

Kinetic Studies of Calixarene-based Cyclic and Non-cyclic 'Super-uranophiles'

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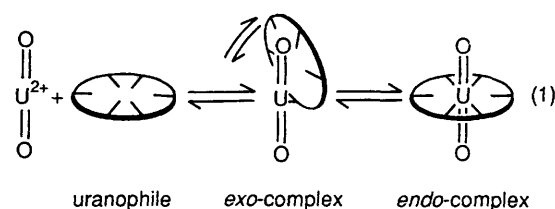
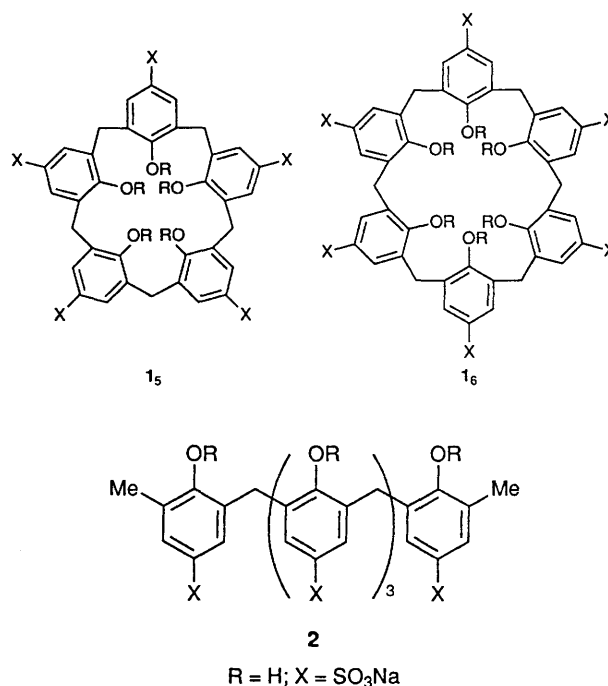
The kinetic parameters for the binding of UO_2^{2+} to calixarene-based 'super-uranophiles', *para*-sulphonatocalix[*n*]arenes ($n = 5, 6$ and 8 ; **1_n**) and their non-cyclic analogue, 3,5-bis{[2-hydroxy-3-(2-hydroxy-3-methyl-5-sulphonatophenyl)methyl-5-sulphonatophenyl]methyl}-4-hydroxybenzene-sulphonate (**2**) have been evaluated at 25 °C and pH 10.40. The reaction of UO_2^{2+} and **2** is speeded up by a factor of 85 compared to that of UO_2^{2+} and **1₆**.

The selective extraction of uranium from sea water has attracted extensive attention from chemists because of its importance in relation to energy problems. In order to design such a ligand that is capable of selective extraction of uranyl ion (UO_2^{2+}), one faces a difficult problem: *i.e.* the ligand must strictly discriminate UO_2^{2+} from other metal ions present in great excess in sea water. It has been established that UO_2^{2+} complexes adopt either a pseudoplanar pentacoordinate or hexacoordinate structure.¹ 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).² Calixarenes are cyclic oligomers made up of phenol units.³ We recently found that calix[5]arene-*p*-pentasulphonate (**1₅**) and calix[6]arene-*p*-hexsulphonate (**1₆**) have remarkably large, record-breaking stability constants ($K_{\text{uranyl}} = 10^{18.7-19.2} \text{ dm}^3 \text{ mol}^{-1}$) and selectivity factors ($K_{\text{uranyl}}/K_{\text{M}^{2+}} = 10^{10-17}$) in water.⁴ The results are attributed to the moderately rigid skeleton of calix[5]arene and calix[6]arene which can provide the pre-organized penta- and hexa-coordination geometry for the binding of UO_2^{2+} . A preliminary kinetic study on **1₆** indicated that the binding rate is relatively slow, the half-life at room temperature being *ca.* 1 h. This is supposed to be the sole defect of the calixarene-based uranophiles. What is taking so long? Rebek *et al.*⁵ found that the reaction rate for the binding of 18-crown-6 to $\text{Hg}(\text{CN})_2$ or $\text{Hg}(\text{CF}_3)_2$ (linear guest cation) is very slow. As UO_2^{2+} is also a linear guest cation ($\text{O}=\text{U}=\text{O}^{2+}$), the slow binding rate may be a characteristic of a reaction between linear guest cations and cyclic host ligands. If so, this phenomenon would be attributed, as pointed out by Rebek *et al.*,⁵ to the slow *exo*- to *endo*-complex (rotaxane-type complex) step which must experience a high-energy conformation in order to permit UO_2^{2+} to penetrate the calixarene ring [as in eqn. (1)]. As an attempt to remove this defect, we have designed a non-cyclic calixarene analogue **2** which does not necessarily experience such a high-energy conformation as an obligatory path and compared its equilibrium and kinetic parameters with those of **1_n** ($n = 5, 6$ and 8).

Preparations of **1_n** have been described previously.^{4,6} Compound **2** was prepared by sulphonation of 2,6-bis{[2-hydroxy-3-(2-hydroxy-3-methylphenyl)methylphenyl]methyl}phenol.†

† This compound was prepared by de-*tert*-butylation of 2,6-bis{[2-hydroxy-3-(2-hydroxy-3-methyl-5-*tert*-butylphenyl)methyl-5-*tert*-butylphenyl]methyl}-4-*tert*-butylphenol. The methods used for de-*tert*-butylation and sulphonation are similar to those used for the syntheses of **1_n**.⁴

‡ M.p. > 300 °C, yield 49%; IR (Nujol) ν_{SO} /cm⁻¹ 1050, 1170; ¹H NMR (D_2O , internal standard DSS) δ 2.27 (6 H, s, CH_3), 4.05 and 4.07 (4 H and 4 H, s and s, ArCH_2Ar), 7.40, 7.42, 7.45, 7.48 and 7.51 (2 H each, all s, ArH) (Found: C, 36.5; H, 3.7%. Calc. for $\text{C}_{36}\text{H}_{29}\text{O}_{20}\text{S}_5\text{Na} \cdot 7\text{H}_2\text{O}$: C, 36.55; H, 3.66%).



The product was identified as **2** by IR, ¹H NMR spectroscopy and elemental analysis.‡

The measurements were carried out at pH 10.40 (adjusted with carbonate buffer) and 25 °C. The stoichiometry for the uranyl complexes was studied by a continuous variation method. The stability constants ($K_{\text{uranyl}} = [\text{UO}_2^{2+}\text{-uranophile}]/[\text{UO}_2^{2+}][\text{uranophile}]$) were evaluated by a displacement method (described in ref. 4). The reaction of uranophiles and $\text{UO}_2(\text{CO}_3)_3^{4-}$ in carbonate buffer solution was followed by monitoring the appearance of a new absorption band at 449 nm. Under the pseudo-first-order conditions ($[\text{uranophile}] \ll [\text{UO}_2(\text{CO}_3)_3^{4-}]$) the reaction obeyed first-order kinetics for up to three half-lives. Although the equilibrium reaction for eqn.

Table 1 Stoichiometry, kinetic parameters and stability constants for the complexes of UO_2^{2+} and calixarene derivatives

Calixarene	Stoichiometry ^a UO_2^{2+} :uranophile	$k_{\text{obs}}/10^{-3} \text{ s}^{-1}$	$k_f/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$k_r/10^{-3} \text{ s}^{-1}$	$\log K_{\text{uranyl}}$
1₅	1:1	1.15	1.05	0.138	18.9 ^c
1₆	1:1	0.111	0.0762	0.0504	19.2 ^c
1₈	1:2	2.74 ^d	— ^e	— ^e	18.7 (= $\log K_1$) ^f 18.1 (= $\log K_2$) ^f
2	1:1	9.38	2.13	7.13 ^g	17.7

^a Determined by a continuous variation method at $[\text{UO}_2(\text{CO}_3)_3^{4-}] + [\text{calixarene}] = 1.34 \times 10^{-3} \text{ mol dm}^{-3}$. ^b Pseudo first-order rate constant at $[\text{UO}_2(\text{CO}_3)_3^{4-}] = 4.90 \times 10^{-3} \text{ mol dm}^{-3}$ in $0.030 \text{ mol dm}^{-3}$ carbonate buffer. ^c Cited from ref. 4. ^d Since the reaction obeyed first-order kinetics, it is unlikely that k_{f1} (the pseudo first-order rate constant for the formation of the $\text{UO}_2^{2+} \cdot \mathbf{1}_8$ complex) $> k_{f2}$ [the pseudo first-order rate constant for formation of the $(\text{UO}_2^{2+})_2 \cdot \mathbf{1}_8$ complex]. Thus, the possible kinetic situation is either $k_{f1} \approx k_{f2}$ or $k_{f1} < k_{f2}$. ^e The kinetic equation for the two-step UO_2^{2+} -binding, $\text{UO}_2(\text{CO}_3)_3^{4-} + \mathbf{1}_8 \rightleftharpoons \text{UO}_2^{2+} \cdot \mathbf{1}_8 + 3\text{CO}_3^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-} + \text{UO}_2^{2+} \cdot \mathbf{1}_8 \rightleftharpoons (\text{UO}_2^{2+})_2 \cdot \mathbf{1}_8 + 3\text{CO}_3^{2-}$, is too complicated to determine k_f and k_r . ^f $K_1 = [\text{UO}_2^{2+} \cdot \mathbf{1}_8]/[\text{UO}_2^{2+}][\mathbf{1}_8]$ and $K_2 = [(\text{UO}_2^{2+})_2 \cdot \mathbf{1}_8]/[\text{UO}_2^{2+}][\text{UO}_2^{2+} \cdot \mathbf{1}_8]$. These values were estimated by a computer simulation (non-linear least-squares method) of a plot of OD_{449} vs. $[\mathbf{1}_8]$ at $[\text{UO}_2(\text{CO}_3)_3^{4-}] = 1.11 \times 10^{-4} \text{ mol dm}^{-3}$ (constant), where $\epsilon_1 (= 1320 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ for $\text{UO}_2^{2+} \cdot \mathbf{1}_8$ and $\epsilon_2 (= 2290 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ for $(\text{UO}_2^{2+})_2 \cdot \mathbf{1}_8$, which were needed for the simulation, were determined from the absorbances at $[\text{UO}_2^{2+}] \ll [\mathbf{1}_8]$ and $[\text{UO}_2^{2+}] \gg [\mathbf{1}_8]$, respectively. ^g $k_r[\text{CO}_3^{2-}]$ (at $[\text{CO}_3^{2-}] = 0.030 \text{ mol dm}^{-3}$) $= 7.13 \times 10^{-3} \text{ s}^{-1}$. Thus, k_r [in eqn. (5)] $= 0.238 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

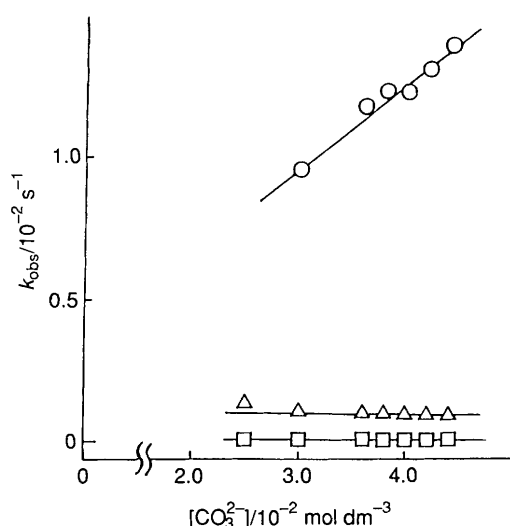


Fig. 1 Plots of k_{obs} vs. $[\text{CO}_3^{2-}]$: 25 °C, pH 10.40 with $0.030 \text{ mol dm}^{-3}$ carbonate, $\mu = 0.15$, $[\mathbf{1}_n \text{ or } \mathbf{2}] = 9.30 \times 10^{-5} \text{ mol dm}^{-3}$ $[\text{UO}_2(\text{CO}_3)_3^{4-}] = 8.75 \times 10^{-4} \text{ mol dm}^{-3}$

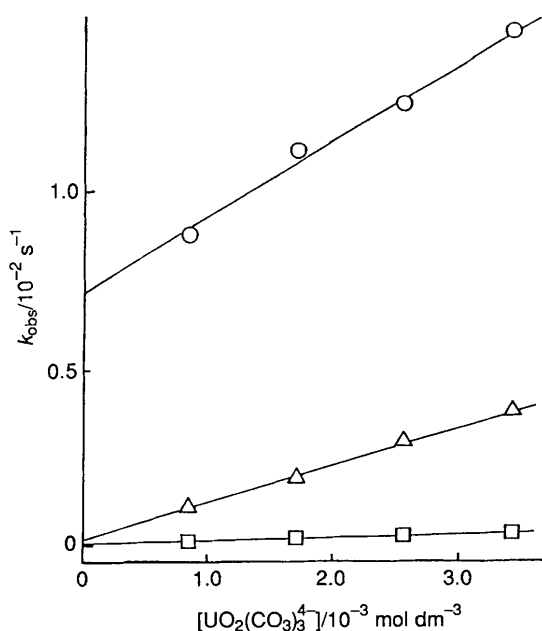
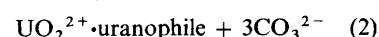
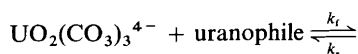


Fig. 2 Plots of k_{obs} vs. $[\text{UO}_2(\text{CO}_3)_3^{4-}]$: 25 °C, pH 10.40 with $0.030 \text{ mol dm}^{-3}$ carbonate, $\mu = 0.15$, $[\mathbf{1}_n \text{ or } \mathbf{2}] = 4.00 \times 10^{-4} \text{ mol dm}^{-3}$

(2) is formally expressed by eqn. (3), the third-order dependence on the carbonate concentration is actually inconceivable. We thus determined k_{obs} as a function of $[\text{CO}_3^{2-}]$. As shown in Fig. 1 $[\text{UO}_2(\text{CO}_3)_3^{4-}]$ is maintained constant, k_{obs} for **2** showed a first-order dependence whereas that for **1₅** and **1₆** showed a zero-order dependence. This implies that in the $\text{UO}_2^{2+} \cdot \mathbf{2}$ complex the non-cyclic chain surrounding the UO_2^{2+} ion is displaced bimolecularly by the nucleophilic attack of CO_3^{2-} whereas in the rotaxane-type $\text{UO}_2^{2+} \cdot \mathbf{1}_5$ and $\text{UO}_2^{2+} \cdot \mathbf{1}_6$ complexes the UO_2^{2+} ion is protected by the calixarene ring from nucleophilic attack by CO_3^{2-} . The complexes feature unimolecular demetallation followed by association with CO_3^{2-} . Thus, the equilibrium reaction for **1₅** and **1₆** is expressed by eqn. (4) and that for **2** by eqn. (5).

Plots of k_{obs} vs. $[\text{UO}_2(\text{CO}_3)_3^{4-}]$ are illustrated in Fig. 2. From the slope and the intercept one can determine k_f and k_r , respectively. The results are summarized in Table 1.



$$k_{\text{obs}} = k_f[\text{UO}_2(\text{CO}_3)_3^{4-}] + k_r[\text{CO}_3^{2-}]^3 \quad (3)$$

$$k_{\text{obs}} = k_f[\text{UO}_2(\text{CO}_3)_3^{4-}] + k_r \quad (4)$$

$$k_{\text{obs}} = k_f[\text{UO}_2(\text{CO}_3)_3^{4-}] + k_r[\text{CO}_3^{2-}] \quad (5)$$

The stoichiometry in Table 1 establishes that **1₅**, **1₆** and **2** form a 1:1 UO_2^{2+} /calixarene complex, whereas **1₈**, having a large calix[8]arene ring, forms a 2:1 UO_2^{2+} /calixarene complex. The stability constants for $\text{UO}_2^{2+} \cdot \mathbf{1}_8$ (K_1 and K_2 , respectively) are comparable with those for **1₅** and **1₆**. It is known that the calix[8]arene ring is more flexible than the smaller calixarene rings.³ Although the phenolic oxygens are not suitably arranged for coordination to UO_2^{2+} , the flexibility would allow an induced-fit type complexation with UO_2^{2+} . In contrast, K_{uranyl} for non-cyclic **2** is somewhat smaller than those values for cyclic **1_n**.

As expected, the rate constants for non-cyclic **2** are greater than those for cyclic **1_n**. Examination of kinetic parameters reveals that the rapid equilibration in **2** is not only due to the fast forward complexation rate but also due to the more enhanced reverse decomplexation rate: for example, k_f and $k_r[\text{CO}_3^{2-}]$ (at $[\text{CO}_3^{2-}] = 0.030 \text{ mol dm}^{-3}$) for **2** are greater by 28-fold and 141-fold, than k_f and k_r for **1₆**, respectively. This means that carbonate ligands in $\text{UO}_2(\text{CO}_3)_3^{4-}$ are easily

replaced by noncyclic **2**, but **2** in the $\text{UO}_2^{2+}\cdot\text{2}$ complex is more easily replaced by carbonate ligands. The results establish that the reaction of **2** and UO_2^{2+} has a transition state much lower than those for **1_n** and UO_2^{2+} . The difference is explained because non-cyclic **2** does not need to experience an energetically unfavourable *exo*- to *endo*-complex step as an obligatory path.

Surprisingly, compound **1₅** gave kinetic parameters much greater than those for **1₆**. Why are the kinetic parameters for **1₅** so peculiar? Previously, we found that in the binding of **1₅** to UO_2^{2+} four OH groups are dissociated at pH 6 and one OH group remains undissociated; at pH 9 the last OH group is dissociated to form the fully-saturated pentacoordinate complex. In contrast, six OH groups in **1₆** are all dissociated at pH 6. This suggests that the calix[5]arene ring *a priori* is distorted and in the binding to UO_2^{2+} the initial and the final state are both destabilized. This view explains well the relatively fast equilibration in **1₅**.

In conclusion, the present study demonstrated that non-cyclic **2** and calixarene **1₅** act as better uranophiles for experiments including dynamic processes (*e.g.*, solvent extraction, membrane transport, *etc.*). Thus, they may be more useful for extracting UO_2^{2+} from sea water.

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