3475. De Angelis, S.; Solari, E.; Gallo, E.; Fiorani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1996**, *35*, 5995–6003. Gallo, E.; Solari, E.; Re, N.; Fiorani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1997**, *119*, 5144–5154.

[9] Albrecht, M.; Mirtschin, S.; de Groot, M.; Janser, I.; Runsink, J.; Raabe, G.; Kogej, M.; Schalley, C. A.; Fröhlich, R. *J. Am. Chem. Soc.* **2005**, *127*, 10371–10387. Albrecht, M.; Baumert, M.; Klankermayer, J.; Kogej, M.; Schalley, C. A.; Fröhlich, R. *Dalton. Trans.* **2006**, 4395–4400.

[10] Cametti, M.; Nissinen, M.; Dalla Cort, A.; Mandolini, L.; Rissanen, K. *J. Am. Chem. Soc.* **2007**, *129*, 3641–3648. Cametti, M.; Nissinen, M.; Dalla Cort, A.; Mandolini, L.; Rissanen, K. *J. Am. Chem. Soc.* **2005**, *127*, 3831–3837.

[11] Takao, K.; Ikeda, Y. *Inorg. Chem.* **2007**, *46*, 1550–1562.

Table 1. Results of the ESI-Mass Spectrometry Experiments for Complexes **1** and **2** in MeCN[a]

complex **1**	[**1**-H]$^-$	[(**1**)$_2$-H]$^-$	[(**1**)$_2$-2H+K]$^-$	[(**1**)$_2$-2H+Na]$^-$	[(**1**)$_2$-2H+Li]$^-$
1. 10 equiv K; 1 equiv Na	100		55	86	
2. 10 equiv K; 1 equiv Li	100		4		77
3. 10 equiv Na; 1 equiv Li	67			100	75
4. 1 equiv K/Na/Li	93			2	100
complex **2**	[**2**-H]$^-$	[(**2**)$_2$-H]$^-$	[(**2**)$_2$-2H+K]$^-$	[(**2**)$_2$-2H+Na]$^-$	[(**2**)$_2$-2H+Li]$^-$
5. 1 equiv K/Na/Li	100	7	2.2	1.8	0.4

[a] The intensity is reported as a percentage with respect to the main peak (100). Metal salts were added from a concentrated solution in water of the corresponding carbonate (M_2CO_3).

Table 2. Results of the ESI-Mass Spectrometry Competition Experiments between Complexes **1** and **3** in MeCN[a]

peak formula	+1 equiv Li$^+$	+2 equiv Li$^+$
[(**3**)$_2$-H]$^-$	34	68
[(**1**)(**3**)-H]$^-$	66	15
[(**1**)$_2$-H]$^-$	3	
[(**3**)$_2$-2H+Li]$^-$	13	4
[(**1**)(**3**)-2H+Li]$^-$	80	52
[(**1**)$_2$-2H+Li]$^-$	100	100

[a] The intensity is reported as a percentage with respect to the main peak (100). Li_2CO_3 was added from a concentrated solution in water.

properties toward alkali metal ions by ESI-mass spectrometry and to assess the cation's effect on the dimer formation equilibrium.

When 10 equiv of the alkali metal cation are added to a 2 × 10^{-5} M solution of UO_2 complex **1** in MeCN, the ESI-mass spectrum shows an intense [(**1**)$_2$-2H+M]$^-$ peak, at an *m*/*z* value of 1236.4 (100/100), 1253.46 (95.5/100), and 1269.47 (76/100) for M = Li$^+$, Na$^+$, and K$^+$, respectively. The [(**1**)$_2$-H]$^-$ peak instead almost disappears in all three cases. Under these conditions, it is apparent that a metal complex, responsible for the appearance of the ESI-mass spectrometry peak, is formed in all cases. If a specific interaction is responsible for the complex formation, then a certain metal selectivity could be expected. Therefore, a second set of experiments, where mixtures with different ratios of alkali metal cations were added to **1**, was then undertaken in order to verify this hypothesis.

The results are summarized in Table 1 (see also, the Supporting Information). The addition of 10 equiv of K$^+$ and 1 equiv of Na$^+$ to a 2 × 10^{-5} M solution of **1** in MeCN forms the [(**1**)$_2$-2H+K]$^-$ and [(**1**)$_2$-2H+Na]$^-$ species whose relative peaks' intensity is 0.64:1 (Table 1, entry 1). A rough and qualitative estimate of the selectivity factor can be simply done by considering the relative height of the main isotopic peaks of two metal-bound species together with the relative concentration of the metal added with respect to the salophen−UO_2 complex. Therefore, from these data, it appears that the [(**1**)$_2$-2H+Na]$^+$ species is more stable than the analogue with K$^+$. Similar considerations, derived from experiments with K$^+$/Li$^+$ and Na$^+$/Li$^+$ ratios of 10:1 (Table 1, entries 2 and 3), allow us to say that Li$^+$ is better bound than K$^+$ and Na$^+$. Finally, when **1** is sprayed with an equimolar solution of K$^+$, Na$^+$, and Li$^+$ (entry 4), the Li adduct, [(**1**)$_2$-2H+Li]$^-$, is almost exclusively formed, thus confirming that the Li$^+$ cation binds best to the dimeric complex by far, with a selectivity which is considerably high, especially over K$^+$.

To verify these data and to be confident in the nature of the interactions observed in the ESI-mass spectrometry experiments, we tested the isomeric complex **2** under the same conditions. This UO_2 complex still possesses the OH groups, but their position prevents any double mutual coordination, and the resulting dimer is supposed to be much less favorable. Indeed, the ESI-mass spectrometry data (entry 5, Table 1) show a very weak [(**1**)$_2$-H]$^-$ peak and, more importantly, even weaker metal-adduct peaks. These low-intensity peaks show an opposed affinity trend if compared to those of complex **1**, with more intense peaks for the K$^+$ and Na$^+$ adducts rather than for Li$^+$. This strongly indicates that the peak observed at 1237 *m*/*z* is corresponding to a Li$^+$-bound species of composition [(**1**)$_2$-2H+Li]$^+$ and that the crown-ether-like arrangement of the oxygens is a likely explanation for its formation. Assistance in the interaction with Li$^+$ from the weakly basic uranyl oxygens can also be present.[12]

The observed selectivity for the Li$^+$ cation may also be due to a Coloumbic effect, often predominant in solution for charged receptors,[13] rather than due to the dimension of the binding site.

As for crown ethers, the conformation of our dimeric species upon metal binding may change, and it may not quite resemble the one occurring in the solid state structure shown in Figure 1. Indeed, a convergent arrangement of the oxygen donor atoms seems more favorable for binding, as found, for example, in the X-ray structure of the 12-crown-4 complex with Li$^+$. Here, a flat pyramidal coordination around the metal is found, with the cation lying 0.8 Å above the plane of the four oxygen atoms.[14] We believe that this picture from the solid state could be a fairly good model for the Li$^+$ binding in our case, at least until we will be able to obtain any suitable crystal of the Li complex with our systems, a task which has eluded us so far. However, if a conformational change is necessary for metal binding, the flexibility of the system may have an important role.

We have already demonstrated in a previous work that the replacement of the *o*-phenylene moiety on the top of the salophen ligand with a simple two-methylene bridge can have an effect on the guest recognition in the solid state.[15] The enhanced flexibility of the salen derivative results in a less preorganized system, but also it can give access to different conformations which might induce changes in the affinity.

---

[12] Bram, A.; Bruederl, G.; Burzlaff, H.; Lange, J.; Rothammel, W.; Spengler, R.; Karayannis, M. I.; Veltsistas, P. G. *Acta Crystallogr.* **1994**, *C50*, 178–180.

[13] Gokel, G. W.; Goli, D. M.; Minganti, C.; Echegoyen, L. *J. Am. Chem. Soc.* **1983**, *105*, 6786–6788.

[14] Chivers, T.; Eisler, D. J. *Angew. Chem., Int. Ed.* **2005**, *43*, 6686–6689.

[15] Cametti, M.; Nissinen, M.; Dalla Cort, A.; Rissanen, K.; Mandolini, L. *Inorg. Chem.* **2006**, *45*, 6099–6101.

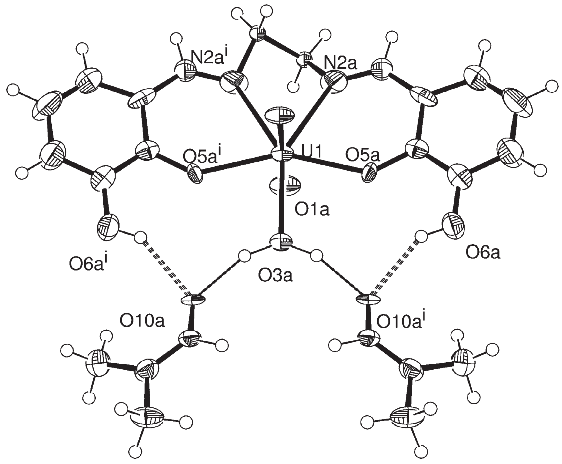


Figure 2. Ortep plot of the $3\cdot(H_2O)\cdot(DMF)_2$ crystal structure (thermal ellipsoids at 50% probability level).

We therefore have synthesized complex **3** and tested its affinity for Li^+ in the presence of **1**. The 2×10^{-5} M mixture of equimolar complex **1** and **3** provides an ESI-mass spectrum in which peaks of the three dimers (two homo- and one hetero-) are present, with *m*/*z* values of 1135.10, 1183.06, and 1231.11, corresponding to $[(\mathbf{3})_2\text{-H}]^-$, $[(\mathbf{1})(\mathbf{3})\text{-H}]^-$, and $[(\mathbf{1})_2\text{-H}]^-$ species, and with intensity ratios of 1:1.3:0.9 with respect to each other. The predicted statistical distribution (1:2:1) is not strictly followed by the systems, which shows a lower predominance for the heterodimeric species.

Upon the addition of 1 and then 2 equiv of Li^+, peaks corresponding to the $[(\mathbf{3})_2\text{-2H+Li}]^-$, $[(\mathbf{1})(\mathbf{3})\text{-2H+Li}]^-$, and $[(\mathbf{1})_2\text{-2H+Li}]^-$ species appear. The $[(\mathbf{1})_2\text{-2H+Li}]^-$ peak is the most intense in both experiments, and this allows for a quick comparison. The peaks intensities are reported in Table 2. The addition of the first equivalent of Li^+ shows that the **1** homodimer is a better binder for Li^+ than the **3** homodimer. The heterodimer also has some affinity for Li^+, but considering the intensity of the remaining peaks for the $[(\mathbf{1})(\mathbf{3})\text{-H}]^-$ and $[(\mathbf{1})_2\text{-H}]^-$ species, 66/100 and 3/100, respectively, it is clear that the **1** homodimer is the best binder among the three. The second equivalent of Li^+ added has the effect of shifting the equilibrium toward the formation of the $[(\mathbf{1})_2\text{-2H+Li}]^-$ at the expense of the other two Li^+-containing species whose relative intensities decrease. Interestingly, the intensity of $[(\mathbf{1})(\mathbf{3})\text{-H}]^-$ also decreases, while, on the contrary, the intensity of $[(\mathbf{3})_2\text{-H}]^-$ increases (see the Supporting Information). The shift of the equilibrium toward the formation of $[(\mathbf{1})_2\text{-2H+Li}]^-$ sequesters **1** from the system, and therefore complex **3** cannot dimerize other than with itself, with the consequent increase of the **3** homodimeric species's intensity on the ESI-mass spectrum.

The increased flexibility in the salen derivative has therefore a pronounced, detrimental effect on the Li^+-binding ability under the experimental conditions; this is also confirmed by the weaker binding observed for Na^+ and K^+ cations.

The slow evaporation of salen derivative **3** from a mixture of DMF and MeCN produced, instead, good quality single crystals of the solvated **3**. The complex, whose structure is shown in Figure 2, presents a butterfly curvature of the organic framework. This feauture, although only slightly pronounced,[16] is unprecedented in salen derivatives, which usually adopt a nearly planar Z-type conformation,[17] and it is generally observed for more rigid salophen complexes.[10] Interestingly, the oxygen atoms of the OH groups in **3** are found to be 0.4 Å farther apart than in the case of the dimeric salophen$-UO_2$ complex. This, in addition to the overall nearly planar structure, may affect the dimer formation process, and it also may explain the difference in affinity with Li^+ observed by ESI-mass spectrometry experiments. However, the peculiar H-bond network,[18] which the two DMF and the one water molecules form, may have a role in fixing the complex conformation, and therefore this direct comparison has, unfortunately, limited value.

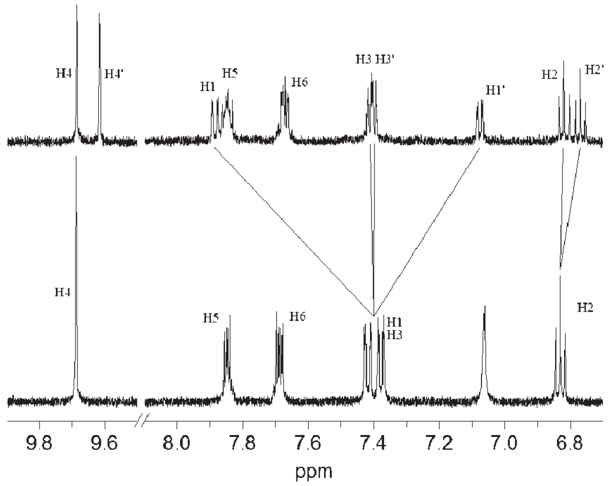


Figure 3. Portion of 500 MHz ^{1}H NMR spectra of a 2 mM solution of **1** in deuterated MeCN; before (bottom) and after (top) the addition of 1 equiv of Li^+ (as Li_2CO_3 aq.).

Figure 3 shows the ^{1}H NMR spectra at 500 MHz of a 2×10^{-3} M solution of **1** in MeCN-D_3 before (bottom) and after (top) the addition of 1 equiv of Li_2CO_3. The addition of the salt induces several shifts and splittings of the signals. In particular, significant shifts were found for the imine proton (from one singlet at 9.68 ppm to two singlets at 9.67 and 9.60 ppm) and for the H2 proton (from a triplet at 6.83 ppm to two triplets at 6.80 and 6.75 ppm). Intense shifts are also found for one of the H1 and one of the H3 protons, whose doublet signal shifts from approximately 7.40 ppm (each of the H1 and H3 protons present a doublet) to 7.06 ppm and 7.87 ppm. This new signal pattern can be easily explained by the fact that the dimer formation induces a symmetry break (see Scheme 2).[19] Whereas such a loss of symmetry is responsible for the induced splitting of the signals belonging to the salophen moiety protons, the chemical shift difference, $\Delta\delta$, is due to the sum of two effects: first, an increased electron density on the molecular framework due to the

---

(16) The curvature for **3** is described by butterfly angles (defined as the angle formed by the N_2O_2U plane and the two benzenoid rings) of 13.2 and 16.7°, clearly smaller when compared with those found in the salophen units of the **1**-dimer (39.5 and 43.4°).

(17) Evans, D. J.; Junk, P. C.; Smith, M. K. *Polyhedron* **2002**, *21*, 2421–2431.

(18) The carbonyl oxygen of the DMF molecule is H-bonded to both the UO_2-coordinated water and the phenolic OH. The $C{=}O\cdots O$ distances are 2.6 and 2.7 Å (O10a to O3a and O6a) and 2.6 and 2.8 Å (O10b to O3b and O6b), indicating quite strong H-bonding (see Figure 2).

(19) At intermediate additions of Li_2CO_3 (0.2−0.8 equiv with respect to Li^+), the monomeric and dimeric species are simultaneosly visible on the NMR spectrum, indicating a slow equilibrium on the 250−500 MHz NMR chemical shift time scale.

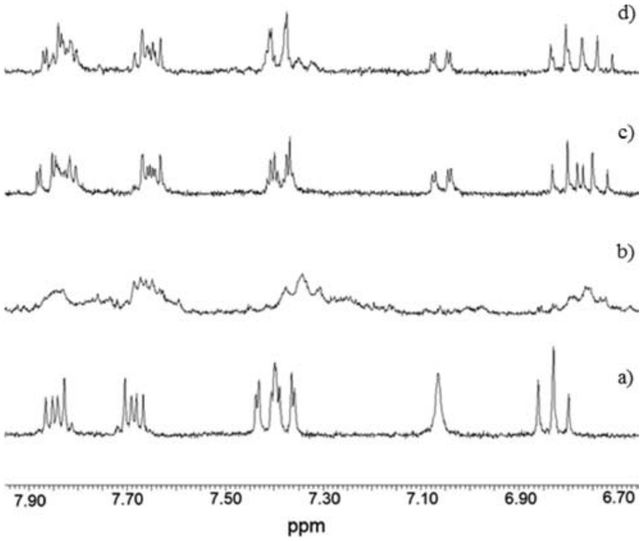


Figure 4. Selection of the 250 MHz ^{1}H NMR spectra of a 2 mM solution of **1** in MeCN (a), after the addition of 1 equiv of K_2CO_3 (b), after the addition of 1 equiv of Li_2CO_3 (c), and after the addition of 1 equiv of K_2CO_3 and $LiClO_4$ (d).

coordination on the UO_2 center (a downfield effect, already documented in similar cases when anions are coordinated to the U atom) and, second, the different chemical environment in the dimer compared with the monomeric form. Since more pronounced $\Delta\delta$ values can be reasonably expected for the protons closer to the center of the dimer, this allows for the assignment of the signals for protons H1 and H1′ (see Scheme 2).[20] A similar behavior is also observed in DMSO$-D_6$.

The possibility to study the same binding phenomenon with different techniques, which work at different concentrations and in different environments, is usually rewarding. While under the ESI-mass spectrometry high dilution conditions, the observation of the $[(\mathbf{1})_2\text{-H}]^-$ peak does not require the addition of a base; the situation is different at higher concentrations. As noted in the ^{1}H NMR spectrum of **1** in MeCN (see Figure 3), the OH proton's signal is present (at $\delta = 7.06$ ppm). This suggests that the majority of **1** is in its monomeric form under these conditions. Moreover, the sole addition of Li^+ in the form of $LiClO_4$ (ClO_4 is a very weak base) does not alter significantly the spectrum. This is a strong indication that a noncoordinative base is necessary to induce the dimerization process. At the same time, the cation must have a role too, as the ESI-mass spectrometry experiments appear to suggest.

Figure 4 shows ^{1}H NMR spectra at 250 MHz of a 2×10^{-3} M solution of **1** in MeCN-D_3 before (a), after the addition of 1 equiv of K_2CO_3 (b), and after the addition of 1 equiv of Li_2CO_3 (c). As noted before, the presence of a base induces the formation of the dimeric species, but this equilibrium is also dependent on the nature of the alkali metal cation. If the addition of 1 equiv of Li^+ quantitatively forms the dimeric species, this does not happen when K^+ is added at the same concentration. Indeed, a situation with broader signals and less significant shifts is present in this case. However, the addition of 1 equiv of $LiClO_4$ to the sample already containing K_2CO_3 produces a spectrum (d) almost identical to the one containing Li_2CO_3. This latter sample, when diluted 100-fold and sprayed, shows only the $[(\mathbf{1})_2\text{-2H+Li}]^-$ peak in the ESI-mass spectrum. These data therefore suggest the presence of a cooperative effect exerted by the $CO_3{}^{2-}$, as a base, and by the metal as a templating species for the formation of the dimer. This effect, stronger with Li^+ than with K^+, must involve a specific interaction between the metal and the UO_2 complex, in line with the selectivity trend found with the ESI-mass spectrometry experiments.

Conclusion

In this paper, we have demonstrated that the salophen$-UO_2$ complex **1** can self-assemble into a dimeric species via mutual coordinative U$-$O bonds. As noted by inspection of the X-ray determined structure, the dimer formation creates a site with a high density of O-donor atoms, in a psedo-crown-ether arrangement.

ESI-mass spectrometry experiments have shown that this rigid dimeric species, $(\mathbf{1})_2$, is able to bind the Li^+ cation with good selectivity over larger Na^+ and K^+ ions. When the OH groups are *misplaced*, as in compound **2**, the self-assembly and the metal binding are not favorable processes. The rigidity of the salophen framework seems to be beneficial to the binding, since the more flexible salen derivative **3** shows a relatively lower affinity for Li^+ than does **1**. However, the structural features by which salen and salophen complexes differ, as evidenced by X-ray analyis, also have a role.

^{1}H NMR experiments, performed in polar organic solvents (MeCN and DMSO), are in line with the ESI-mass spectrometry data. Under these higher concentration range conditions, the dimer formation requires a base, but consistently with the ESI-mass spectrometry experiments, the metal cation has a significant effect, and the Li^+/K^+ selectivity is qualitatively confirmed.

A specific interaction with the Li^+ cation must be responsible for the observed behavior, and we believe that the pseudo-crown-ether arrangement of the oxygens in the dimer can be the likely source of interaction with the metal. In order to prove this, attempts to obtain single crystals of the Li^+-$(\mathbf{1})_2$ species suitable for X-ray structural determination are underway.

Experimental Section

Synthesis. General procedure for the synthesis of UO_2 complexes **1**$-$**3**: A solution (50 mL, MeOH) of the corresponding bis-amine (10 mmol) was added to a refluxing solution (MeOH, 100 mL) of the corresponding aldehyde (20 mmol). After 1 h, $UO_2(OAc)_2 \cdot 2H_2O$ (10 mmol) was added. The refluxing was maintained for 1 h, and then the mixture was left to cool, under stirring, overnight. The red-brown precipitate which formed was filtered, washed with Et_2O, and then dried in vacuo. Complex **3** was recrystallized from the MeCN/DMF mixture.

Complex 1. Yield: 75%. ^{1}H NMR (500 MHz, DMSO-d6): δ 9.58 (s, 2H), 8.48 (s, 2H), 7.75$-$7.78 (m, 2H), 7.52$-$7.56 (m, 2H), 7.28 (dd, 2H, $J_1 = 1.6$ Hz, $J_2 = 8.1$ Hz), 7.16 (dd, 2H, $J_1 = 1.6$ Hz, $J_2 = 7.5$ Hz), 6.57 ppm (t, 2H, $J = 7.7$ Hz). ^{13}C NMR (126 MHz, DMSO-d6): δ 166.83, 158.91, 148.15, 146.72, 128.74, 125.75, 123.46, 120.22, 118.91, 116.42 ppm. MS(ES) m/z calcd for $C_{20}H_{13}O_6N_2U$: 615.4 $[M - H]^-$. Found: 615.3. Anal. Calcd for $C_{20}H_{14}O_6N_2U-H_2O$ (MW = 634.418): C, 37.86; H, 2.54; N, 4.42. Found: C, 38.24; H, 2.70; N, 4.50.

---

[20] Alternative assignments are also possible (see the Supporting Information).

Complex 2. Yield: 70%. ^{1}H NMR (250 MHz, DMSO-d6): δ 9.46 (s, 2H), 8.79 (s, 2H), 7.73 (m, 2H), 7.51 (m, 2H), 7.13 (m, 4H), 6.82 (d, 2H, 9.5 Hz). ^{13}C NMR (63 MHz, DMSO-d6): δ 165.97, 163.69, 147.83, 146.73, 128.53, 125.04, 123.29, 120.90, 120.138, 118.75 ppm. MS(ES) m/z calcd. for $C_{20}H_{13}O_6N_2U$: 615.4 $[M - H]^-$. Found: 615.2. Anal. Calcd. for $C_{20}H_{14}O_6N_2U{-}CH_3OH$ (MW = 648.41): C, 38.90; H, 2.80; N, 4.32. Found: C, 38.54; H, 2.60; N, 4.55.

Complex 3. Yield: 60%. ^{1}H NMR (250 MHz, DMSO-d6): ^{1}H NMR (250 MHz, DMSO-d6): δ 9.45 (s, 2H), 8.19 (s, 2H), 7.11 (m, 4H), 6.55 (t, 2H, $J = 7.5$ Hz), 4.51 (s, 4H). ^{13}C NMR (63 MHz, DMSO-d6): δ 168.88, 157.39, 148.20, 124.53, 122.46, 117.64, 115.92, 63.63 ppm. MS(ESI) m/z calcd. for $C_{16}H_{13}N_2O_6U$: 567.14 $[M - H]^-$. Found: 567.12. Anal. Calcd. for $C_{16}H_{13}N_2O_6U{-}DMF$ (MW = 641.41): C, 35.58; H, 3.30; N, 6.55. Found: C, 35.85; H, 3.70; N, 6.50.

Negative ESI Mass Spectrometry. ESI mass spectra were recorded on an LCT TOF mass spectrometer with an electrospray ion source (Micromass LCT). MeCN served as a spray solvent in all cases. Ionization parameters were adjusted as follows: capillary voltage, 3000 V; cone voltage, 20 V; sample cone, 7 V; RF lens, 800 V. Desolvation and source temperature were 120 and 80 °C, respectively. The S/N ratio was improved by scan average. Metal carbonates (M_2CO_3, M = Li, Na, and K) were added from highly concentrated water solutions.

NMR. Proton NMR spectra were recorded on 250 and 500 MHz Bruker Advance machines.

Crystallography. Data were recorded with a Bruker-Nonius Kappa APEX II diffractometer using graphite-monochromatized Mo Ka radiation [λ = 0.071073 nm)] at 173.0(1) K. The data were processed with Denzo-SMN v0.95.373,[21] and the structure was solved by direct methods.[22] Refinements based on F^2 were made using full-matrix least-squares techniques.[23] Multiscan absorption correction (SADABS2008) was applied.[24] The hydrogen atoms were calculated to their idealized positions with isotropic temperature factors (1.2 or 1.5 times the C temperature factor) and refined as riding atoms. The salen **3** complex was solved and refined as a racemic twin in a polar space group. Any attempts to solve the structure in the centric space group *Pbmm* failed. The two halves of the molecule **3** are situated on a mirror plane leading to a disorder of the salen moiety. Some geometrical restraints were applied, and the disordered salen carbon atoms were refined isotropically.

Crystal data for $[(Et)_3NH^+)_2(\mathbf{1}_2\text{-}2H)^{2\text{-}}]\cdot(acetone)_2$. Formula, $C_{58}H_{70}N_6O_{14}U_2$; crystal size, 0.15 × 0.20 × 0.30 mm; orthorhombic; space group, *Pbca*; a = 11.4824(1) Å; b = 17.2116(3) Å; c = 29.8556(6) Å; V = 5900.4(2) Å^3; Z = 4; D_{calcd} = 1.746 g/cm^{-3}; μ = 5.551 mm^{-1}; 52 057 reflections measured ($2\theta_{max}$ = 28.5); 7399 independent; 4177 with $I > 2\sigma(I)$; number of parameters, 346; three restraints; R_{int} = 0.1439; R = 0.0732 [$I > 2\sigma(I)$]; wR^2 = 0.1505 [all data]; GOF = 1.027. Maximum and minimum peaks in the difference map, 1.363 (near U) and −1.013 eÅ^{-3}.

Crystal data for $\mathbf{3}\cdot(H_2O)\cdot(DMF)_2$. Formula, $C_{22}H_{30}N_4O_9U$; crystal size, 0.08 × 0.15 × 0.25 mm; orthorhombic; space group, *Pb*2$_1$*m*; a = 7.3241(2) Å; b = 13.6857(3) Å; c = 25.6837(6) Å; V = 2574.4(1) Å^3; Z = 4; D_{calcd} = 1.890 g/cm^{-3}; μ = 6.361 mm^{-1}; 16 496 reflections measured ($2\theta_{max}$ = 25°); 4521 independent; 3695 with $I > 2\sigma(I)$; number of parameters 343; 19 restrainsts; R_{int} = 0.0372; R = 0.0260 [$I > 2\sigma(I)$]; wR^2 = 0.0621 [all data]; GOF = 1.062. Maximum and minimum peaks in the difference map, 0.812 and −0.947 eÅ^{-3}. Flack x parameter, 0.47(2).

Acknowledgment. The authors gratefully acknowledge the Academy of Finland (proj. no. 212588) for financial support.

Supporting Information Available: ESI-mass spectra for the complexation and competition experiments with complexes **1**−**3**. Alternative assignment for the ^{1}H NMR spectrum of dimeric **1**. CIF files of $[(Et)_3NH^+)_2(\mathbf{1}_2\text{-}2H)^{2\text{-}}]\cdot(acetone)_2$ and $\mathbf{3}\cdot(H_2O)\cdot$-$(DMF)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(21) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307–326.

(22) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.

(23) Sheldrick, G. M.; Schneider, T. R. *Methods Enzymol.* **1997**, *277*, 319–343.

(24) Sheldrick, G. M. *Acta Crystallogr., Sect A* **2008**, *64*, 112–122.