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Synthesis of mono-, di-, and trinitro tricarboxymethyl calix[6]arenes for the complexation of uranium(VI)

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Abstract—Mono-, di-, and trinitro tricarboxymethyl calix[6]arenes **3**(**a**–**c**) have been synthesised and their acid-base behaviour determined by potentiometric investigations. It was shown that the nitro groups do not play a major role on the acid-base properties. Preliminary complexation of uranyl is presented.

Calixarenes represent a class of macrocyclic molecules formed by 4-20 *para*-substituted phenolic units linked by methylene bridges *ortho* to the OH functions.[1–5] The parent phenolic calixarenes as well as their chemically modified derivatives, obtained by substitution of the phenolic hydrogens with various types of ligating groups, are efficient in complexing, extracting or transporting metal cations.[1–5] Reports on the binding of actinide metal ions with calixarenes show their potential utility on various practical grounds. Thus, in relation to energy problems, by exploiting the property of the UO_2^{2+} ion to form an equatorial garland of five or six ligand donor atoms held in a nearby planar array, Shinkai et al. have studied various parent and modified calix[*n*]arenes ($n=5$, 6, 8) bearing carboxylic acid, phosphonate or hydroxamic acid groups, which act as specific ligands for uranyl ions.[6–12] On the basis of these findings these calixarenes were investigated as optical sensors[13] and for decontamination.[14] Similarly, we reported complexation and extraction studies of UO_2^{2+} with a dicarboxylated calix[4]arene[15] and a tricarboxylated calix[6]arene.[16–18] Connected to the problem of determination of uranium in urine for routine monitoring of workers exposed to the risk of internal contamination in the nuclear industry, 1,3,5-trimethoxy-2,4,6-tricarboxymethyl-*p*-*tert*-butyl calix[6]arene was shown to be selective for the extraction of UO_2^{2+} in the presence of divalent cations such as Zn^{2+}, Cu^{2+}, Mg^{2+}, Ca^{2+} and competing anions such as phosphates and sulphates.[19]

In the present paper we report the synthesis and preliminary complexation studies of calixarenes **3**(**a**–**c**) related to 1,3,5-trimethoxy-2,4,6-tricarboxymethyl-*p*-*tert*-butyl calix[6]arene by introduction of nitro groups into the *para* position on the calix ring. This was decided to evaluate a possible electron withdrawing effect on the complexation behaviour and to introduce chemically modifiable functions for further synthetic work such as grafting these macrocycles on solid phases.

The synthetic route to **3**(**a**–**c**) is given in Scheme 1.

According to reference 19, 1,3,5-trimethoxy-*p*-*tert*-butyl calix[6]arene[18] was reacted with a 1:1 mixture of HNO_3/H_2SO_4 in CH_2Cl_2 at room temperature to give mononitro (**1a**) calix[6]arene (~1.5 equiv. of HNO_3, reaction time 20 min), dinitro (**1b**) calix[6]arene (~3 equiv. of HNO_3, reaction time 30 min) and trinitro (**1c**) calix[6]arene (~3 equiv. of HNO_3, reaction time 50 min) in 19, 17 and 28% yields, respectively, after purification on silica with 2:4:4 AcOEt/hexane/CH_2Cl_2 as eluent.[20]

Calixarenes **1**(**a**–**c**) were reacted with ~12–13 equiv. of $BrCH_2CO_2CH_3$ in CH_3CN in the presence of an excess of K_2CO_3 at reflux to give the trimethyl ester **2a** (77%), **2b** (86%) and **2c** (86%) by precipitation with Et_2O/hexane.

The trimethyl ester derivatives **2**(**a**–**c**) were hydrolysed by reaction with a large excess of KOH in a 1:1 mixture of H_2O/CH_3OH to give the triacid derivatives **3a** (73%), **3b** (79%) and **3c** (64%) by precipitation in the reacting medium with 1N HCl.

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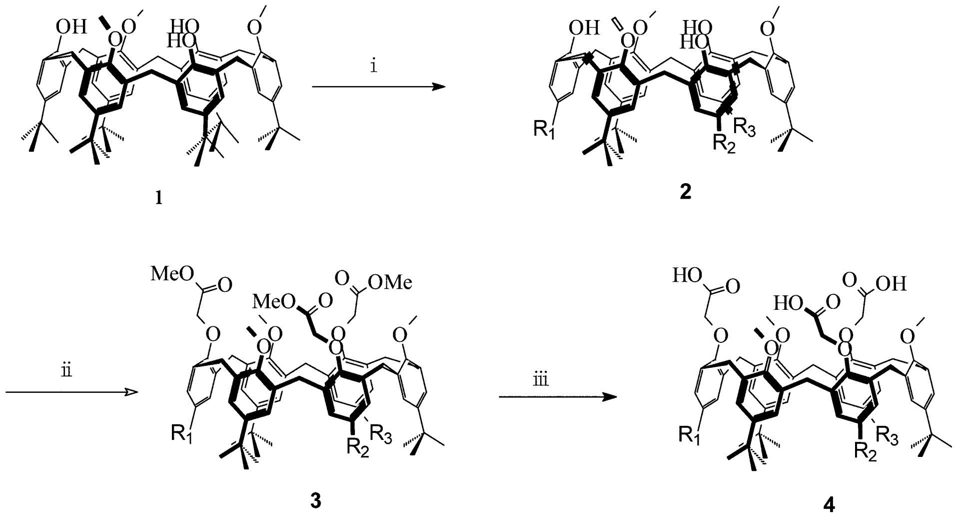

	R_1	R_2	R_3
a	NO_2	t-Bu	t-Bu
b	NO_2	NO_2	t-Bu
c	NO_2	NO_2	NO_2
d	t-Bu	t-Bu	t-Bu

Scheme 1. *Reagents and conditions*: (i) HNO_3/H_2SO_4, CH_2Cl_2, rt; (ii) $BrCH_2CO_2CH_3$, K_2CO_3, CH_3CN, reflux; (iii) KOH, H_2O/CH_3OH, reflux.

All the analytical data were in agreement with the proposed structures **1**(**a**–**c**)–**3**(**a**–**c**). ^{1}H NMR data revealed that **1**(**a**–**c**)–**3**(**a**–**c**) have no preferred conformation and are flexible.

The acid–base behaviour of **3**(**a**–**c**) and of the unsubstituted 1,3,5-trimethoxy-2,4,6-tricarboxymethyl-*p*-*tert*-butyl calix[6]arene **3d** taken as reference compound has been determined from pHmetric titrations in methanol in the presence of Et_4NCl as background electrolyte as already described.[21] The interpretation of the titration curves by the program Hyperquad[22] led to the pK_i values (i = 1–3) given in Table 1. These values are lower for **3**(**a**–**c**) than for **3d** (except pK_3 for **3c**). As expected from the electron-withdrawing character of the nitro groups, the three nitro compounds are thus more acidic than their *tert*-butyl counterpart. However these differences in pK_i are very small and show only little influence of the nitro groups certainly due to their large distance from the carboxylic sites.

Table 1. pK_i values[a] of the calix[6]arene carboxylic acids **3**(**a**–**d**) in MeOH (T=25°C, I=0.01 M (Et_4NCl))

pK_i	**3d**	**3a**	**3b**	**3c**
pK_1	7.88±0.04	7.5±0.3	7.56±0.03	7.61±0.04
pK_2	8.37±0.06	8.39±0.03	8.19±0.04	8.10±0.01
pK_3	9.23±0.05	9.17±0.09	9.06±0.04	9.33±0.01

[a] Arithmetic mean of at least two independent experiments with the corresponding standard deviation.

Complexation of several bivalent metal ions is presently under study in methanol by the same technique and the preliminary results show a strong binding of $UO_2(NO_3)_2 \cdot 6H_2O$ with **3**(**a**–**d**). However, the precipitation which occurred with the **3**(**b**–**d**) did not allow any reliable interpretation. Only the titration curves corresponding to ligand **3a** used in excess with respect to the metal ion (ratio of 0.5) could be interpreted taking into account the simultaneous formation of four methoxo species[23] of the metal ion and the three complexes [UO_2(**3a**)]$^-$ ($\log \beta_{110} = 9.93$), [UO_2(**3a**)H] ($\log \beta_{111} = 17.14$) and [UO_2(**3a**)OMe]$^{2-}$ ($\log \beta_{11-1} = -1.19$). The distribution curves of these species versus pH (see Fig. 1) show the predominance of the 1:1 species in the range $4 \leq \mathrm{pH} \leq 11$. The formation of the neutral protonated species, which is the major species between pH 5 and 7, is in full agreement with the two proton exchange mechanism which was proposed for the extraction of uranium from water into benzene.[16]

Further work is directed toward: (a) the synthesis of related derivatives including the 1,3,5-tricarboxylic acid calix[6] unit to be grafted on solid phases and (b) the complexation studies of toxic metals which will be published in due course.

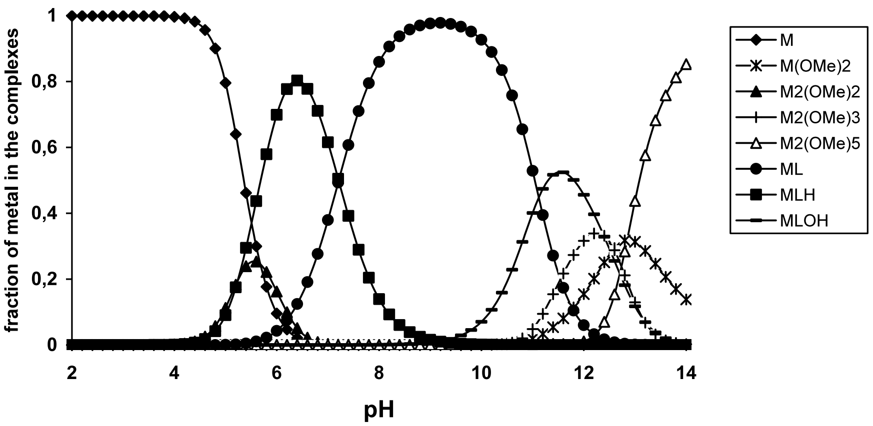

Figure 1. Speciation curves of the system uranyl/**3a** in MeOH ($C_l = 10^{-3}$ M, $C_{uranyl} = 5\times10^{-4}$ M).

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20. **General**. The melting points were taken on a Büchi apparatus in a capillary sealed under nitrogen. ^{1}H NMR spectra were recorded in $CDCl_3$ at 200 MHz on a Bruker SY200 spectrometer. δ are given in ppm and J are given in Hz. FAB(+) mass spectra were obtained on a VG-Analytical ZAB HF. Elemental analyses were performed at the Service de Microanalyse of the Institut de Chimie de Strasbourg. All the reactions were run under nitrogen. All reagents were commercial and used without further purification. 1,3,5-Trimethoxy *p*-*tert*-butyl calix[6]arene was prepared as already published.[18]
Mononitro (1a) calix[6]arene. 1,3,5-Trimethoxy *p*-*tert*-butyl calix[6]arene (2.00 g, 1.97 mmol) was dissolved in dry CH_2Cl_2 (40 ml). A 1:1 mixture of HNO_3/H_2SO_4 (0.132 ml containing 0.186 g, 2.95 mmol of HNO_3) was added to at room temperature. The mixture was stirred for 20 min. Then the solvents were removed to dryness. The crude residue was quenched with H_2O (40 ml), extracted with CH_2Cl_2 (3×30 ml) and washed with brine (3×20 ml). The organic layer was dried over Na_2SO_4, filtered and evaporated to dryness. The residue was chromatographed with a 2:4:4 AcOEt/hexane/CH_2Cl_2 mixture as eluent to give **1a** a powder (0.371 g, 0.369 mmol, 19%). Mp 218–219°C (Et_2O/Hexane). ^{1}H NMR ($CDCl_3$): $\delta=$ 8.84 (s, 1H, ArO*H*), 7.96 (s, 2H, ArO*H*), 7.10 (d, $J=2.4$ Hz, 2H, Ar*H*), 7.03 (d, $J=2.2$ Hz, 2H, Ar*H*), 7.00 (d, $J=2.2$ Hz, 2H, Ar*H*), 6.97 (d, $J=2.4$ Hz, 2H, Ar*H*), 6.91 (s, 2H, *p*-NO_2Ar*H*), 6.45 (s, 2H, Ar*H*), 3.90 (s, 8H, ArC*H*$_2$Ar), 3.78 (s, 4H, ArC*H*$_2$Ar), 3.43 (s, 3H, OC*H*$_3$), 1.55 (s, 6H, OC*H*$_3$), 1.25 (s, 18H, C(C*H*$_3$)$_3$), 1.10 (s, 18H, C(C*H*$_3$)$_3$), 1.01 (s, 9H, C(C*H*$_3$)$_3$). Anal calcd for $C_{65}H_{81}NO_8$: C, 77.73; H, 8.13; N, 1.39. Found: C, 77.80; H, 8.13; N,1.43. **Dinitro (1b) calix[6]arene**. Same procedure as for **1a** with 1,3,5-trimethoxy *p*-*tert*-butyl calix[6]arene (4.00 g, 3.94 mmol), CH_2Cl_2 (80 ml), 1:1 HNO_3/H_2SO_4 (0.528 ml, 0.740 g, 11.82 mmol of HNO_3), reaction time (30 min), column chromatography 2:4:4 AcOEt/hexane/CH_2Cl_2, **1b** (0.65 g, 0.66 mmol, 17%). Mp 220–221°C (Et_2O/Hexane). ^{1}H NMR ($CDCl_3$): $\delta=8.73$ (s, 2H, *p*-NO_2ArO*H*), 8.05 (d, $J=2.7$ Hz, 2H, *p*-NO_2Ar*H*), 7.92 (d, $J=2.7$ Hz, 2H, *p*-NO_2Ar*H*), 7.14 (s, 2H, Ar*H*), 7.07 (s, 2H, Ar*H*), 7.03 (d, $J=2.4$ Hz, 2H,

Ar*H*), 6.93 (d, $J=2.4$ Hz, 2H, Ar*H*), 5.73 (s, 1H, ArO*H*), 3.95 (m, 12H, ArCH_2Ar), 3.58 (s, 6H, OCH_3), 3.19 (s, 3H, OCH_3), 1.31(s, 9H, C(CH_3)$_3$), 1.20 (s, 9H, C(CH_3)$_3$), 1.09 (s, 18H, C(CH_3)$_3$). Anal calcd for $C_{61}H_{72}N_2O_{10}$: C, 73.77; H, 7.31; N, 2.82. Found: C,73.22; H,7.52; N,2.70. **Trinitro (1c) calix[6]arene**. Same procedure as for **1a** with 1,3,5-trimethoxy *p-tert*-butyl calix[6]arene (0.51 g, 0.5 mmol), CH_2Cl_2 (10 ml), 1:1 HNO_3/H_2SO_4 (0.067 ml, 0.095 g, 1.5 mmol of HNO_3), reaction time (50 min), column chromatography 2:4:4 AcOEt/hexane/CH_2Cl_2, **1c** (0.138 g, 0.14 mmol, 28%). Mp 221–222°C (Et_2O/Hexane). Mp$_{\mathrm{lit.}}$ 226–227°C.[19] ^{1}H NMR ($CDCl_3$): $\delta=8.2$ (s, 3H, ArO*H*), 8.04 (s, 6H, *p*-NO_2ArH), 7.02 (s, 6H, ArH), 3.96 (s, 12H, ArCH_2Ar), 3.57 (s, 9H, OCH_3), 1.14 (s, 27H, C(CH_3)$_3$). FAB-MS *m*/*z* 1041.6 [(M+C(NH$_2$)$_3$)$^+$, 1041.5]. Anal calcd for $C_{57}H_{63}N_3O_{12}$: C, 69.71; H, 6.46; N, 4.28. Found: C, 69.97; H, 7.14; N, 3.61. **Mononitro tri-methyl ester (2a) calix[6]arene**. **1a** (0.523 g, 0.5 mmol), K_2CO_3 (3.96 g, 28.62 mmol) and CH_3CN (80 ml) were refluxed for 30 min. Then $BrCH_2CO_2CH_3$ (1.03 g, 6.72 mmol) was added to the reaction mixture. After 18 h, the reaction mixture was acidified with 1N HCl and extracted with CH_2Cl_2. The organic layer was washed with H_2O, dried over Na_2SO_4, filtered and concentrated to give a residue which was precipitated with Et_2O/Hexane to afford **2a** (0.467 g, 0.38 mmol, 77%). Mp 212–213°C. ^{1}H NMR ($CDCl_3$): $\delta=7.57$(s, 2H, *p*-NO_2Ar*H*), 7.27 (s, 2H, Ar*H*), 7.28 (s, 2H, Ar*H*), 7.19 (s, 2H, Ar*H*), 6.70 (d, $J=2.1$ Hz, 2H, Ar*H*), 6.61 (d, $J=2.1$ Hz, 2H, Ar*H*), 4.59 (s, 2H, OCH_2), 4.39 (s, 4H, ArOCH_2), 3.96 (broad s, 12H, ArCH_2Ar), 3.77 (s, 3H, ArOCH_3), 3.72 (s, 6H, ArOCH_3), 2.65 (s, 6H, CO$_2$CH_3), 2.46 (s, 3H, CO$_2$CH_3), 1.36 (s, 18H, C(CH_3)$_3$), 1.30 (s, 9H, C(CH_3)$_3$), 0.84 (s, 18H, C(CH_3)$_3$.

Anal calcd for $C_{74}H_{93}NO_{14}$: C, 72.82; H, 7.68; N, 1.15. Found: C, 72.84; H, 7.84; N, 1.07. **Dinitro tri-methyl ester (2b) calix[6]arene**. Same procedure as for **2a** with **1b** (0.512 g, 0.50 mmol), K_2CO_3 (3.99 g, 28.92 mmol), CH_3CN (80 ml), $BrCH_2CO_2CH_3$ (1.05 g, 6.79 mmol), reaction time (18 h), precipitation with Et_2O/hexane, **2b** (0.452 g, 0.37 mmol, 86%). Mp 178–179°C. 7.67 (d, $J=2.7$ Hz, 2H, *p*-NO_2Ar*H*), 7.61 (d, $J=2.7$ Hz, 2H, *p*-NO_2Ar*H*), 7.25 (s, 2H, Ar*H*), 7.21 (d, $J=2.4$ Hz, 2H, Ar*H*), 7.17 (d, $J=2.4$ Hz, 2H, Ar*H*), 6.53 (s, 2H, Ar*H*), 4.46 (br s, 6H, ArOCH_2), 4.00 (broad s, 12H, ArCH_2Ar), 3.75 (s, 6H, CO$_2$CH_3), 3.66 (s, 3H, CO$_2$CH_3), 2.88 (br s, 6H, ArOCH_3), 2.70 (br s, 3H, ArOCH_3), 1.33 (br s, 9H, C(CH_3)$_3$), 1.28 (br s, 18H, C(CH_3)$_3$), 0.75 (br s, 9H, C(CH_3)$_3$). Anal calcd for $C_{70}H_{84}N_2O_{16}$: C, 69.52; H, 7.00; N, 2.32. Found: C, 70.20; H, 6.95; N, 2.47. **Trinitro tri-methyl ester (2c) calix[6]arene**. Same procedure as for **2a** with **1c** (0.284 g, 0.28 mmol), K_2CO_3 (2.17 g, 14.47 mmol), CH_3CN (40 ml), $BrCH_2CO_2CH_3$ (0.563 g, 3.64 mmol), reaction time (18 h), precipitation with Et_2O/hexane; **2c** (0.29 g, 0.24 mmol, 86%). Mp 158–160°C. ^{1}H NMR ($CDCl_3$): $\delta=7.67$ (s, 6H, *p*-NO_2Ar*H*), 7.18 (s, 6H, Ar*H*), 4.32 (s, 6H, OCH_2), 4.00 (s, 12H, ArCH_2Ar), 3.67 (s, 39H, CO$_2$CH_3), 3.01 (s, 9H, OCH_3), 1.29 (s, 27H, C(CH_3)$_3$). FAB-MS *m*/*z* = 1198.7 [(M+H), 1198.5]. Anal calcd for $C_{66}H_{75}N_3O_{18}$: C, 66.15; H, 6.31; N, 3.51, Found: C, 66.54; H, 6.68; N, 2.73. **Mononitro tri-carboxylic acid (3a) calix[6]arene**. **2a** (0.101 g, 0.08 mmol), KOH (0.25 g, 4.47 mmol), H_2O (2.98 ml) and CH_3OH (2.98 ml) were refluxed for 4 h. After cooling to room temperature, H_2O (10 ml) was added and the mixture was acidified with 1N HCl. After precipitation the residue was filtered to afford **3a** (0.721 g, 0.06 mmol, 73%). Mp 215–216°C. ^{1}H NMR ($CDCl_3$): $\delta=7.82$ (s, 2H, *p*-NO_2Ar*H*), 7.03 (s, 2H, Ar*H*), 7.00 (broad d, $J=3.5$ Hz, 4H, Ar*H*), 6.82 (broad d, $J=7.0$ Hz, 4H, Ar*H*), 3.74 (br s, 18H, ArCH_2Ar and OCH_2), 3.74 (s, 9H, ArOCH_3), 1.15 (s, 9H, C(CH_3)$_3$), 1.14 (s, 18H, C(CH_3)$_3$), 1.01 (s, 18H, C(CH_3)$_3$). FAB-MS *m*/*z* 1176.6 (M+H$^+$). Anal calcd for $C_{71}H_{87}NO_{14}$: C, 72.36; H, 7.44; N, 1.19. Found: C, 71.70; H, 7.51; N, 1.07. **Dinitro tri-carboxylic acid (3b) calix[6]arene**. Same procedure as for **3a**, with **2b** (0.264 g, 0.22 mmol), KOH (0.665 g, 11.71 mmol), H_2O (7.8 ml), CH_3OH (7.8 ml), reflux time (4 h), **3b** (0.206 g, 0.17 mmol, 79%). Mp 218–219°C. ^{1}H NMR ($CDCl_3$): $\delta=7.88$ (s, 2H, *p*-NO_2Ar*H*), 7.77 (s, 2H, *p*-NO_2Ar*H*), 7.11 (s, 2H, Ar*H*), 6.96 (s, 4H, Ar*H*), 6.73 (s, 2H, Ar*H*), 4.13–4.02 (l, 18H, ArCH_2Ar and OCH_2), 3.72 (s, 9H, ArOCH_3), 1.17 (s, 18H, C(CH_3)$_3$), 1.09 (s, 9H, C(CH_3)$_3$), 0.89 (s, 9H, C(CH_3)$_3$). FAB-MS *m*/*z* 1165.5 (M+H$^+$). Anal calcd for $C_{67}H_{78}N_2O_{16}$: C, 68.94; H, 6.73; N, 2.40. Found: C, 68.85; H, 6.87; N, 2.34. **Trinitro tri-carboxylic acid (3c) calix[6]arene**. Same procedure as for **3a**, with **2c** (0.472 g, 0.39 mmol), KOH (1.25 g, 21.36 mmol), H_2O (15 ml), CH_3OH (15 ml), reflux time reaction (4 h), **3c** (0.291 g, 0.25 mmol, 64%). Mp 220–221°C. ^{1}H NMR ($CDCl_3$): $\delta=7.73$ (s, 6H, *p*-NO_2Ar*H*), 7.06 (s, 6H, Ar*H*), 4.26–3.57 (broad s, 18H, ArCH_2Ar and OCH_2), 3.56 (s, 9H, ArOCH_3), 1.17 (s, 27H, C(CH_3)$_3$). FAB-MS *m*/*z* 1154.5 (M+H$^+$). Anal calcd for $C_{63}H_{69}N_3O_{18}$: C, 65.43; H, 6.01; N, 3.63. Found: C, 64.23; H, 6.33; N, 3.05.

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23. The following methoxo species of uranyl have been taken into account: M(OMe)$_2$ ($\log \beta_{10-2}=-16.79$), M$_2$(OMe)$_2$ ($\log \beta_{20-2}=-7.75$), M$_2$(OMe)$_3$ ($\log \beta_{20-3}=-17.46$), M$_2$(OMe)$_5$ ($\log \beta_{20-5}=-42.93$).