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Molecular Design of a Calix[6]arene-Based Super-Uranophile with C_3 Symmetry. High UO_2^{2+} Selectivity in Solvent Extraction

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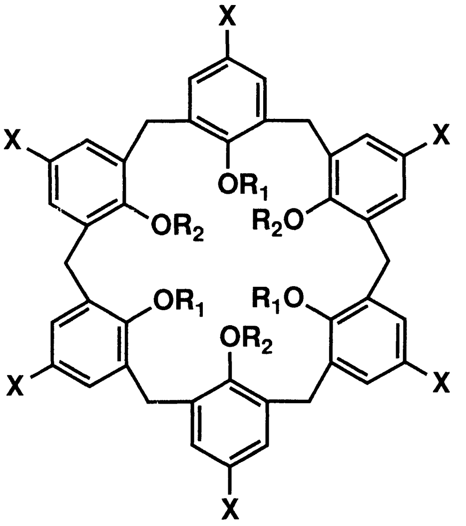
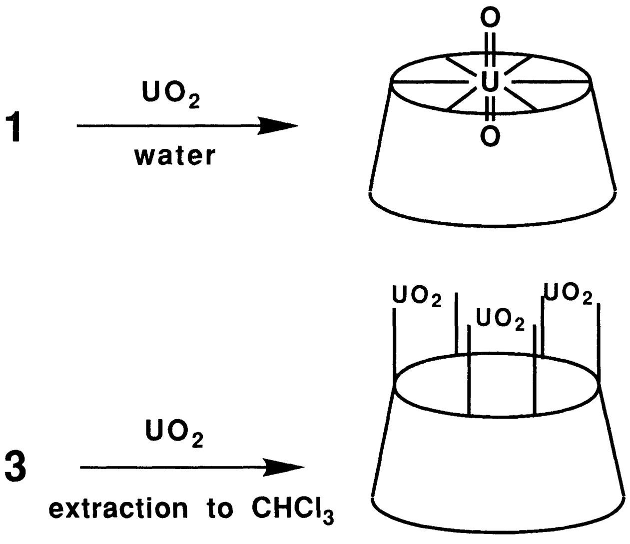
Calix[6]arene bearing three carboxylate groups arranged in C_3 symmetry formed a 1:1 complex with UO_2^{2+} and showed much more excellent selectivity factors for UO_2^{2+} in solvent extraction than calix[6]arene bearing six carboxylate groups. This establishes that the essence of "super-uranophiles" is related to the molecular design of C_3 symmetry.

X-Ray crystallographic studies have established that UO_2^{2+} complexes adopt either a pseudoplanar pentacoordinate or hexacoordinate structure, which is quite different from the coordination structures of other metal ions. This suggests that a macrocyclic host molecule having a nearly coplanar arrangement of either five or six ligand groups would serve as a specific ligand for UO_2^{2+} (i.e., as a uranophile). This approach has been investigated by several groups.[1-7] We previously found that water-soluble calix[6]arene **1**, which exactly satisfies the above prerequisite, forms a 1:1 complex with UO_2^{2+} and has a remarkably high stability constant ($K_{\mathrm{uranyl}} = 10^{18.7}\ \mathrm{dm^3\ mol^{-1}}$) and selectivity factors ($K_{\mathrm{uranyl}} / K_{\mathrm{M}^{n+}} > 10^{12}$) in water.[3] Based on these findings, we designed lipophilic calix[6]arenes **2** and **3**.[4,7] Although these calix[6]arenes could efficiently extract UO_2^{2+} from aqueous solution to organic phase, the extracted species turned out to be a 1:3 calix[6]arene/UO_2^{2+} complex and the selectivity factors in two-phase solvent-extraction were not so excellent as those in **1** in an aqueous system.[4,7] We thus considered that to imitate the structure of the stable uranyl tricarbonate complex, $UO_2(CO_3)_3^{4-}$ three carboxylate groups suffice and extra three carboxylate groups in **2** rather hamper the selectivity factors. Conceivably, more important is to arrange these three essential carboxylate groups in C_3 symmetry to yield the hexaccodinate structure. Here, we synthesized compound **4** in which three carboxylate groups are arranged in C_3 symmetry and tested the UO_2^{2+} selectivity in a two-phase solvent-extraction system.



1: $R_1=R_2=CH_2COOH$, $X=SO_3Na$
2: $R_1=R_2=CH_2COOH$, X=*t*-Bu
3: $R_1=R_2=CH_2CONHOH$, X=*t*-Bu
4: R_1=OMe, $R_2=CH_2COOH$, X=*t*-Bu



Compound **4** was synthesized according to the literature[8)] and identified by IR, ^1H NMR, and elemental analysis. The details of solvent extraction and analysis of metal concentrations were described previously.[4)] The pH dependence for UO_2^{2+} extraction (Fig. 1) shows that the extractability of **4** is a little inferior to those of **2** and **3** but reaches nearly 100% at pH 7. At pH 5.9 (buffered with 10 mmol dm^{-3} potassium acetate) we carried out extraction in the absence and the presence of UO_2^{2+} in the aqueous phase. In the absence of UO_2^{2+} we detected 1.2 equiv. of K^+ in the chloroform phase whereas in the presence of UO_2^{2+} we detected **4** : UO_2^{2+} : K^+ = 1.0 : 0.85 : 1.2 in the chloroform phase. The results support the following extraction scheme including the formation of the 1:1 calix[6]arene/UO_2^{2+} complex: UO_2^{2+} (aq) + $K^+ \cdot \mathbf{4}H_2^-$(org) $\longrightarrow$ $2H^+$(aq) + $UO_2^{2+} \cdot K^+ \cdot \mathbf{4}^{3-}$((org) where $\mathbf{4}H_3$ denotes undissociated species of **4**. The formation of the 1:1 calix[6]arene/UO_2^{2+} complex is further confirmed by the molar ratio plot in Fig. 2, which gives a breakpoint at $[\mathbf{4}]/[UO_2^{2+}]$ = 1.0. These results indicate that **4** bearing three carboxylate groups in C_3 symmetry forms the 1:1 complex as **1** did in homogeneous aqueous solution.[3)]

We confirmed if the $UO_2^{2+} \cdot M^+ \cdot \mathbf{4}^{3-}$ complex adopts C_3 symmetry similar to the $UO_2(CO_3)_3^{4-}$ complex. $Cs^+ \cdot \mathbf{4}H_2^-$ and $UO_2(NO_3)_2$ (1:1 mole ratio) were dissolved in a mixed solvent of DMSO-d_6 and $CDCl_3$ (1:1 v/v) and the resultant solution was subjected to ^1H NMR measurement (30 °C, 250 MHz): δ 0.78 and 1.37 (*t*-Bu, s each, 27H each), 4.46 (OCH_2 and endo-$ArCH_2Ar$, br s, 12H; exo-$ArCH_2Ar$ protons are overlapped with water protons in solvent (ca. 3.4 ppm)), 6.61 and 8.21 (ArH, s each, 6H each). The spectral finding that three carboxylate groups are equivalent supports the view that the complex adopts C_3 symmetry (Fig. 3).

Table 1. Solvent extraction of UO_2^{2+} in the presence of competing metal cations at 30 °C[a)]

Metal(mmol dm^{-3})	Ex%/Ex% without competing metal	
	2	**4**
Mg^{2+}(100)	72	92
Ni^{2+}(0.25)	93	98
Ni^{2+}(1.00)	77	98
Zn^{2+}(0.73)	63	98

a) pH 5.9 with 10 mmol dm^{-3} acetate buffer. For other conditions see a footnote to Fig. 1.

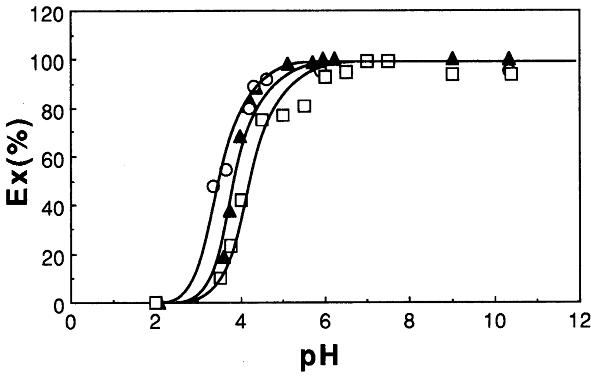


Fig. 1. pH Dependence for UO_2^{2+} extraction from water (25 cm^3) to chloroform (5 cm^3) at 30 °C: $[K_4UO_2(CO_3)_3]$ = 0.106 mmol dm^{-3} in water, [**2**(○), **3**(▲), **4**(□)] = 0.530 mmol dm^{-3} in chloroform.

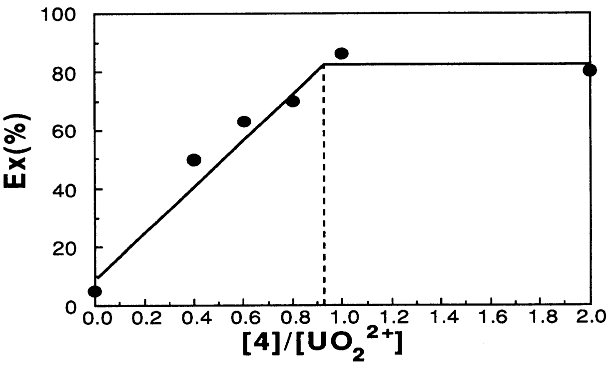


Fig. 2. Plot of Ex% vs. [calixarene]/[UO_2^{2+}]: pH 6.2 with 10 mmol dm^{-3} acetate buffer. The concentraion of UO_2^{2+} (added) as $K_4UO_2(CO_3)_3$) was maintained constant (1.06 x 10^{-4} mol dm^{-3}).

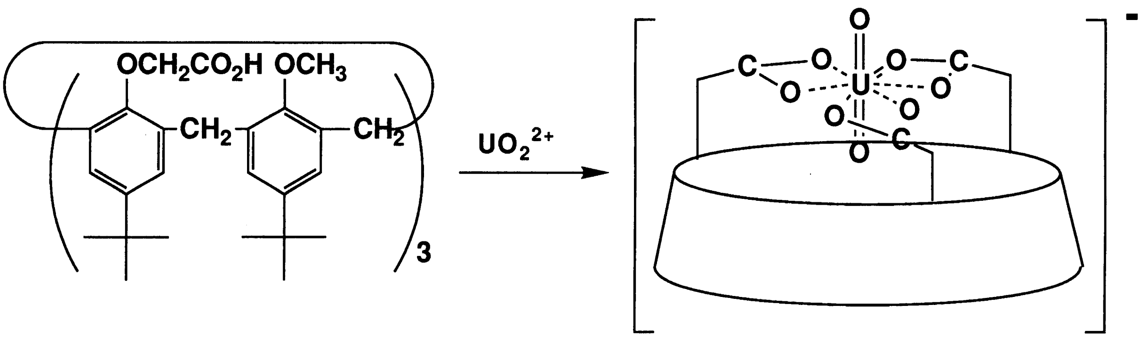


Fig. 3. Complex structure with C_3 symmetry proposed for the $UO_2^{2+}\cdot 4^{3-}$ complex.

The UO_2^{2+} selectivities in a two-phase solvent-extraction system are summarized in Table 1. As mentioned previously,7) the Ex% values for **2** were significantly reduced, indicating that these metal cations can significantly compete with UO_2^{2+} for a binding-site in **2**. Since **2** forms the 1:3 calix[6]arene/UO_2^{2+} complex, the advantage of the calix[6]arene skeleton that can provide a pseudoplanar hexacoordination structure is not ultimately used. In contrast, the Ex% values for **4** were scarcely affected by these metal cations, indicating the high UO_2^{2+} affinity of three carboxylate groups arranged in C_3 symmetry.

In conclusion, the present paper demonstrated that in molecular design of super-uranophiles it is important to arrange three carboxylate groups in C_3 symmetry and the presence of extra carboxylate groups rather decreases the selectivity factor in a two-phase solvent-extraction system. We believe that the rigid skeleton of calix[6]arene is indispensable to firmly maintain the C_3 symmetry.

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