Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Preorganized metallomacrocycles: Selective receptor for NH_3

Frank C. J. M. Van Veggel[a]; Gabriela Chiosis[a]; Beth R. Cameron[a]; David N. Reinhoudt[a]
[a] Faculty of Chemical Technology, Department of Organic Chemistry, University of Twente, AE Enschede, The Netherlands

To cite this Article Van Veggel, Frank C. J. M. , Chiosis, Gabriela , Cameron, Beth R. and Reinhoudt, David N.(1994) 'Preorganized metallomacrocycles: Selective receptor for NH_3', Supramolecular Chemistry, 4: 3, 177 — 183

To link to this Article: DOI: 10.1080/10610279408029470

URL: http://dx.doi.org/10.1080/10610279408029470

SUPRAMOLECULAR CHEMISTRY, Vol. 4, pp. 177–183
Reprints available directly from the publisher
Photocopying permitted by license only

Preorganized metallomacrocycles: selective receptor for NH_3

FRANK C.J.M. VAN VEGGEL, GABRIELA CHIOSIS, BETH R. CAMERON and DAVID N. REINHOUDT*

University of Twente, Faculty of Chemical Technology, Department of Organic Chemistry, P. O. Box 217, 7500 AE Enschede, The Netherlands

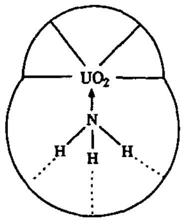
(Received December 6, 1993; Revised May 4, 1994)

Three preorganized metallomacrocycles (9a-c) have been prepared with an immobilized uranyl cation (UO_2^{2+}) as an electrophilic center. The macrocyclization in MeOH was accomplished starting from the dialdehyde 7 and the diamines 11a-c using Ba^{2+} as template ion. Subsequently the Ba^{2+} complexes 8a-c were reacted with 1 equiv of $UO_2(OAc)_2$ to give the uranyl complexes 9a-c in 70-80% yield. The association constants of the complexes 9a-c with ammonia, benzylamine, and n-propylamine, determined by ^1H NMR spectroscopy in $CDCl_3$, range from 20 to 990 $l \cdot mol^{-1}$. The highest selectivity for ammonia was observed for 9b ($K_{ass}(NH_3):K_{ass}(BnNH_2)$ = 33). Molecular mechanics calculations., performed using Quanta/CHARMm, predict that the substitution of the complexed water molecule in the uranyl complex 9a by ammonia is thermodynamically the most favorable.

INTRODUCTION

Since the first publication on crown ethers and their interaction with guest species[1] many publications on complexes of (alkyl)ammonium salts and synthetic hosts have appeared.[2] In sharp contrast is the small number of studies on the complexation of ammonia (NH_3) or (primary) amines. Stoddart and others[3] have investigated the second sphere coordination of crown ethers to ammonia that is complexed to boron derivatives or transition metal ions. These second sphere interactions lack selectivity. Reetz and co-workers[4] have recently described an elegant approach in which a boron center was incorporated in a crown ether to provide both an electrophilic center for coordination of the lone pair of amines and oxygen donor atoms for the formation of hydrogen bonds. However, these receptors are not highly preorganized.[5] Previously, we have demonstrated that a uranyl cation (UO_2^{2+}), immobilized in metallomacrocycles,[6] can be used for the complexation of polar neutral guests like urea (derivatives), amides, and barbiturates. Ring-size selectivity has been observed in a number of cases. The incorporation of the uranyl cation in metalloclefts[7] provides receptors for the complexation of species like pyridines and isoquinolines. So far our metallomacrocycles were either too large or too flexible to achieve selectivity for ammonia over (primary) amines. Therefore, we decided to synthesize metallomacrocycles with an immobilized uranyl cation and a small highly preorganized cavity that has additional sites for hydrogen bonding (see Chart). Based on the 2,2',2"-trimethoxyterphenyl unit, which is well known for its degree of preorganization,[5] CPK models indicate that the cavity can accommodate ammonia or the polar part of a primary amine. The synthesis, complexation behavior, and molecular mechanics calculations of three new metallomacrocycles will be described.

Chart



RESULTS AND DISCUSSION

1. Synthesis

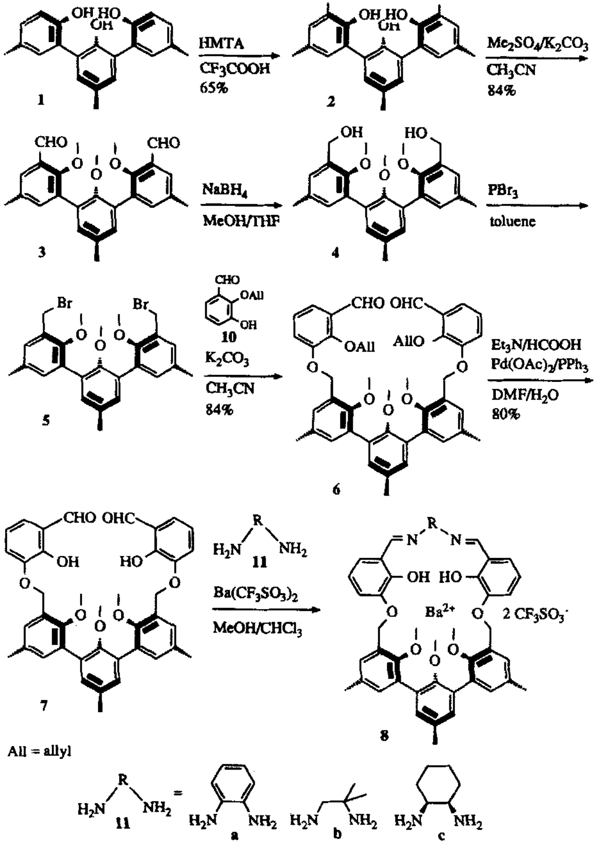
The synthesis of the dialdehyde 3 has been reported[8a] via methylation of terphenyl **1**, followed by formylation (Scheme 1). We found it more convenient to synthesize first the dialdehyde **2** by formylation using hexamethyl-

---

*Corresponding author.

enetetramine in CF_3COOH, followed by methylation with dimethyl sulfate in acetonitrile under basic conditions. The conversion of the dialdehyde **3** via **4** into the dibromide **5** has been performed as described.[8b] The synthesis of **7** has been published[9] starting from **5** and 2,3-dihydroxybenzaldehyde in only 23% yield. The two-step synthesis via **6** gave an overall yield of 67%. Reaction of the dibromide **5** with the protected 2,3-dihydroxybenzaldehyde **10**[6a] under basic conditions provided the dialdehyde **6** in 84% yield. Deallylation using $Et_3N/HCOOH$ and $Pd(OAc)_2$[10] afforded the dialdehyde **7**, which was subsequently cyclized to the Schiff bases **8a-c** by reaction with an appropiate diamine (**11a-c**). The macrocyclization was promoted by using $Ba(CF_3SO_3)_2$ as template salt.[11] The Ba^{2+} complexes **8a-c** all showed the $[M\text{-}CF_3SO_3]^+$ peak in the FAB-MS spectra. The loss of one triflate anion is characteristic for these types of complexes. The properties of the Ba^{2+} complex **8a** have been described.[9] The ^1H NMR spectrum of **8b** showed the expected imine absorptions at δ 8.25 and 8.20 ppm and the AB systems for the benzylic protons at δ 5.57, 4.76 and 5.43, 4.90 ppm (J = 11.0 Hz). The NCH_2 absorption was observed as an AB system at δ 3.79 and 3.68 ppm (J = 13.1 Hz). Compound **8c** was obtained as a mixture of conformers in a ratio of 2 to 1. The spectral data are similar to those of **8b**. Reaction of the Ba^{2+} complexes **8a-c** with uranyl acetate resulted in the formation of the uranyl complexes **9a-c** in 70 – 80% isolated yield (Scheme 2). All three uranyl complexes showed the $[M+H]^+$ peak in the FAB-MS spectra, indicating that the uranyl cation is tightly bound. The absorptions of the imine protons of **9a-c** are shifted downfield in comparison with the barium complexes **8a-c** (8.20 – 8.40 ppm in **8a-c** and 9.20 – 9.40 ppm in **9a-c**). The absorptions of the imine stretch frequencies in the IR spectra were shifted by 15 – 25 cm^{-1} to lower wave numbers with respect to the Ba^{2+} complexes, as normally found upon complexation of a cation in the salophen or salen moiety. In principle two conformations of the uranyl complexes **9a-c** are possible, one with the outer methoxy groups of the terphenyl unit at the concave side of the salophen or salen unit[6] and the other with the inner methoxy group at this side. The ^1H NMR spectra of **9a-c** showed only signals of one compound and most probably the conformer with the outer methoxy groups at the concave side of the salophen or salen unit (see Molecular Mechanics calculations).

Scheme 1



2. Binding studies

The first indications that binding of ammonia in the uranyl hosts **9a-c** occurs were obtained from the ^1H NMR spectra in $CDCl_3$ in the presence of excess ammonia. The free ammonia was observed at δ 0.75 ppm and the complexed ammonia in **9a** as a broad singlet at δ 4.10 ppm, with an integral corresponding to a 1:1 complex. Furthermore shifts of the benzylic AB system of **9a** and the two benzylic AB systems of **9b** in addition to upfield shifts of the outer MeO groups were observed. The imine absorptions showed small but significant upfield shifts. The inner MeO absorptions showed only marginal shifts, which indicates that this group is not or only very weakly interacting with the guest. The AB system of the NCH_2 group in **9b** changes almost completely into an A_2 system. An unresolved (broadened) absorption was observed at δ 4.40 ppm with a very small signal at either side. The broad absorption of the benzylic protons in **9c** clearly resolved into two AB systems upon complexation of ammonia and for the OMe signals similar observations were made as for **9a** and **9b**. Also the addition of propylamine or benzylamine showed significant shifts of the outer OMe, the benzylic protons, and imine protons.

Scheme 2

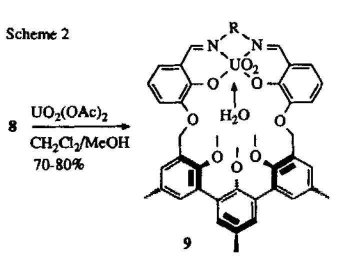


Table 1 Association constants ($l \cdot mol^{-1}$)[a] for the complexation of **9a-c** with amines in $CDCl_3$ at 293 K.

	NH_3	$BnNH_2$	$n\text{-}PrNH_2$
9a	350±25	20±5	80±5
9b	990±50	30±5	60±5
9c	650±50	30±10	40±10

a) The estimated error was determined by averaging the calculated K_{ass}'s using the various probes (see experimental section). All experiments were performed in duplicate.

The association constants of the hosts **9a-c** and ammonia, benzylamine, and propylamine in $CDCl_3$ were determined by ^1H NMR titrations (Table 1).[12] For all three hosts the observed selectivity was ammonia > propylamine and benzylamine. The highest selectivity was observed for **9b** [$K_{ass}(NH_3) : K_{ass}(BnNH_2) = 33$]. The highest selectivity for "2-boron-1,3-xylylcrown ethers" observed by Reetz[4] in CCl_4 was 10.

3. Molecular mechanics calculations

In order help us rationalize these data molecular mechanics calculations were performed on **9a** with various guests using Quanta/Charmm.[13-15] Before introducing a guest the free uranyl complex **9a** was minimized. The conformation (conf. 1) has an energy of 33.62 kcal·mol⁻¹ and it has a cavity that is accessible for the complexation of a small guest. The minimum found for the conformation in which the inner OMe group is at the concave side of the molecule (conf. 2) has an energy of 45.85 kcal mol⁻¹. These calculations suggest that only one conformer will exist and this is in agreement with the observations in solution (*vide supra*). We decided to use conformation 1 only. The calculations are summarized in Table 2.

In the minimized complexes one hydrogen of the guest was found hydrogen bonded to the phenolate and the benzylic oxygen atoms (see Figure 1), as has been observed in a number X-ray structures of complexes of metallomacrocycles with urea, DMSO, MeOH, and water.[6] A second hydrogen forms a hydrogen bond with one or two outer methoxy oxygens. The calculated ΔE values defined in equation 1 are ≤ 1 kcal·mol⁻¹ and indicate that both host and guest do not undergo major conformational changes. The fact that the ΔE values are almost zero could be purely accidental. However, as can be seen from Table 2 the energy of the host as well as the guest are almost the same as for the individually minimized host and guest. Visual inspection of host and guest shows that only minor conformational changes occur upon complexation. This clearly indicates that the host is preorganized for complexation of water, ammonia, and primary amines.

$$\Delta E = E_{interaction} - E_{complex} + (E_{host} + E_{guest}) \qquad (1)$$

$E_{interaction}$ = sum of vanderWaals and eletrostatic interactions between host and guest.
$E_{complex}$ = total energy of the complex.
E_{host} = total energy of the host.
E_{guest} = total energy of the guest.

The obtained calculated coordination distances between the uranium ion and the donor atom of the guest (2.36 – 2.69 Å) are in good agreement with experimental

Table 2 Calculated energies (kcal·mol⁻¹) from molecular mechanics and coordination distance $UO_2^{2+} \cdots D_{guest}$(Å).

	E_{tot}[a]	E_{host}[b]	E_{guest}[c]	E_{int}[d]	ΔE[e]	$U - D_{guest}$[f]
H_2O	0.0		0.0			
NH_3	0.0		0.0			
$BnNH_2$	1.72		1.72			
9a(conf. 1)	33.62	33.62				
9a(conf. 2)	45.58	45.58				
9a(Conf.1)·H_2O	7.46	33.83	0.36	-26.72 -28.88[g] 2.15[h]	-0.56	2.61
9a(Conf.1)·NH_3	1.47	33.76	0.89	-33.18 -38.44[g] 5.26[h]	-0.97	2.40
9a(Conf.1)·$BnNH_2$	17.17	33.99	1.44	-18.26 -8.06[g] -10.20[h]	-0.09	2.69

a) total energy
b) energy of the host
c) energy of the guest
d) interaction energy between host and guest
e) $\Delta E = E_{int} - E_{complex} + (E_{host} + E_{guest})$
f) coordination distance between UO_2^{2+} and hetero atom of the guest (Å)
g) the electrostatic contribution to E_{int}.
h) the vanderWaals contribution to E_{int}.

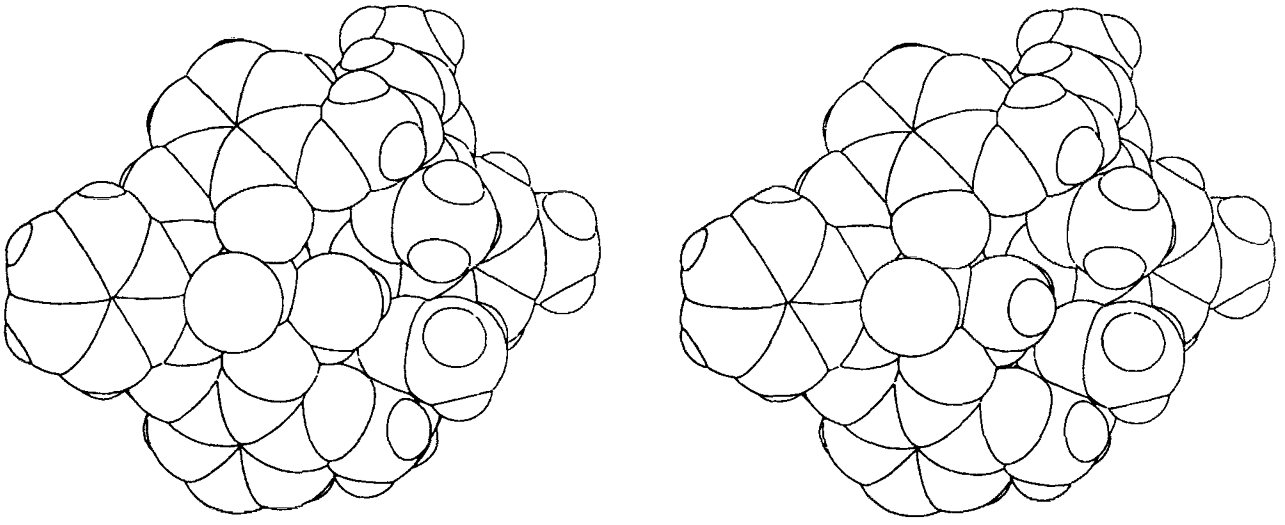


Figure 1 Space filling representation of **9a**(conf. 1)$\cdot H_2O$ (a) and **9a**(conf. 1)$\cdot NH_3$ (b).

values.[6,7] The calculated value of $E_{9a.ammonia} - E_{9a.water}$ of -5.99 kcal·mol^{-1} is of the same order of magnitude as the experimentally $\Delta\Delta G(NH_3 - H_2O)$ = -RTln(350/1) = -3.41 kcal·mol^{-1} and this suggests that entropy effects do not play a dominant role. Since the complexation of a molecule of ammonia in **9a-c** liberates a molecule of water and assuming that the solvations of the two guests are similar in $CDCl_3$ it is not unlikely that this is indeed the case. Since host and guest do not reorganize, the selectivity is determined by the interaction energy (E_{int}), which is dominated by the electrostatic contribution. With respect to the selectivity of benzylamine versus water this assumption will certainly not hold and further experiments have to be awaited to draw sound conclusions. From the longer coordination distance between the uranium cation and the nitrogen atom of the guest it is clear that the guest can not penetrate the host as deeply as ammonia and water. This will result in a smaller electrostatic contribution to the interaction energy. The increased vanderWaals interaction can not compensate this loss. We predict that entropy effects are dominant factors in the displacement of water by benzylamine.

CONCLUSIONS

The concept of immobilizing an electrophilic center combined with the concept of preorganization of the host resulted in three new uranyl complexes (**9a-c**) as hosts for ammonia and primary amines. The uranyl complex **9b** has the highest reported selectivity for ammonia over primary amines. It is anticipated that modifying the substituents on the outer phenyl rings of the terphenyl moiety will increase the selectivity towards ammonia.

EXPERIMENTAL SECTION

General

All solvents were of analytical grade and used as received. Reagent were used without further treatment. All NMR spectra were taken in $CDCl_3$ (^1H: 250 MHz). Only characteristic peaks in the ^{13}C NMR spectra are given. FAB mass spectra were taken in NBA.

Syntheses

3,3"-(2,2',2"-Trihydroxy-5,5',5"-trimethyl[1,1':3',1"-terphenyl]dialdehyde (2). A solution of **1** (20.0 g, 62.5 mmol) and hexamethylenetetramine (26.3 g, 187.9 mmol) in 150 mL of CF_3COOH was heated for 3.5 days at 90°C. The reaction mixture was cooled to 60°C and 100 mL of water were added. The mixture was stirred for 2.5 h and poured into 1 L of ethyl acetate. The acid was neutralized with a solution of $NaHCO_3$. The organic layer was separated off, washed with brine and dried with $MgSO_4$. The solvent was removed and the residue was purified by column chromatography (SiO_2,CH_2Cl_2) to give **2** as a slightly yellow solid in 65% yield. mp = 209-210°C; ^1H NMR δ 11.62 (s, 2 H), 9.90 (s, 2 H), 7.49 (d, 2 H, J = 2.0 Hz), 7.39 (d, 2 H, J = 2.0 Hz), 7.14 (s, 2 H), 6.46 (bs, 1 H), 2.38 (s, 6 H), 2.39 (s, 3 H); ^{13}C NMR δ 196.9 (d), 156.1, 149.1 (s), 20.6, 20.3 (q); IR (KBr) 3490 (OH), 1655 (C=O) cm^{-1}. FAB mass spectrum, *m/e* 377.0 [$(M+H)^+$ calcd 377.1].

3,3”-(2,2’,2”-Trimethoxy-5,5’,5”-trimethyl[1,1’:3’,1”-terphenyl]dialdehyde (3). A mixture of **2** (14,3 g, 38.0 mmol), dimethyl sulfate (19.2 g, 152 mmol), and K_2CO_3 (21.0 g, 152 mmol) was refluxed in CH_3CN for 3 h. After cooling to room temperature the salts were filtered off and the filtrate concentrated to dryness. Upon standing the residue solidified and was purified as described.[8a] Spectral data were all identical to literature.[8a]

3,3”-((2,2’,2”-Trimethoxy-5,5’,5”-trimethyl[1,1’:3’,1”]terphenyl]-3,3”-diyl)bis(methyleneoxy))bis[2-(2-propenyloxy)benzaldehyde] (6). A mixture of 2.6 g (14.6 mmol) 2-(2-propenyloxy)-3-hydroxybenzaldehyde (**10**) and 10.0 g (72.5 mmol) K_2CO_3 in 75 mL of acetonitrile was refluxed for 30 min. The dibromide **5** (4.0 g, 7.3 mmol), dissolved in 10 mL of acetonitrile, was added and the resulting mixture was refluxed for another 4 h. The reaction mixture was cooled to room temperature, poured in water and extracted with CH_2Cl_2. The organic layer was separated, washed with brine, 10% $NaOH_{aq}$, and dried with $MgSO_4$. The solvent was removed to give pure **6** as a slightly yellow oil in 84% yield. ^{1}H NMR δ 10.45 (s, 2 H), 7.44 (d, 2 H, *J* = 7.8 Hz), 7.32 (s, 2 H), 7.27 (d, 2 H, *J* = 7.8 Hz), 7.17 (s, 4 H), 7.12 (dd, 2 H, *J* = 7.8 Hz, *J* = 7.8 Hz), 6.12-5.95 (m, 2 H), 5.37-5.22 (m, 4 H), 5.22 (s, 4 H), 4.71 (d, 4 H), 3.49 (s, 6 H), 3.20 (s, 3 H), 2.38 (s, 3 H), 2.35 (s, 6 H); ^{13}C NMR δ 190.5 (d), 153.5 153.2, 152.3, 152.6 (s), 75.2, 66.6 (t), 61.1, 60.6, 20.9, 20.8 (q); IR (KBr) 1688 (CHO) cm^{-1}. FAB mass spectrum, *m/e* 743.3 [$(M+H)^+$ calcd 743.3].

3,3”-((2,2’,2”-Trimethoxy-5,5’,5”-trimethyl[1,1’:3’,1”]terphenyl]-3,3”-diyl)bis(met hyleneoxy))bis(2-hydroxybenzaldehyde) (7). A mixture of **6** (2.20 g, 2.90 mmol), HCOOH·NEt$_3$ (1.30 g, 8.90 mmol), $Pd(OAc)_2$ (7 mg), and PPh_3 (35 mg) was heated at 90°C in a mixture of DMF and water (5:1) for 2.5 h. The reaction mixture was cooled to room temperature, poured into water and extracted with CH_2Cl_2. The organic layer was dried with $MgSO_4$ and concentrated to dryness to give an oil. This oil was treated with MeOH to give **7** as a white powder, which was further purified by recrystallization from EtOH (80%). Spectral data were identical to literature.[9]

The Ba^{2+} complexes **8a-c** were obtained using the method described in literature.[9] **(37,38,39-Trimethoxy-5,5,18,22,27-pentamethyl-13,31-dioxa-3,6-diazahexacyclo[30.3.1.1^{8,12}.1^{15,19}.1^{20,24}.1^{25,29}]tetraconta-1(36),2,6,8,10,12(40),15,17,19(39),20,22,24(38),25,27,29(37),32,34-heptadecaene-36,40-diol-O^{13},O^{31},O^{36},O^{37},O^{38},O^{39},O^{40})barium(2+)Bis(trifluoromethanesulfonate) (8b):** ^{1}H NMR δ 8.25, 8.20 (s, 2 H), 7.26 (s, 4 H), 7.19-7.15 (m, 2 H), 7.11 (s, 2 H), 6.90 (m, 2 H), 6.73-6.61 (m, 2 H), 5.57, 5.43, 4.90, 4.76 (2 x AB-q, *J* = 11.0 Hz), 3.79, 3.68 (AB-q, 4 H, *J* = 13.1 Hz), 3.63 (s, 6 H), 3.03 (s, 3 H), 2.48 (s, 3 H), 2.37 (s, 6 H), 1.39, 1.38 (s, 3 H); ^{13}C NMR δ 167.5 (d), 154.3, 154.0, 149.8, 149.9 (s), 71.4, 69.6, 63.7 (t), 63.2, 62.9, 24.7, 22.9, 20.9 (q); IR (KBr) 1632 (C=N) cm^{-1}; FAB mass spectrum, *m/e* 1001.2 [$(M-CF_3SO_3))^+$ calcd 1001.1]. Anal. calcd for $C_{46}H_{46}BaF_6N_2O_{13}S_2$: C, 48.03; H, 4.03; N, 2.44. Found: C, 48.08; H, 3.99; N, 2.41.

(*cis*-33a,34,35,36,37,37a-Hexahydro-39,40,41-trimethoxy-12,17,22-trimethyl-25*H*-3,7:10,14;15,19:20,24:27,31-pentametheno-9*H*-8,26,1,33-benzodioxadiazacyclopentatriacontine-38,42-diol-O^8,O^{26},O^{38},O^{39},O ^{40}, O^{41},O^{42})barium(2+) Bis(trifluoromethanesulfonate) (8c): mp=220-228 °C ; ^{1}H NMR (predominent conformer) δ 8.41, 8.28 (s, 1 H), 7.28 (s, 2 H), 7.25 (s, 2 H), 7.24-7.12 (m, 2 H), 7.17-6.97 (m, 2 H), 6.90 (s, 2 H), 6.71-6.68 (m, 2 H), 5.60, 4.79 (AB-q, 4 H, J = 12.0 Hz), 4.10-3.98 (m, 2 H), 3.62 (s, 6 H), 3.09 (s, 3 H), 2.48 (s, 3 H), 2.32 (s, 6 H), 1.82-1.25 (m, 8 H); ^{13}C NMR δ 167.1 (d), 153.4, 148.9 (s), 72.2 (t), 63.4, 61.6 (q), 62.3 (d), 29.8, 27.8 (t), 20.9 (q); IR (KBr) 1642 (C=N) cm^{-1}. FAB mass spectrum, *m/e* 1027.1 [$(M-CF_3SO_3)^+$, calcd 1027.3]. Anal. calcd for $C_{50}H_{48}BaF_6N_2O_{13}S_2$: C, 50.03; H, 4.03; N, 2.33. Found: C, 50.09; H, 3.99; N, 2.30.

General procedure for the synthesis of 9a-c.

To a solution of 0.20 g of the Ba^{2+} complex **8** in 4 mL of CH_2Cl_2 and 4 mL of MeOH, was added 1 equiv of $UO_2(OAc)_2{\cdot}2H_2O$ dissolved in 4 mL MeOH. The mixture was stirred for 15 min and concentrated to dryness. The red powder was recrystallized from a mixture of MeOH, CH_2Cl_2, and petroleum ether (bp = 60 – 80°C) to give the uranyl complex as red crystals in a yield of 70 – 80%.

(39,40,41-Trimethoxy-12,17,22-trimethyl-25*H*-3,7:10,14:15,19:20,24:27,31-pentametheno-9*H*-8,26,1,33-benzodioxadiazacyclopentatriacontine-38,42-diolato(2-)-N^1,N^{33},O^{38},O^{42})dioxouranium (9a): mp = 195-210°C. ^{1}H NMR δ 9.4 (s, 2 H), 7.61-7.57 (m, 2 H), 7.53 (dd, 2 H, *J* = 1.5 and *J* = 7.6 Hz), 7.49-7.46 (m, 2 H), 7.45 (d, 2 H, *J* = 2.0 Hz), 7.41 (dd, 2 H, *J* = 1.5 and *J* = 7.6 Hz), 7.27 (d, 2 H, *J* = 2.0 Hz), 7.24 (s, 2 H,), 6.67 (dd, 2 H, *J* = 7.6 and *J* = 7.6 Hz), 5.57, 4.95 (AB-q, 4 H), 3.61 (s, 6 H), 3.15 (s, 3 H), 2.46 (s, 6 H), 2.44 (s, 3 H); ^{13}C NMR δ 165.8 (d), 164.4, 154.9, 154.3, 150.1 (s), 70.9 (t), 62.2, 61.2, 20.9 (q); IR (KBr) 1602(C=N), 903 (O-U-O) cm^{-1}. FAB mass spectrum, *m/e* 1003.2 [$(M+H)^+$, calcd 1003.3]. Anal. calcd for $C_{46}H_{40}N_2\,O_9U{\cdot}H_2O{\cdot}CH_2Cl_2$: C, 51.58; H, 3.97; N, 2.51. Found: C, 51.96; H, 4.04; N, 2.50. Upon standing the CH_2Cl_2 molecule was exchanged for a molecule of water. Anal. calcd for $C_{46}H_{40}N_2O_9U{\cdot}2H_2O$: C, 53.18; H, 4.27; N, 2.70. Found: C, 53.09; H, 4.20; N, 2.66. **(37,38,39-Trimethoxy-5,5,18,22,27-pentamethyl-13,31-dioxa-3,6diazahexacyclo[30.3.1.1^{8,12}.1^{15,19}.1^{20,24}.1^{25,29}]tetraconta-1(36),2,6,8,10,12(40),**

15,17,19(39),20,22,24(38), 25,27,29(37),32,34-heptadecaene-36,46-diolato(2-)-N^3,N^6,O^{36},O^{40})dioxouranium (9b): mp = 160-170 °C. ^{1}H NMR δ 9.29, 9.22 (s, 1 H), 7.51-7.44 (m, 2 H), 7.40-7.36 (m, 2 H), 7.29-7.24 (m, 4 H), 7.23 (s, 2 H), 6.72 (m, 2 H), 5.40, 5.30, 5.28 (2 x AB-q, 4 H), 4.54, 4.33 (AB-q, 2 H), 3.59 (s, 6 H), 3.08 (s, 3 H), 2.44 (s, 6 H), 2.44 (s, 6 H), 2.43 (s, 3 H), 1.71, 1.66 (s, 3 H); ^{13}C NMR 169.3, 165.8 (d), 155.4, 154.7, 150.8, 150.5 (s), 76.5, 71.7, 71.5 (t), 65.3 (s), 62.3, 61.5, 26.6, 26.4, 21.24 (q); IR (KBr) 1617 (C=N), 896 (U-O-U) cm^{-1}. FAB mass spectrum, *m/e* 983.2 [(M+H)$^+$ calcd 983.4]. Anal. calcd for $C_{44}H_{44}N_2O_9U{\cdot}2H_2O$: C, 51.87; H, 4.75; N, 2.75. Found: C, 51.82; H, 4.80; N, 2.76.

[*cis*-33a,34,35,36,37,37a-Hexahydro-39,40,41-trimethoxy-12,17,22-trimethyl-25*H*-3,7:10,14:15,19:20,24:27,31-pentametheno-9*H*-8,26,1,33-benzodioxadiazacyclopentatriacontine-38,42-diolato(2-)-N^1,N^{33},O^{38},O^{42}]dioxouranium (9c): mp = 205-210 °C. ^{1}H NMR δ 9.33 (s, 2 H), 7.50-7.46 (m, 2 H), 7.40-7.37 (m, 2 H), 7.31-7.27 (m, 2 H), 7.24-7.20 (m, 2 H), 7.23 (s, 2 H), 6.69 (m, 2 H), 5.34 (s, 4 H), 4.72-4.64 (m, 2 H), 3.59 (s, 6 H), 3.07 (s, 3 H), 2.47-2.18 (m, 2 H) 2.44 (s, 9 H), 2.06-1.77 (m, 6 H); ^{13}C NMR δ 168.2 (d), 155.0, 153.3, 150.2 (s), 71.8, 71.0 (d), 71.3 (t), 61.9, 61.1 (q), 20.89, 20.84 (q); IR (KBr) 1617 (C=N), 899 (O-U-O) cm^{-1}. FAB mass spectrum, *m/e* 1009.4 [(M+H)$^+$, calcd 1009.3]. Anal. calcd for $C_{48}H_{46}N_2O_9U.2H_2O$: C, 53.93; H, 4.91; N, 2.62. Found: C, 53.82; H, 5.01; N, 2.65.

^{1}H NMR titrations

The ^{1}H NMR titrations were performed in dry $CDCl_3$ (molsieves) at room temperature (293 K). During the titrations the concentration of the host was kept constant and the concentration of the guest was increased stepwise in a molar ratio of guest over host of 0.2-20. For the experiments 9-12 samples were prepared of which the outer MeO and/or the benzylic AB-q and/or the imine absorptions of the host were used as probe. The association constants were obtained with a nonlinear two parameter fit of the chemical shift and the association constant.[12] The results gave good fits for a 1:1 stoichiometry as could be concluded from the *function values*[12] (< 0.01), which can be regarded as the "goodness of fit parameter". All experiments were performed in duplicate. The calculated association constants using the two probes showed good agreement. The obtained association constants were averaged and the error bars estimated. For the determination of the $K_{ass}(NH_3)$'s a solution had to be prepared in $CDCl_3$ of known concentration. A flask was first purged with nitrogen and weighted. The same was done using ammonia gas. The difference in weight combined with the law of a perfect gas gave us the amount of ammonia in the flask. Injection of a known volume of $CDCl_3$ through a stopper gave a concentration of 0.050 mol·l^{-1}. The method was verified by acid-base titration of this solution (0.046 mol·l^{-1}). Since all three uranyl complexes were obtained as dihydrate the concentration of water in all experiments is the same and therefore the numbers can be compared.

MM calculations

The molecular mechanics calculations have been performed using Quanta/CHARMm.[13-15] The coordinates of the salophen moiety with the complexed uranyl cation were taken from literature[6a] and kept constant during the minimizations by imposing atomic constraints. The nonbonded parameters for the uranyl cation[16] were taken from literature:[6b] $q_o = 0.0$ and $q_u = 2.0$, $R_{min} = 3.00$ Å and $E_{min} = -1.00$ kcal·mol^{-1}. These parameters correctly reproduce the hydration energy of the uranyl cation in water and coordination distances are similar to those in crystal structures.[6] The terphenyl moiety has been generated in Quanta, minimized, and attached to the salophen unit. The TIP3P model for water has been used. The charges used are the so called *charge templates* as provided by Quanta, except for the uranyl cation and the phenolate oxygen ($q_{phenolate} = -0.9$).[6c] Small "excess" charge was smoothed to non-polar hydrogen and carbon atoms. The complexes were made by placing the guest manually in the host with the donor atom of the guest in the first coordination sphere of the uranium cation and hydrogen bonds to the two outer methoxy groups of the terphenyl unit. In this way a complex with approximately a plane of symmetry was obtained as observed in the ^{1}H NMR spectra. Minimizations were run with a distance dependent dielectric constant and an $\epsilon = 1$. No cutoff was applied. The structures were minimized by *conjugate gradient* and terminated when the rms on the gradient was < 0.01.

REFERENCES

1 Pedersen, C.J. *J. Am. Chem. Soc.*, **1967**, *89*, 7017.

2 See for example: (a) Vögtle, F. *Supramoleculare Chemie*, Teubner, Stuttgart, **1989**. (b) Patai, S.; Rappoport, Z. (Eds) *Crown Ethers and Analogs*, Wiley, Chichester, England, **1989**. (c) Gokel, G.W. (Ed) *Advances in Supramolecular Chemistry*, JAI Press Inc., London, **1990**. (d) Balzani, V.; De Cola, L. (Eds) *Supramolecular Chemistry*, Kluwer Academic Publishers, Dordrecht, The Netherlands, **1992**. (e) Hiraoka, M. (Ed) *Crown Ethers and Analogous Compounds*, Elsevier, Amsterdam, **1992**.

3 (a) Colquhoun, H.M.; Stoddart, J.F.; *J. Chem. Soc., Chem. Commun.*, **1981**, *612*. (b) Colquhoun, H.M.; Stoddart, J.F.; Williams, D.J.; *J. Chem. Soc., Chem. Commun.*, **1981**, *847*. (c) Colquhoun, H.M.; Stoddart, J.F.; Williams, D.J.; *Angew. Chem., Int. ed. Eng.*, **1986**, *25*, 487. (d) Alston, D.R.; Stoddart, J.F.; Wolstenholme, J.B.; Williams, D.J.; *Tetrahedron* **1984**, *41*, 2923.

4 Reetz, M.T.; Niemeyer, C.M.; Hermes, M.; Goddard, R.; *Angew. Chem., Int. Ed. Eng.*, **1992**, *31*, 1017.

5 Cram, D.J.; *Angew. Chem.*, **1988**, *100*, 1041.

6 (a) van Staveren, C.J.; van Eerden, J.; van Veggel, F.C.J.M.; Harkema, S.; Reinhoudt, D.N.; *J. Am. Chem. Soc.*, **1988**, *110*, 4994. (b) van Doorn, A.R.; Rushton, D.J.; van Straaten-Nijenhuis, W.F;, Verboom, W.; Reinhoudt, D.N.; *Recl. Trav. Chim. Pays-Bas* **1992,** *111*, 421. (c) Reichwein, A.R.; Verboom, W.; Reinhoudt, D.N.; *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 358. (d) van Doorn,

A.R.; Schaafstra, R.; Bos, M.; Harkema, S.; van Eerden, J.; Verboom, W.; Reinhoudt, D.N.; *J. Org. Chem.*, **1991**, *56*, 6083. (e) van Doorn, A.R.; Verboom, W.; Harkema, S.; Reinhoudt, D.N.; *Synthesis* **1992**, *119*, (f) Reichwein, A.R.; Verboom, W.; Reinhoudt, D.N.; *Recl. Trav. Chim. Pays-Bas*, **1993**, *112*, 595.

7 van Doorn, A.R.; Bos, M.; Harkema, S.; van Eerden, J.; Verboom, W.; Reinhoudt, D.N.; *J. Org. Chem.*, **1991**, *56*, 2371.

8 (a) Dijkstra, P.J.; Skowronska-Ptasinska, M.; Reinhoudt, D.N.; den Hertog, H.J., Jr.; van Eerden, J.; Harkema, S.; de Zeeuw, D.; *J. Org. Chem.*, **1987**, *52*, 4913. (b) Koenig, K.E.; Lein, G.M.; Stuckler, P.; Kaneda, T.; Cram, D.J.; *J. Am. Chem. Soc.*, **1979**, *101*, 3553.

9 van Veggel, F.C.J.M.; Harkema, S.; Bos, M.; van Staveren, C.J.; Gerritsma, G.J.; Reinhoudt, D.N.; *Inorg. Chem.*, **1989**, *28*, 1133.

10 Yamada, T.; Goto, K.; Mitsuda, Y.; Tsuji, J.; *Tetrahedron Lett.*, **1987**, *28*, 4557.

11 van Staveren, C.J.; Reinhoudt, D.N.; van Eerden, J.; Harkema, S.; *J. Chem. Soc., Chem. Commun.*, **1987**, *974*, and references 6a and 9.

12 de Boer, J.A.A.; Reinhoudt, D.N.; Harkema, S.; van Hummel, G.J.; de Jong, F.; *J. Am. Chem. Soc.* **1982**, *104*, 4073.

13 Quanta 3.3/CHARMm 22.0 package, Molecular Simulations, Waltham, USA, 1992.

14 Brooks, B.R.; Bruccoleri, R.E.; Olafson, B.D.; States, D.J.; Swaminathan, S.; Karplus, M.; *J. Comput. Chem.*, **1983**, *4*, 187.

15 Momary, F.A.; Rone, R.; *J. Comput. Chem.*, **1993**, *13*, 888.

16 Guilbaud, P.; Wipff, G.; *J. Phys. Chem.*, **1993**, *97*, 5685.