Synthesis and Solvent Extraction Studies of Novel Calixarene-based Uranophiles Bearing Hydroxamic Groups†

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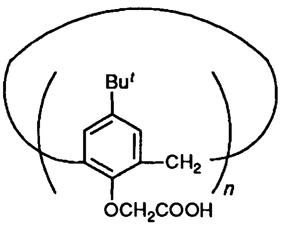
Calix[*n*]arene-based uranophiles bearing hydroxamic groups on the lower rim ($\mathbf{2}_n$; $n = 4$ and 6) have been synthesized and the extractability (Ex%) and the selectivity towards uranyl ion (UO_2^{2+}) estimated in a two-phase (water–chloroform) solvent-extraction system. Ex% for $\mathbf{2}_4$ and $\mathbf{2}_6$ increases from pH 2 and saturation is reached at around pH 5 where 100% extractability occurs. Since the pK_a values for hydroxamic acids are 8–9, the apparent pK_a shift caused by the UO_2^{2+}-complexation amounts to 6–7 pK units. Extraction of UO_2^{2+} from aqueous carbonate solution established that $\mathbf{2}_6$ in the organic phase can compete efficiently with CO_3^{2-} ions in the aqueous phase for UO_2^{2+} whereas in $\mathbf{2}_4$ and a calix[6]arene-based uranophile bearing six carboxy groups ($\mathbf{1}_6$) UO_2^{2+} is re-extracted to the aqueous phase. The difference indicates that $\mathbf{2}_6$, which has the hexacoordination geometry preorganized for the binding of UO_2^{2+}, is superior to $\mathbf{2}_4$ as a uranophile. We also found that the selectivity of $\mathbf{2}_6$ is superior to $\mathbf{1}_6$: the Ex% values for $\mathbf{2}_6$ is scarcely affected by the addition of competing metal cations (except Fe^{3+}). These results show that $\mathbf{2}_6$ serves as an excellent UO_2^{2+}-selective extraction reagent.

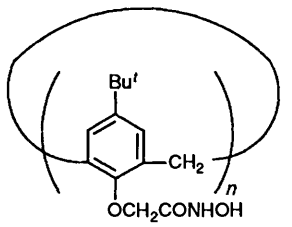
The selective extraction of uranium has attracted extensive attention from chemists because of its importance in relation to energy problems. In order to design a ligand that can selectively extract uranyl ion (UO_2^{2+}), one has to overcome a difficult problem: that is, the ligand must discriminate strictly between UO_2^{2+} and other metal ions present in great excess in sea water. A possibly unique solution to this difficult problem is provided by the unusual coordination structure of UO_2^{2+} complexes which require either a pseudoplanar pentacoordinate or hexacoordinate structure.[1–3] This suggests that a macrocyclic host molecule having a nearly coplanar arrangement of either five or six ligand groups would act as a specific ligand for UO_2^{2+} (*i.e.*, as a uranophile). This approach has been investigated by several groups.[4–8] We previously found that calix[5]arene-*p*-pentasulphonate derivatives and calix[6]arene-*p*-hexasulphonate derivatives have remarkably large stability constants ($K_{uranyl} = 10^{18.7-19.2}$ dm^3 mol^{-1}) and selectivity factors ($K_{uranyl}/K_{M^{n+}} = 10^{10-17}$) in water.[7,8] The remarkably high selectivity is attributed to the 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+}. This concept can be extended to two-phase solvent extraction: a lipophilic hexacarboxylate derivative of *p*-*tert*-butylcalix[6]arene ($\mathbf{1}_6$) can extract UO_2^{2+} efficiently and selectively from water into organic media.[9] Meanwhile, it has been established in the field of polymer chemistry that the hydroxamate group acts as an efficient ligand for adsorbing UO_2^{2+} on a chelate resin.[10,11] This tempted us to synthesize new uranophiles bearing hydroxamate groups on calix[*n*]arene rings ($\mathbf{2}_n$: $n = 4$ and 6). We report here the synthesis and extraction properties of $\mathbf{2}_n$.

Experimental

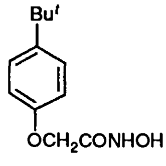
Materials.—Compounds $\mathbf{2}_4$ and $\mathbf{2}_6$ were synthesized from $\mathbf{1}_4$ and $\mathbf{1}_6$,[7,8] respectively, *via* the acid chlorides (see Scheme 1).



$\mathbf{1}_n$



$\mathbf{2}_n$



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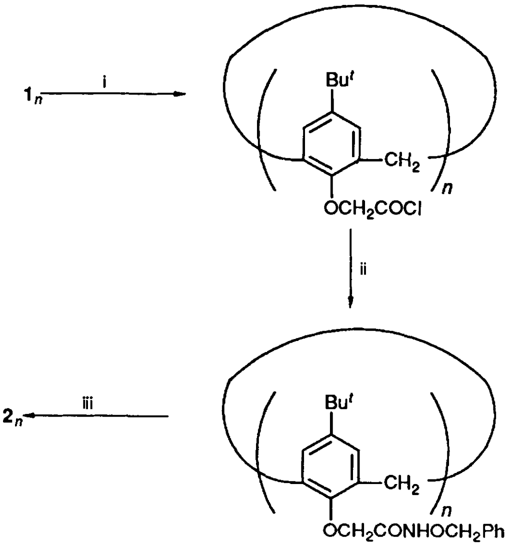

Scheme 1 *Reagents:* i, $(COCl)_2$; ii, *O*-benzylhydroxylamine; iii, H_2/Pd–C

25,26,27,28-*Tetrakis*(N-*benzyloxycarbamoylmethoxy*)-p-tert-*butylcalix*[4]*arene*.—Compound $\mathbf{1}_4$ (1.0 g; 1.13 mmol) and oxalyl chloride (25 cm^3) in carbon tetrachloride (50 cm^3) were refluxed for 6 h. After being cooled, the solution was concentrated under a stream of nitrogen. The residual acid

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† *Preliminary communication:* T. Nagasaki, S. Shinkai and T. Matsuda, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2617.

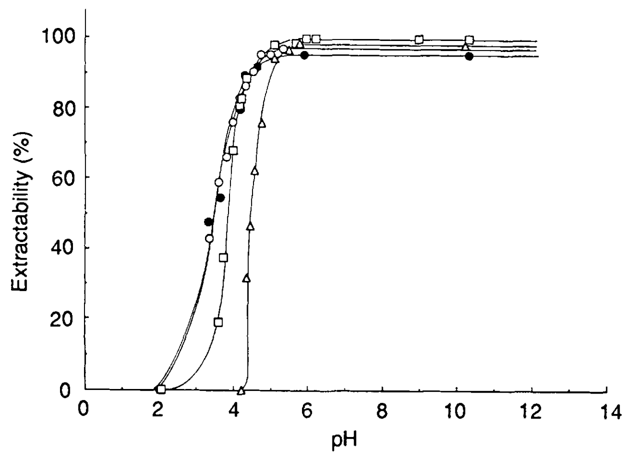

Fig. 1 pH Dependence for UO_2^{2+} extraction from water (25 cm^3) to chloroform (25 cm^3) at 30 °C; [1_6 (●), 2_4 (○) or 2_6 (□)] = 5.30×10^{-4} mol dm^{-3}, [3(△)] = 3.18×10^{-3} mol dm^{-3} (= $6 \times 5.30 \times 10^{-4}$ mol dm^{-3})

chloride (confirmed by IR spectroscopy: no ν_{O-H}) was dissolved in THF (30 cm^3). The solution was added dropwise to a THF solution containing *O*-benzylhydroxylamine (1.60 g, 1.82 mmol) and pyridine (0.70 g, 8.85 mmol). The solution was heated at 35 °C for 30 h. After cooling, the precipitate was removed by filtration, the filtrate being concentrated to dryness under reduced pressure. The residue was dissolved in chloroform (300 cm^3). The solution was washed with water and then dried over $MgSO_4$. The solution was concentrated under reduced pressure, the residue being recrystallized from chloroform–hexane: m.p. 213–214 °C, yield 63%; ν_{max}(KBr)/cm^{-1} 3210 (NH) and 1675 (C=O); δ($CDCl_3$, 30 °C) 1.04 (9 H, s, Bu^t), 3.13 and 4.28 [2 H, d each (J = 12.8 Hz), $ArCH_2Ar$], 4.25 (2 H, s, OCH_2CO), 4.86 (2 H, s, CH_2Ar), 6.75 (2 H, s, ArH), 7.27–7.34 (5 H, m, ArH in benzyl) and 10.77 (1 H, s, NH) [Found: C, 73.7; H, 7.2; N, 4.3. Calc. for $(C_{20}H_{23}NO_3)_4$: C, 73.82; H, 7.12; N, 4.30%].

37,38,39,40,41,42-Hexakis(N-*benzyloxycarbamoylmethoxy*)-p-tert-*butylcalix*[6]*arene*.—This compound was synthesized from 1_6 in a manner similar to that described for the tetramer: m.p. 212–215 °C, yield 36%; ν_{max}(Nujol)/cm^{-1} 3220 (NH) and 1680 (C=O); δ[$(CD_3)_2SO$, 150 °C] 1.02 (9 H, s, Bu^t), 3.97 (2 H, br s, $ArCH_2Ar$), 4.33 (2 H, s, OCH_2CO), 4.85 (2 H, s, CH_2Ar), 7.01 (2 H, s, ArH) and 7.23–7.34 (5 H, m, ArH in benzyl) [Found: C, 73.95; H, 7.1; N, 4.3%. Calc. for $(C_{20}H_{23}NO_3)_6$: C, 73.82; H, 7.12; N, 4.30%].

25,26,27,28-*Tetrakis*(N-*hydroxycarbamoylmethoxy*)-p-tert-*butylcalix*[4]arene (2_4).—The benzyl group was deprotected by catalytic hydrogenation with Pd on charcoal in acetic acid–methanol (1:2 v/v) at 35 °C: m.p. 214 °C (decomp.), yield 91%; ν_{max}(KBr)/cm^{-1} 2400–3600 (OH and NH) and 1665 (C=O); δ($CDCl_3$, 25 °C) 0.72–1.18 (9 H, m, Bu^t), 3.04–4.90 (4 H, m, $ArCH_2Ar$, OCH_2), 6.50–7.15 (2 H, m, ArH) and 8.03 (1 H, s, NH) [Found: C, 65.15; H, 7.25; N, 5.60. Calc. for $(C_{13}H_{17}NO_3)_4$· MeOH (recrystallized from MeOH): C, 65.41; H, 7.46; N, 5.76%].

37,38,39,40,41,42-*Hexakis*(N-*hydroxycarbamoylmethoxy*)-p-tert-*butylcalix*[6]*arene* (2_6).—This compound was synthesized in a manner similar to that described for 2_4: m.p. 207 °C (decomp.), yield 80%; ν_{max}(Nujol)/cm^{-1} 2500–3600 (OH and NH) and 1660 (C=O); δ[$(CD_3)_2SO$, 150 °C] 0.79–1.37 (9 H, m, Bu^t), 3.34–3.85 (2 H, m, $ArCH_2Ar$), 4.25 (2 H, s, OCH_2) and 6.48–7.65 (2 H, m, ArH) [Found: C, 66.05; H, 7.15; N, 5.5%. Calc. for $(C_{13}H_{17}NO_3)_6$·EtOH (recrystallized from hexane–ethanol): C, 65.96; H, 7.40; N, 5.76%].

(p-tert-*Butylphenoxy*)*acetohydroxamic Acid* (**3**).—This compound was synthesized from (*p-tert*-butylphenoxy)acetic acid *via* benzyl (*p-tert*-butylphenoxy)acetohydroxamate in a manner similar to that described for 2_4: benzyl (*p-tert*-butylphenoxy)-acetohydroxamate, m.p. 107–108 °C, yield 76%; ν_{max}(KBr)/cm^{-1} 3220 (NH) and 1655 (C=O); δ($CDCl_3$, 30 °C) 1.29 (9 H, s, Bu^t), 4.51 (2 H, s, OCH_2CO), 4.92 (2 H, s, CH_2Ar), 6.73 and 7.28 (4 H, d each, J = 9.6 Hz, ArH), 7.32 (5 H, s, ArH in benzyl) and 8.87 (1 H, br s, NH) (Found: C, 73.0; H, 7.45; N, 4.5. Calc. for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47%). For **3**: m.p. 140–141 °C, yield 97%; ν_{max}(KBr)/cm^{-1} 3360 (NH), 2300–3500 (OH) and 1655 (C=O); δ($CDCl_3$, 30 °C) 1.29 (9 H, s, Bu^t), 4.56 (2 H, s, OCH_2) and 6.79 and 7.38 (4 H, d each, J = 9.0 Hz, ArH), 8.38 (2 H, br s, OH and NH) (Found: C, 64.15; H, 7.65; N, 6.25. Calc. for $C_{12}H_{17}NO_3$: C, 64.56; H, 7.67; N, 6.27%).

Two-phase Solvent Extraction.—An organic solution (chloroform, 5 cm^3) containing calixarene-based uranophiles was mixed with an aqueous solution [buffered with 10 mmol dm^{-3} acetate (pH 3.7–6.2), Tris (pH 9.0) and ammonia (pH 10.4), 25 cm^3] containing $K_4UO_2(CO_3)_3$ (and competing metal cations, if necessary). The mixture was vigorously stirred for 12 h at 30 °C (the extraction equilibria were usually attained within 3 h). The aqueous phase was separated and subjected to analysis with Arsenazo III to determine the decrease in the UO_2^{2+} concentration. The decrease in other metal cations was determined by atomic absorption spectroscopy.

Results and Discussion

pH *Dependence*.—Fig. 1 shows the extractability (Ex%) of UO_2^{2+} plotted against pH in the aqueous phase. Ex% for 1_6 increases from pH 2 and saturation is reached at around pH 5 showing the 100% extractability. This pH dependence is apparently correlated with the dissociation of the carboxy groups (*e.g.*, phenoxyacetic acid has pK_a = 3.12 in water).[12] Ex% for 2_4 and 2_6 shows a similar pH dependence. The pK_a values for hydroxamic acids are 8–9.[12] Thus, the Ex% 'jump' for 2_4 and 2_6 appears in an unusually low pH region, indicating that the dissociation of the hydroxamic groups in 2_4 and 2_6 is remarkably facilitated (by 6.7 pK units) by the binding to UO_2^{2+}. Acyclic **3** also extracted UO_2^{2+} from the aqueous phase to the organic (chloroform) phase. However, the Ex% 'jump' was observed above pH 4, indicating that the dissociation of **3** is less facilitated by the binding to UO_2^{2+}.

The foregoing results indicate that 2_4 and 2_6 bearing hydroxamic acids as ligand groups on the lower rim can act as excellent uranophiles even in the acidic pH region.

Stoichiometry of Extraction Species.—Plots of log D (distribution ratio = [UO_2^{2+}] in the organic phase/[UO_2^{2+}] in the aqueous phase) *vs.* pH are illustrated in Fig. 2. The plots for 1_6 showed a slope of unity, indicating that one carboxy group is dissociated upon extraction of UO_2^{2+}. This extraction process is shown in Fig. 3(*a*). To confirm this, we repeated the extraction experiments in the absence of UO_2^{2+} ion. The organic layer was separated and then re-extracted with aqueous 0.1 mol dm^{-3} HCl. The analysis of the aqueous solution by atomic absorption spectrometry established that, at pH 3.0–4.5, 1_6 does extract K^+, the concentration being always equal to that of UO_2^{2+} observed in the presence of UO_2^{2+}. This implies that in two-phase solvent extraction with 1_6, an exchange between UO_2^{2+} and K^+ plus H^+ takes place at the water–chloroform interface. On the other hand, the plots for 2_6 and acyclic **3** showed a slope of 2, indicating that two hydroxamic groups are dissociated upon extraction of UO_2^{2+}: that is, neutral 2_6 (or **3**) releases two protons to form a neutral UO_2^{2+} complex. The extraction process is shown in Fig. 3(*b*). In fact, the

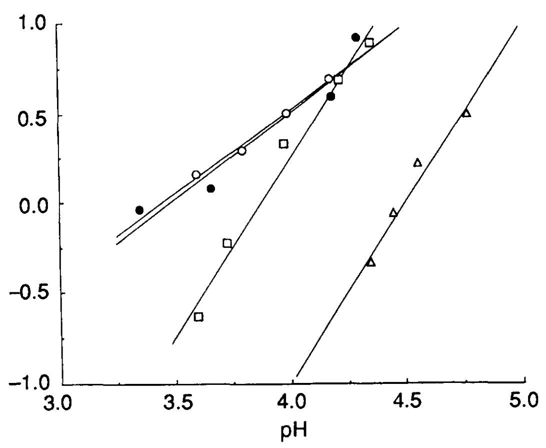

Fig. 2 Plots of log D vs. pH; (●) $\mathbf{1}_6$, (○) $\mathbf{2}_4$, (□) $\mathbf{2}_6$, (△) $\mathbf{3}$

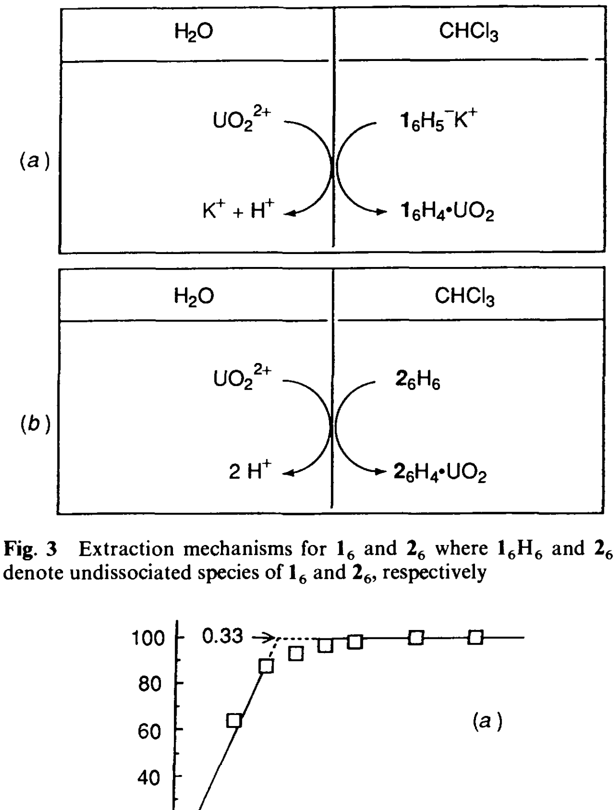

Fig. 3 Extraction mechanisms for $\mathbf{1}_6$ and $\mathbf{2}_6$ where $\mathbf{1}_6H_6$ and $\mathbf{2}_6H_6$ denote undissociated species of $\mathbf{1}_6$ and $\mathbf{2}_6$, respectively

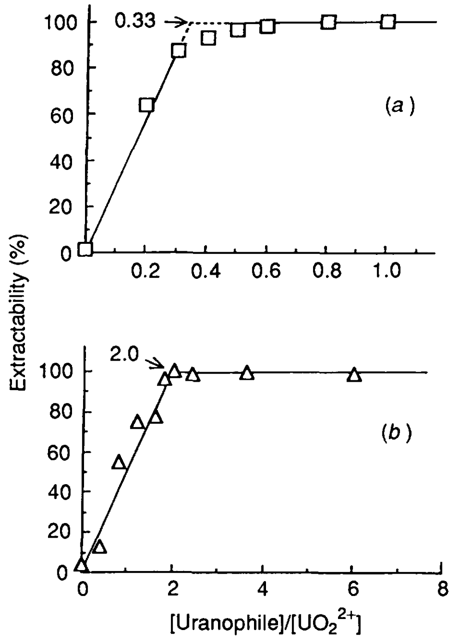

Fig. 4 Plots of Ex% vs. [uranophile]/[UO_2^{2+}]; pH 6.2 with 0.01 mol dm^{-3} acetate buffer, 30 °C. The concentration of UO_2^{2+}([$K_4UO_2(CO_3)_3$] = 1.06×10^{-4} mol dm^{-3}) was maintained constant while that of the uranophile was varied.

K^+ ion was not extracted at all with $\mathbf{2}_6$ or with acyclic $\mathbf{3}$ in the absence of UO_2^{2+} (confirmed by atomic absorption spectrometry). This indicates that in two-phase solvent extraction with $\mathbf{2}_6$ or acyclic $\mathbf{3}$ an exchange between UO_2^{2+} and $2H^+$ takes place at the water–chloroform interface. The difference in the extraction mechanism is accounted for by the difference in the pK_a values between the carboxy group and the hydroxamic group.

Strangely, $\mathbf{2}_4$ bearing hydroxamic groups resulted in a slope of unity. The extraction experiments in the absence of UO_2^{2+} established that $\mathbf{2}_4$ does extract K^+ at pH 3.0–4.5. This implies that extraction of UO_2^{2+} with $\mathbf{2}_4$ proceeds according to mechanism (*a*) in Fig. 3: that is, the pK_a values of the hydroxamic groups in $\mathbf{2}_4$ are lower than those in $\mathbf{2}_6$ and acyclic $\mathbf{3}$. We have previously estimated pK_a values of the OH groups in calix[4]arenes[13–15] and found that the dissociation of the first proton occurs at very acidic pH region.[13–15] This is caused by strong intramolecular hydrogen-bonding interactions among the OH groups.[13–15] In other words, the skeleton of calix[4]arenes is preorganized so that the OH groups can efficiently form intramolecular hydrogen bonds. The formation of such efficient intramolecular hydrogen bonds as the OH groups would not be expected for the hydroxamic groups in $\mathbf{2}_4$ and $\mathbf{2}_6$ but the hydroxamic groups in $\mathbf{2}_4$, arranged on the narrow lower rim of the calix[4]arene ring, would form intramolecular hydrogen bonds more strongly than those in $\mathbf{2}_6$. The difference would lower the pK_{a1} of the hydroxamic group in $\mathbf{2}_4$.

In the above extraction experiments, we selected reaction conditions under which one uranophile can extract less than one UO_2^{2+} ion. When an excess of the UO_2^{2+} ion is present in the aqueous phase, how many UO_2^{2+} ions can these uranophiles extract? As shown in Fig. 4, we determined Ex% as a function of [uranophile]/[UO_2^{2+}]. When $\mathbf{2}_6$ was used as a uranophile, a break-point appeared at 0.33. This indicates that one $\mathbf{2}_6$ molecule can bind three UO_2^{2+} ions. In $\mathbf{2}_4$ the break-point appeared at 0.50 (data not shown), indicating that one $\mathbf{2}_4$ molecule can bind two UO_2^{2+} ions. On the other hand, when acyclic $\mathbf{3}$ was used as the uranophile, the break-point appeared at 2.0. Thus, the extraction species is $(\mathbf{3})_2\cdot UO_2$. These results consistently show that UO_2^{2+} is extracted so that the complex can always maintain 'neutrality.' For example, extraction of UO_2^{2+} with $\mathbf{2}_6$ occurs according to eqns. (1)–(3) in response to the [$\mathbf{2}_6$]/[UO_2^{2+}] ratio.

$$\mathbf{2}_6H_6 + UO_2^{2+} \rightleftharpoons \mathbf{2}_6H_4\cdot UO_2 + 2H^+ \tag{1}$$

$$\mathbf{2}_6H_4\cdot UO_2 + UO_2^{2+} \rightleftharpoons \mathbf{2}_6H_2\cdot(UO_2)_2 + 2H^+ \tag{2}$$

$$\mathbf{2}_6H_2\cdot(UO_2)_2 + UO_2^{2+} \rightleftharpoons \mathbf{2}_6\cdot(UO_2)_3 + 2H^+ \tag{3}$$

UO_2^{2+} *Extraction from Aqueous Carbonate Solution.*—In order to compare relative UO_2^{2+} affinities we carried out two-phase solvent extraction experiments under more severe conditions. It is known that carbonate ions form a stable, water-soluble complex, $UO_2(CO_3)_3^{4-}$, with UO_2^{2+}.[16] We thus determined Ex% as a function of the carbonate concentration (Fig. 5). The Ex% for $\mathbf{1}_6$ was reduced to 5.7% at [CO_3^{2-}] = 4.27×10^{-4} mol dm^{-3} and 0% at 1.22×10^{-3} mol dm^{-3}. This shows that $\mathbf{1}_6$ cannot be used practically for the extraction of UO_2^{2+} from carbonate solution. In extraction with $\mathbf{2}_6$, in contrast, Ex% was 87.9% at [CO_3^{2-}] = 5.92×10^{-4} mol dm^{-3} and 26.1% was still retained even at [CO_3^{2-}] = 4.33×10^{-3} mol dm^{-3}. This extraction result shows that $\mathbf{2}_6$ is able to compete with CO_3^{2-} ions for UO_2^{2+}. On the other hand, $\mathbf{2}_4$ and acyclic $\mathbf{3}$ showed an affinity intermediate between $\mathbf{1}_6$ and $\mathbf{2}_6$. Clearly, $\mathbf{2}_6$, which has hexacoordination geometry preorganized for binding to UO_2^{2+}, is superior to $\mathbf{2}_4$ as a uranophile.

UO_2^{2+} *Selectivity.*—We carried out solvent extraction of

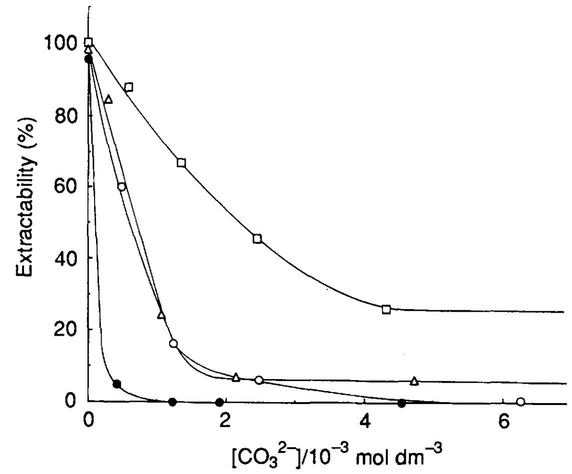

Fig. 5 UO_2^{2+} Extraction from carbonate buffer solution at 30 °C and pH 10.4; $[K_4UO_2(CO_3)_3] = 1.06 \times 10^{-5}$ mol dm^{-3}. At $[CO_3^{2-}] = 0$, $UO_2(CH_3COO)_2$ was used instead of $K_4UO_2(CO_3)_3$ and the solution was buffered with 10 mol dm^{-3} ammonia. The symbols for each uranophile are recorded in the caption to Fig. 1.

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

Metal	$([M^{n+}]/[UO_2^{2+}])$	Ex% of UO_2^{2+}	
		$\mathbf{1}_6$	$\mathbf{2}_6$
None		100	100
Mg^{2+}	(1000)	100	100
Ni^{2+}	(10)	77	98
Zn^{2+}	(12)	51	96
Fe^{3+}	(10)	—	66
Fe^{3+}	(1)	—	100

[a] $[UO_2(CH_3COO)_2] = 2.00 \times 10^{-5}$ mol dm^{-3} in the aqueous phase (25 cm^3), pH 5.9 with 10 mmol dm^{-3} acetate buffer, $[\mathbf{1}_6$ or $\mathbf{2}_6] = 1.00 \times 10^{-4}$ mmol dm^{-3} in chloroform (5 cm^3).

UO_2^{2+} in the presence of competing metal cations. The results are summarized in Table 1. Previously, we found that the absorption spectrum of the UO_2^{2+} complexes with a hexacarboxylate derivative of calix[6]arene-*p*-hexasulphonate in water is not affected at all by the addition of an excess of competitor metal cations.[7,8] The finding illustrates the remarkably high selectively of the hexacarboxylate derivative towards UO_2^{2+}. In contrast, the Ex% values for $\mathbf{1}_6$ were significantly reduced by the addition of competing metal cations.[9] The disagreement was rationalized in terms of the special requirement for the two-phase solvent-extraction system that the extraction species must be always 'neutral': that is, even though $\mathbf{1}_6H_6$* forms the UO_2^{2+} complex selectively ($[\mathbf{1}_6H_{4-n}\cdot UO_2]^{n-}$; the anionic complex results because more than two carboxy groups are dissociated at pH 5.9) it can further extract other metal cations. We consider that the specific affinity for UO_2^{2+} is reduced in the ternary $\mathbf{1}_6\cdot UO_2\cdot M$ complex and UO_2^{2+} is displaced to some extent by competing metal cations. As shown in Table 1, Ex% for $\mathbf{1}_6$ is scarcely affected by the addition of Mg^{2+} but significantly reduced by the addition of Ni^{2+} or Zn^{2+}. In contrast, Ex% for $\mathbf{2}_6$ is reduced by only 2–4% by the addition of these metal cations. The difference is accounted for by two reasons. The first reason is related to the special coordination ability of the hydroxamic group towards UO_2^{2+}.[10] The second reason is related to the special requirement for the solvent extraction system: that is, the pK_a for the hydroxamic group is much higher than that for the carboxy group, so that the extraction species at pH 5.9 is 'neutral' $\mathbf{2}_6H_4\cdot UO_2$ which cannot further exact other metal cations. These results consistently suggest that $\mathbf{2}_6$ is superior to $\mathbf{1}_6$ as a selective extractant for UO_2^{2+} in the neutral or acidic pH region.

We noted that the Fe^{3+} ion is exceptional as a competing metal cation. Fe^{3+} is effectively extracted by $\mathbf{2}_6$,† an unsurprising observation in view of the fact that hydroxamic acids are known, useful analytical reagents for Fe^{3+}. Thus, Ex% for UO_2^{2+} was reduced to 66% in the presence of an excess of Fe^{3+} (tenfold). In the presence of an equimolar amount of Fe^{3+}, however, the Ex% of UO_2^{2+} was scarcely affected.

Conclusions

In the previous paper of this series,[9] we designed a calix[6]arene-based uranophile ($\mathbf{1}_6$) bearing six carboxy groups on the lower rim. This compound could efficiently extract UO_2^{2+} but the UO_2^{2+} selectivity was not satisfactory.[9] We learned therein that in order to design a uranophile which can selectively extract UO_2^{2+} one must pay more attention to the special requirement that the extraction species be formally neutral. This requirement is satisfied to some extent in a calix[6]arene-based uranophile ($\mathbf{2}_6$) bearing six hydroxamic groups on the lower rim. At neutral or acidic pH region the hydroxamic groups (with pK_a about 9) are not dissociated whereas they are forced to be dissociated when they form a complex with UO_2^{2+}. This situation always results in a neutral $\mathbf{2}_6\cdot UO_2$ complex. As expected, the UO_2^{2+} selectivity of $\mathbf{2}_6$ was excellent. Further elaboration on the molecular design of calixarene-based uranophiles is continuing in this laboratory.

References

1 R. Graziani and E. Forsellini, *J. Chem. Soc., Dalton Trans.*, 1972, 2059.
2 W. H. Zachariasen and H. A. Ptettinger, *Acta Crystallogr.*, 1959, **12**, 526.
3 For a comprehensive review for the X-ray structures of UO_2^{2+} complexes see I. Tabushi and Y. Kobuke, *Nippon Kaisui Gakkaishi*, 1982, **36**, 205.
4 A. H. Alberts and D. J. Cram, *J. Am. Chem. Soc.*, 1977, **99**, 3880.
5 I. Tabushi, Y. Kobuke and T. Nishiya, *Tetrahedron Lett.*, 1979, 3515.
6 I. Tabushi, Y. Kobuke and A. Yoshizawa, *J. Am. Chem. Soc.*, 1984, **106**, 2481.
7 S. Shinkai, H. Koreishi, K. Ueda and O. Manabe, *J. Chem. Soc., Chem. Commun.*, 1986, 233.
8 S. Shinkai, H. Koreishi, K. Ueda, T. Arimura and O. Manabe, *J. Am. Chem. Soc.*, 1987, **109**, 6371.
9 S. Shinkai, Y. Shirahama, H. Satoh, O. Manabe, T. Arimura, K. Fujimoto and T. Matsuda, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1167.
10 H. Egawa, T. Nanaka and M. Ikari, *J. Appl. Polym. Sci.*, 1984, **29**, 2045.
11 For a comprehensive review see H. Egawa, *Nippon Kaisui Gakkaishi*, 1988, **41**, 235.
12 W. P. Jencks and J. Regenstein, *Handbook of Biochemistry and Molecular Biology*, ed. G. D. Fasman, CRC Press, Cleveland OH, 1976, p. 305.
13 S. Shinkai, K. Araki, H. Koreishi, T. Tsubaki and O. Manabe, *Chem. Lett.*, 1986, 1351.
14 S. Shinkai, K. Araki, J. Shibata, D. Tsugawa and O. Manabe, *Chem. Lett.*, 1989, 931.
15 K. Araki, K. Iwamoto, S. Shinkai and T. Matsuda, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 3480.
16 Ref. 6 and related papers cited therein.

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* $\mathbf{1}_6H_6$ denotes the undissociated species of $\mathbf{1}_6$.

† In fact, $\mathbf{2}_6$ selectively extracted Fe^{3+} among transition metal cations. The results will be published elsewhere.