

Dinuclear, Diuranyl-containing Metallomacrocycles: Neutral Receptors for Dicarboxylates

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Dinuclear UO_2 -sal(oph)en metallomacrocycles **1** and **2**, containing flexible and rigid cavities, respectively, have been found linearly to recognise and form strong solution complexes with terephthalate, succinate and fumarate dianions in $(\text{CD}_3)_2\text{SO}$; weaker interactions between these hosts and the shorter malonate and monoanionic benzoate were observed.

In contrast with the complexation of cations, the design and synthesis of biomimetic receptors for anions towards applications in sensing and catalysis is a very recent area of study and is currently receiving much attention.¹ For the recognition of carboxylate anions in particular, virtually all the synthetic host molecules reported thus far have employed at least one H-bonding interaction, mimicking natural systems such as enzymes. Positively charged polyammonium-^{2,3} and guanidinium-^{4,5} containing receptors have also exploited electrostatic interactions, the enhancement allowing interactions with anions in more polar solvents. Another approach has been the development of neutral hosts containing multiple urea⁶⁻⁸ or amide⁹⁻¹¹ binding sites. In addition, a redox-responsive ditopic bis-(cobalticinium) calix[4]arene receptor for dicarboxylates¹² and a chiral, capped metalloporphyrin for the enantioselective recognition of amino acid derivatives¹³ have been reported, both employing the combination of a Lewis acid-anion interaction and favourable amide-anion H-bonding for stability and selectivity in complexation, respectively.

We have previously reported that metallo-macrocycles and -clefts containing an immobilised Lewis acidic UO_2 cation (as a salen or salophen complex) are excellent receptors for the complexation of neutral molecules^{14,15} and inorganic anions such as H_2PO_4^- , Cl^- and NO_2^- .¹⁶ This work has now been extended to the incorporation of two UO_2 -sal(oph)en units into macrocycles **1** and **2**, to our knowledge the first *neutral, dinuclear* Lewis acid-containing hosts for the recognition and binding of dicarboxylates. These receptors are unique in that they have no H-bonding donor sites to complement the Lewis acid-anion interaction; their selectivity therefore is derived from size/shape complementarity. An analogous dinuclear metallocleft **3**, containing two 'naked' UO_2 -salophen units¹⁶ (where each UO_2 centre contains two vacant co-ordination sites) was synthesised for comparison. The syntheses and complexation studies of **1-3** with dicarboxylates is reported.

Results and Discussion

We have previously reported the synthesis of the metal-free macrocycle of **1**,¹⁷ and **1** was prepared by this route with metallation effected by the addition of $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ to a refluxing methanolic solution of the free macrocycle which was formed *in situ*. The coupling of two equivalents of 2-(prop-2-enyloxy)-3-hydroxybenzaldehyde¹⁸ with 1,4-bis(chloromethyl)-benzene and K_2CO_3 as a base in refluxing acetonitrile afforded the dialdehyde **4**, the building block for both **2** and **3**, in 70% yield (Scheme 1). Deprotection of **4** to give the dialdehyde **5** in 67% yield was achieved using $\text{Pd}(\text{OAc})_2\text{-PPh}_3\text{-NEt}_3\text{-HCOOH}$ in refluxing 80% aqueous ethanol.¹⁹ Host **2** was then formed by the Schiff base macrocyclisation of **5** with an equimolar amount of *cis*-cyclohexane-1,2-diamine in refluxing 1:1

$\text{CHCl}_3\text{-MeOH}$ followed by the addition of a methanolic solution of $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$.[†] Reaction of **5** with two equivalents of 2-amino-4-*tert*-butylphenol in refluxing methanol and subsequent metallation yielded metallocleft **3**.[‡] The yields of **1** (orange solid), **2** (red-orange solid) and **3** (brown powder) were 26%, 57% and 87%, respectively. The ^1H NMR spectra [$(\text{CD}_3)_2\text{SO}$] each show a singlet for the imine protons at δ 9.60 (**1**), δ 9.45 (**2**) and δ 9.53 (**3**); in the IR spectra the stretching frequency for the imine double bond is present at 1602 cm^{-1} (**1**), 1615 cm^{-1} (**2**) and 1605 cm^{-1} (**3**). The FAB mass spectra show parent ions at m/z 1373.3, m/z 1449.6 and m/z 1207.2 corresponding to **1** (M^+ , 1372.9), **2** (M^+ , 1449.1) and **3** ($[\text{M} - \text{H}]^-$, 1207.8). The presence of (co-ordinated) water in samples of the three hosts was confirmed by elemental analysis and Karl Fischer titration.

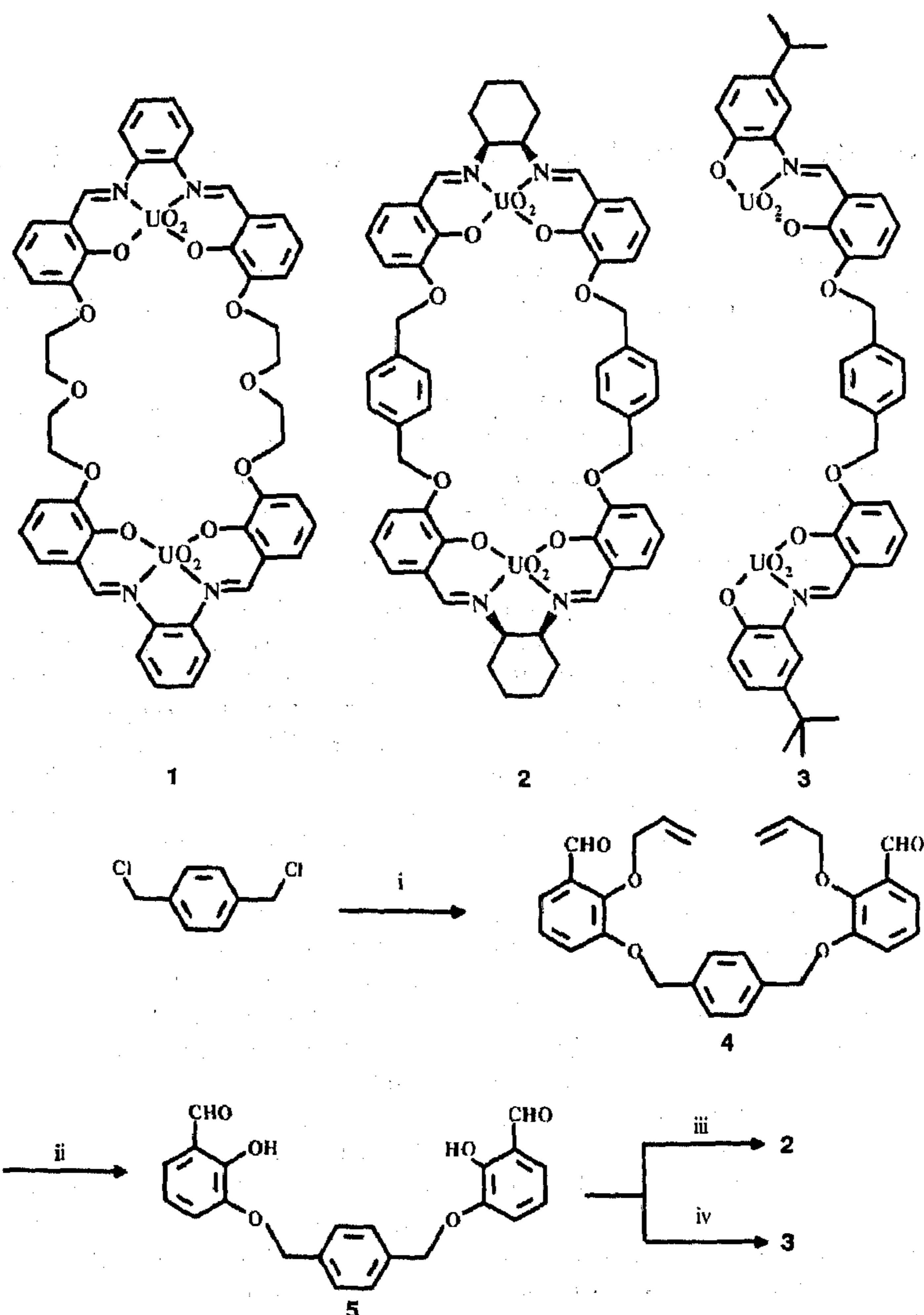
Inspection of CPK molecular models of **1** and **2** reveals that their cavities are similar in shape when the distance between the uranyl centres is at a maximum, with that of **2** being slightly larger. Estimated cavity dimensions for **1** and **2** are *ca.* 15×7.5 Å and *ca.* 17.5×8.8 Å, respectively. The flexible ethylene glycol spacers in **1** allow a great variation in the $\text{UO}_2 \cdots \text{UO}_2$ distance, as is demonstrated in the X-ray crystal structure of a trinuclear dicopper barium sister complex, where the $\text{Cu} \cdots \text{Cu}$ distance is only 3.50 Å due to ligand folding.¹⁷ In contrast, the xylyl spacers in **2** generate a rigid preorganised cavity which is sterically unable to collapse. This cyclo-bis-intercaland² was expected to bind *planar anionic* substrates, such as aromatic carboxylates, in polar aprotic solvents with $\pi\text{-}\pi$ interactions enhancing complex stability which will be derived mainly from the Lewis acid-anion interaction.

Anion complexation was studied by ^1H NMR spectroscopy. The addition of tetrabutylammonium or tetraethylammonium salts of a variety of (mainly di-) carboxylates to solutions of **1** and **2** in $(\text{CD}_3)_2\text{SO}$ resulted in dramatic changes in the ^1H NMR spectra. Virtually all signals of the free and complexed hosts could be observed separately with all those of the complex shifted upfield; for the imine signals $\Delta\delta = 0.06\text{-}0.20$ ppm (Table 1). These observations point to the formation of kinetically stable complexes in $(\text{CD}_3)_2\text{SO}$ on the NMR time-scale.

The association constants (Table 2) determined by ^1H NMR spectroscopy for **1** with the short aliphatic dianions malonate and succinate ($K_{\text{ass}} = 5 \times 10^3\text{ dm}^3\text{ mol}^{-1}$ and $K_{\text{ass}} = 4.5 \times 10^2$

[†] Macrocyclisation of **5** with phenylene-1,2-diamine yielded the salophen analogue of **2**; however, it was found to contain a considerable amount of polymeric impurity (^1H NMR spectroscopy). Their identical and very poor solubilities in common organic solvents thwarted attempts at purification.

[‡] 2-Amino-4-*tert*-butylphenol was used in preference to 2-amino-phenol to improve the solubility of the metallated product.



Scheme 1 Reagents and conditions: i, 2-prop-2-enyloxy-3-hydroxybenzaldehyde, K_2CO_3 , KI, MeCN; ii, $Pd(OAc)_2$, PPh_3 , $HCOOH$, Et_3N , $EtOH-H_2O$, 4:1; iii, *cis*-cyclohexane-1,2-diamine, $UO_2(OAc)_2 \cdot 2H_2O$, $CHCl_3$ -MeOH, 1:1; iv, 2-amino-4-*tert*-butylphenol, $UO_2(OAc)_2 \cdot 2H_2O$, MeOH

Table 1 1H NMR spectroscopic data for the imine signals of 1 and 2 with anions^a

	S	M	TP	B	F	IP
1						
$\delta_{HC=N_f}$	9.60	9.60	9.60	9.60	9.60	9.60
$\delta_{HC=N_c}$	9.45	9.43	9.47	9.54, 9.50	9.47	9.50
$\Delta\delta$	0.15	0.17	0.13	0.06, 0.10	0.13	0.10
2						
$\delta_{HC=N_f}$	9.45	9.45	9.45	9.45	9.45	9.45
$\delta_{HC=N_c}$	9.31	9.25	9.37	9.45	9.33	9.39
$\Delta\delta$	0.14	0.20	0.08	0.00	0.12	0.06

^a $\delta_{HC=N_f}$ and $\delta_{HC=N_c}$ are imine chemical shifts of the free and complexed hosts, respectively. $[1] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$ and for solubility reasons $[2] = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$. S = succinate; M = malonate; TP = terephthalate; B = benzoate; F = fumarate; IP = isophthalate.

$\text{dm}^3 \text{ mol}^{-1}$, respectively) are somewhat larger than the corresponding values for 2 ($K_{\text{ass}} = 2.7 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ and $K_{\text{ass}} = 1.7 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$, respectively) although 2 shows the larger imine complexation-induced shifts. The modest selectivity for succinate over malonate exhibited by both hosts (11 for 1;

Table 2 Association constants ($K_{\text{ass}}/\text{dm}^3 \text{ mol}^{-1}$) of UO_2 metallo-macrocycles determined by 1H NMR spectroscopy in $(CD_3)_2SO$

Host	S ^a	M ^a	F ^a	TP ^b	B ^b
1	5.0×10^3	4.5×10^2	$>10^5$	1.4×10^4	2.0×10^2
2	2.7×10^3	1.7×10^2	1.8×10^4	2.0×10^4	c

^a Tetrabutylammonium and ^b tetraethylammonium salts were used. ^c No visible changes observed in the 1H NMR spectra. Spectra were recorded at 298 K with $[Host] = 0.0025 \text{ mol dm}^{-3}$. Estimated error = $\pm 10\%$.

16 for 2) indicates, most probably, the more favourable (*i.e.*, greater) length of the former for ditopic binding.

The benzoate anion induced no observable changes in the 1H NMR spectra of 2, implying that very little or no complexation was occurring. However, in the case of 1 having aliphatic spacers a K_{ass} value of $2.0 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$ was obtained. Raposo *et al.*⁹ recently reported that benzoate binds more strongly in $(CD_3)_2SO$ by a receptor containing two chromenone fragments ($K_{\text{ass}} = 1.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$). The formation of a 1:1 host-guest complex could be deduced from the pattern of the imine signals in the 1H NMR spectra. Addition of benzoate to 1 gives rise to three imine signals—the free host singlet and two upfield singlets of equal intensity

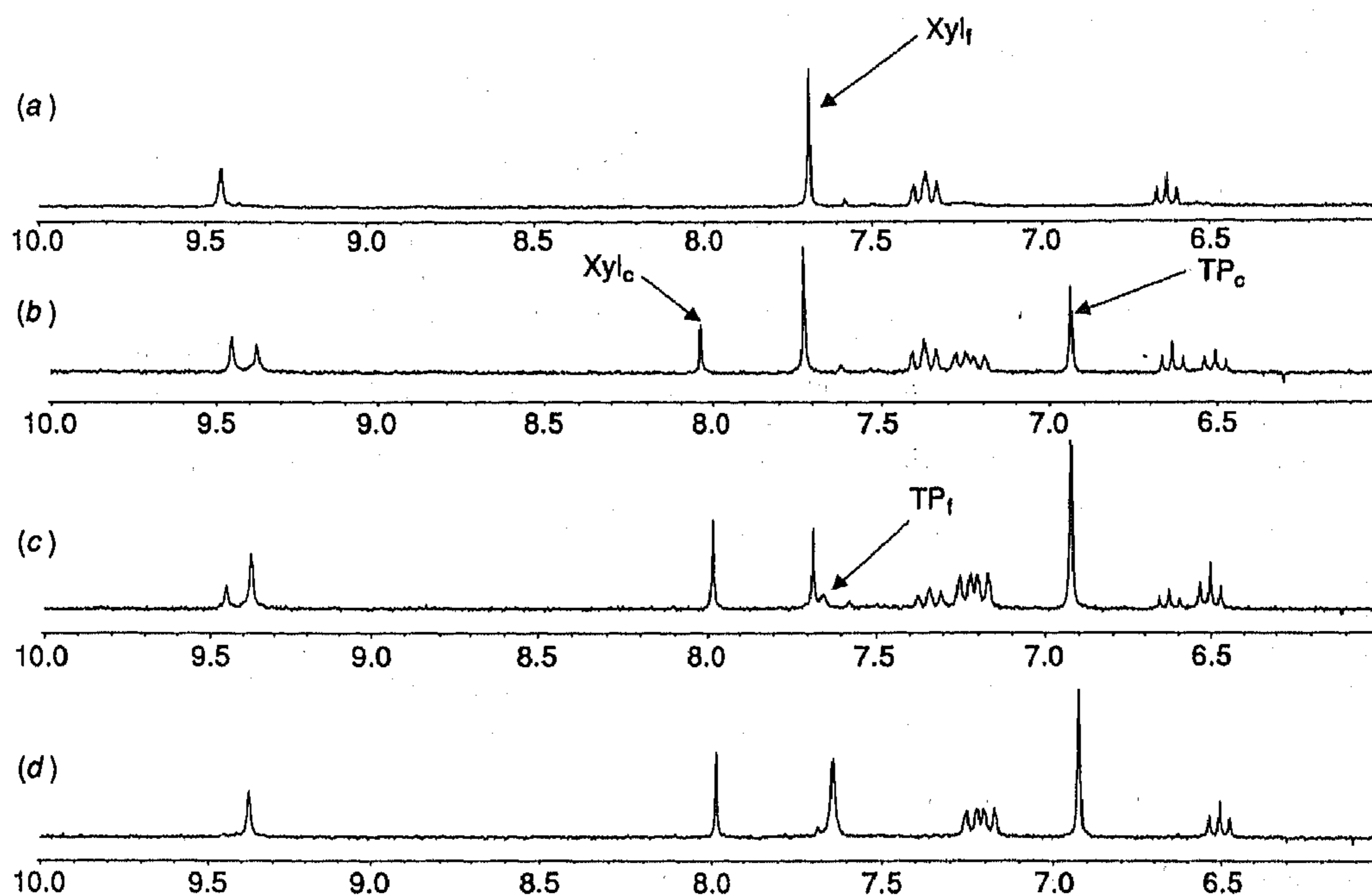


Fig. 1 ^1H NMR spectra $[(\text{CD}_3)_2\text{SO}]$ of (a) **2** only; (b) **2**:TP, 1:0.5; (c) **2**:TP, 1:1.0; (d) **2**:TP, 1:3.0 $[\text{2}] = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$ and TP = terephthalate. Xyl_f and Xyl_c correspond to the free and complexed xylol proton signals of **2**, respectively. TP_f and TP_c refer to the free and complexed terephthalate proton signals, respectively.

corresponding to the complex. Since the benzoate can bind only one UO_2 -salophen of the host, the other UO_2 -salophen will remain free but in a different environment from those in the free host, generating a second shifted imine signal.

Both metallomacrocycles showed the strongest complexation with the terephthalate (TP) dianion ($K_{\text{ass}} = 1.4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ for **1** and $K_{\text{ass}} = 2.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ for **2**). As a probe for investigating the complexation, the behaviour of the aromatic xylol and/or TP proton signals was used. For the xylol spacers of **2**, no change in the singlet was observed in the presence of succinate or malonate, as expected for aliphatic guests. For TP, whose free guest signal is at δ 7.65, addition to **1** results in the dianion singlet first appearing downfield at δ 8.15, with another signal appearing with excess guest at δ 7.65 ($\Delta\delta = 0.50 \text{ ppm}$). Interestingly, the addition of TP to **2** yields a complexed TP singlet with a very marked *upfield* position (δ 6.92, $\Delta\delta = -0.73 \text{ ppm}$), with a concomitant change in the host xylol singlet from δ 7.68 (free) to δ 7.99 (complex). These observations imply the formation of 1:1 complex (Fig. 1). The derived association constants for TP with **1** and **2** ($K_{\text{ass}} = 1.4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ and $K_{\text{ass}} = 2.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$, respectively) do not indicate a significant preference of TP for **2** over **1** as a result of aromatic stacking interactions; both values compare well with that of Schmidtchen's open-chain guanidinium host in CD_3OD ($K_{\text{ass}} = 3.1 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$).⁴ The independent and unambiguous characterisation of the complexed xylol signal was obtained by titration of the acyclic analogue **3** with succinate where the free and complexed host signals (at δ 7.69 and δ 8.00, respectively) match those of **2**. Given that TP dianion is the longest of those studied, it seems very unlikely that the other dicarboxylates would form 2:1 host-guest bridging complexes.

Titration with fumarate dianion also yielded large complexation-induced shifts in the guest singlet. Upon complexation by **1** and **2**, signals at δ 7.08 and δ 7.10, respectively were recorded for the dianion guest; the signal for the free dianion occurs at δ 6.03, giving rise to $\Delta\delta$ values of 1.05 ppm and 1.07 ppm, respectively. An association constant of $1.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ was determined for fumarate

with **2**; that with **1** was too high to be calculated ($>10^5 \text{ dm}^3 \text{ mol}^{-1}$). The slight shift in the xylol signal of **2** with this dianion (from δ 7.68 to δ 7.72) may suggest some weak interaction between the xylol spacer and the alkene group of the guest.[§]

The dinuclear metallocleft **3** was found by analogous ^1H NMR studies to complex succinate, benzoate, TP and H_2PO_4^- (no others were tested). However, the complexity of the derived spectra in general, and the imine signal changes in particular, coupled with a total of four possible Lewis acid binding sites on the host precluded the possibility of gaining further insight into the nature of the complexes formed.[¶]

In conclusion, it has been demonstrated that the incorporation of two Lewis acid centres within simple macrocyclic frameworks can lead to novel neutral receptors for dicarboxylates. With the presence of two UO_2 -sal(oph)en units in proximity it is possible to adjust the binding strength and selectivity

§ As expected from previous work,¹⁶ H_2PO_4^- anion was also bound quite strongly in $(\text{CD}_3)_2\text{SO}$ by both receptors ($K_{\text{ass}} = 1.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ for **1**; $K_{\text{ass}} = 2.3 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ for **2**) with the formation of 1:2 host-guest complexes. A solid 1:2 **1**- H_2PO_4^- complex, **6**, was prepared by stirring **1** with 2 equivalents of $\text{NBu}_4\text{H}_2\text{PO}_4$ in acetonitrile, followed by evaporation of the solution obtained. Complex **6** was fully characterised, with the ^1H NMR imine singlet at δ 9.55, IR $\text{HC}=\text{N}$ stretch at 1603 cm^{-1} and repeated FAB mass spectra showing ions corresponding to $[\text{1} + \text{anion}]^-$ and $[\text{1} + \text{salt}]^+$. Selectivity of almost a decade was found for TP over H_2PO_4^- by both **1** and **2**, suggesting that preorganisation of the Lewis acid sites in mutual proximity offers a slight advantage in the binding of a single linear dianion over that of two monoanions.

¶ Titration of **3** in $(\text{CD}_3)_2\text{SO}$ with neutral guests such as *p*-benzoquinone, DABCO and piperazine resulted in no observable changes in the ^1H NMR spectra. The unavoidable presence of water and/or the $(\text{CH}_3)_2\text{SO}$ solvent may inhibit or block any interaction of **3** with the neutral guests—both molecules have strong Lewis bases and are co-ordinated to all available uranyl sites present before the addition of guest solutions. This 'preco-ordination' of all three hosts by water- $(\text{CH}_3)_2\text{SO}$, which is overcome by anions in the case of **1** and **2** having only one vacant site per UO_2 , must also complicate the interaction of **3** with the anions tested.

of the Lewis acid centres away from the otherwise dominant dihydrogen phosphate towards dicarboxylates.

Experimental

Synthesis.—Melting points were determined using a Reichert melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer with the deuterated solvent signal as the reference. J values are given in Hz. Mass spectra were obtained with a Finnigan MAT 90 spectrometer. Positive and negative ion fast atom bombardment (FAB) mass spectra were recorded using *m*-nitrobenzyl alcohol as a matrix. IR spectra were recorded with a Nicolet SCX FT spectrophotometer. Elemental analyses were carried out by use of a Model 1106 Carlo Erba Strumentazione elemental analyser. CH_2Cl_2 and MeCN were stored over molecular sieves (4 Å) prior to use. All reagents were analytically pure and were used without further purification. Column chromatography was performed with silica gel (Merck: 0.040–0.063 mm). Tetraethylammonium malonate and succinate were prepared by titration of aqueous solutions of the acids with tetraethylammonium hydroxide (20 wt% solution in water, Janssen), followed by evaporation of the solvent and drying over P_2O_5 under vacuum. Tetrabutylammonium terephthalate, isophthalate and fumarate were prepared by titration of methanolic slurries of the acids with tetrabutylammonium hydroxide (1 mol dm^{-3} solution in methanol, Aldrich), followed by evaporation of the solutions formed and drying as described. Tetrabutylammonium dihydrogen phosphate and benzoate were used as purchased from Fluka.

Care should be taken when handling uranyl-containing compounds because of their toxicity and radioactivity.²⁰

^1H NMR Studies.—Stock solutions of guests (1.0 $\times 10^{-2}$ mol dm^{-3}) were added to 0.25 cm^3 or 0.125 cm^3 aliquots of host solutions (1.0 $\times 10^{-2}$ mol dm^{-3} for **1**, 5.0 $\times 10^{-3}$ mol dm^{-3} for **2**), which were then made up to 1.0 cm^3 or 0.5 cm^3 , respectively, with solvent to maintain a constant volume. K_{ass} values were determined by integration of the separated signals of the imine protons of both free ligand and complex.¹⁶ On the basis of repetitive measurements, the estimated error is < 10%.

μ -[8,11,14,22,25,28-Hexaoxa-3,5,17,19-tetraaza- κ^4 -N-1(1,3),4(1,2),7(1,3),15(1,3),18(1,2),21(1,3)-hexabenzencyclooctacosaphane-3,5,16,19-tetraene-1²,7²,15²,21²-tetraolato- κ^4 -O]-tetraoxodiuranium(vi) **1**.—To a refluxing solution of $\text{Ba}(\text{CF}_3\text{SO}_3)_2$ ¹⁸ (0.45 g, 1.04 mmol) in MeOH (200 cm^3) were added simultaneously a solution of 3,3'-[oxybis(2,1-ethanedioxy)]bis(2-hydroxybenzaldehyde)¹⁷ (0.72 g, 2.08 mmol) in THF (50 cm^3) and a solution of 1,2-phenylenediamine (0.22 g, 2.08 mmol) in MeOH (50 cm^3) dropwise over a period of 80 min. The resulting reddish solution was stirred at reflux for 80 min and $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.88 g, 2.08 mmol) was added in one portion. The reflux was continued for a further 1.5 h. The mixture was evaporated to dryness and the residue taken up in CH_2Cl_2 (100 cm^3). An equal volume of water was added and the mixture was stirred overnight to yield an orange slurry. The slurry was filtered and the precipitate washed successively with CH_2Cl_2 , MeOH and CH_2Cl_2 . Drying in the sinter and *in vacuo* gave an orange powdery solid **1** (0.37 g, 26%); m.p. > 291 °C (decomp.) (Found: C, 40.0; H, 3.2; N, 3.8. $\text{C}_{48}\text{H}_{40}\text{N}_4\text{O}_{14}\text{U}_2 \cdot 4\text{H}_2\text{O}$ requires C, 39.90; H, 3.35; N, 3.87%); Karl Fischer titration: Found: 4.7. Calc. for $4\text{H}_2\text{O}$: 4.99; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1602 (N=CH); $\delta_{\text{H}}[250 \text{ MHz}; (\text{CD}_3)_2\text{SO}]$ 9.60 (4 H, s, N=CH), 7.8–7.7 (4 H, m, ArH), 7.6–7.5 (4 H, m, ArH), 7.45 (4 H, d, J 7.1, ArH), 7.34 (4 H, d, J 7.3, ArH), 6.63 (4 H, t, J 7.8, ArH), 4.5–4.4 (8 H, m, CH_2) and 4.2–4.1 (8 H, m, CH_2); m/z (FAB) 1373.3 (M^+).

3,3'-(*p*-Phenylenedimethyldioxy)bis(2-prop-2-enyloxybenzaldehyde) **4**.—A mixture of 3-hydroxy-2-prop-2-enyloxybenzaldehyde¹⁸ (1.78 g, 10.0 mmol), 1,4-bis(chloromethyl)benzene (0.88 g, 5.0 mmol), KI (0.33 g, 2.0 mmol) and K_2CO_3 (2.90 g, 21.0 mmol) in MeCN (50 cm^3) was refluxed under argon for 61 h. The cooled mixture was filtered, the residue washed with MeCN and the combined filtrate and washings were evaporated to dryness. The yellowish residue was purified by flash chromatography (silica gel; CH_2Cl_2) to give **4** as a white solid (1.61 g, 70%); m.p. 138–139 °C (Found: C, 73.0; H, 5.6. $\text{C}_{28}\text{H}_{26}\text{O}_6$ requires C, 73.35; H, 5.72%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1681 (HC=O); $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$ 10.46 (2 H, s, CHO), 7.49 (4 H, s, ArH), 7.46 (2 H, dd, J 7.7 and 1.8, ArH), 7.21 (2 H, dd, J 8.1 and 1.7, ArH), 7.11 (2 H, t, J 7.9, ArH), 6.2–6.0 (2 H, m, $\text{OCH}_2\text{CH=}$), 5.4–5.2 (4 H, m, C=CH_2), 5.17 (4 H, s, ArCH_2O) and 4.70 (4 H, dd, J 6.1 and 1.2, $\text{OCH}_2\text{CH=}$); $\delta_{\text{C}}(62.5 \text{ MHz}; \text{CDCl}_3)$ 190.7 (CHO), 152.4, 152.1, 136.8, 133.5, 130.8, 128.1, 124.6, 120.4, 120.2 (ArC and $\text{OCH}_2\text{CH=}$), 119.5 (C=CH_2), 75.7 ($\text{OCH}_2\text{CH=}$) and 71.3 (ArCH_2O); m/z (EI) 458.2 (M^+).

3,3'-(*p*-Phenylenedimethyldioxy)bis(2-hydroxybenzaldehyde) **5**.—A mixture of **4** (0.85 g, 1.85 mmol), $\text{Pd}(\text{OAc})_2$ (12.4 mg, 0.062 mmol), triphenylphosphine (77.0 mg, 0.31 mmol), triethylamine (2.30 g, 23 mmol) and formic acid (1.02 g, 23 mmol) in 4:1 EtOH– H_2O (40 cm^3) was refluxed for 1.5 h by which time a suspension had formed. The cooled mixture was filtered, the precipitate washed with 4:1 EtOH– H_2O (10 cm^3) and dried in the funnel and *in vacuo* resulting in a pale greenish solid, **5** (0.47 g, 67%); m.p. 193–195 °C (Found: C, 70.2; H, 4.8. $\text{C}_{22}\text{H}_{18}\text{O}_6$ requires C, 69.83; H, 4.79%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1653 (HC=O); $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$ 11.13 (2 H, s, OH), 9.92 (2 H, s, CHO), 7.46 (4 H, s, ArH), 7.20 (2 H, dd, J 7.8 and 1.5, ArH), 7.12 (2 H, dd, J 8.1 and 1.3, ArH), 6.90 (2 H, t, J 7.9, ArH) and 5.19 (4 H, s, CH_2); $\delta_{\text{C}}(62.5 \text{ MHz}; \text{CDCl}_3)$ 196.5 (CHO), 152.3, 147.1, 136.5, 127.7, 125.4, 121.1, 121.0, 119.5 (ArC) and 71.1 (CH_2); m/z (EI) 378.0 (M^+).

μ -[8,12,20,24-Tetraoxa-3,5,15,17-tetraaza- κ^4 -N-1(1,3),7(1,3),10(1,4),13(1,3),19(1,3),22(1,4)-hexabenzena-4(1,2),16(1,2)-dicyclohexanacyclotetracosaphane-2,5,14,17-tetraene-1²,7²,13²,19²-tetraolato- κ^4 -O]-tetraoxodiuranium(vi) **2**.—Solutions of **5** (0.30 g, 0.792 mmol) in CHCl_3 (25 cm^3) and *cis*-cyclohexane-1,2-diamine (0.09 g, 0.792 mmol) in MeOH (25 cm^3) were added dropwise over 1.75 h to a refluxing mixture of 1:1 MeOH– CHCl_3 (100 cm^3) with vigorous magnetic stirring; 0.5 h after the addition was complete, another 100 cm^3 of 1:1 MeOH– CHCl_3 were added. The mixture was refluxed for a further 3 h by which time a bright yellow suspension had formed. A solution of $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.39 g, 0.919 mmol) in MeOH (10 cm^3) was added in one portion and after 0.5 h a red solution was obtained. The solution was allowed to cool slowly in the oilbath with stirring, to yield an orange precipitate. The precipitate was filtered and washed with 1:1 MeOH– CHCl_3 (10 cm^3) and dried in the sinter and *in vacuo*, giving an orange-red solid, **2** (0.33 g, 57%) m.p. 255–257 °C (decomp.) (Found: C, 44.5; H, 3.9; N, 3.7. $\text{C}_{56}\text{H}_{52}\text{N}_4\text{O}_{12}\text{U}_2 \cdot 4\text{H}_2\text{O}$ requires C, 44.22; H, 3.98; N, 3.68%); Karl Fischer titration: Found: 4.5. Calc. for $4\text{H}_2\text{O}$: 4.74; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1615 (N=CH); $\delta_{\text{H}}(250 \text{ MHz}; (\text{CD}_3)_2\text{SO})$ 9.45 (4 H, s, HC=N), 7.68 (8 H, s, ArH), 7.34 (8 H, t, J 8.2, ArH), 6.63 (4 H, t, J 7.8, ArH), 5.38 (8 H, s, ArCH_2O), 4.6–4.5 (4 H, m, C=NCH), 2.4–2.2 (4 H, m, cyclH) and 1.9–1.6 (12 H, m, cyclH); m/z (FAB) 1449.6 (M^+).

μ -[1⁵,13⁵-Di-*tert*-butyl-5,9-dioxa-2,12-diaza- κ^2 -N-1,4(1,3),7(1,4),10(1,3),13-pentabenzena-tridecaphane-2,12-diene-1²,4²,10²,13²-tetraolato- κ^4 -O]-tetraoxodiuranium(vi) **3**.—A mixture of **5** (0.42 g, 1.1 mmol) and 2-amino-4-*tert*-butylphenol (0.37 g,

2.2 mmol) in MeOH (100 cm³) was refluxed for 1 h by which time a bright orange precipitate had formed. A solution of UO₂(OAc)₂·2H₂O (0.93 g, 2.2 mmol) in MeOH (10 cm³) was added in one portion (causing an instant colour change in the precipitate to purple–brown) and refluxing was continued for a further 1 h. After slight cooling the mixture was filtered and the brown precipitate was washed with MeOH. The product was dried in the sinter and *in vacuo* to give **3** as a brown powder (1.17 g, 87%); m.p. > 159 °C (decomp.) (Found: C, 39.2; H, 3.7; N, 2.2. C₄₂H₄₀N₂O₁₀U₂·5H₂O requires C, 39.29; H, 3.93; N, 2.18%); Karl Fischer titration: Found: 7.2. Calc. for 5H₂O: 7.02; ν_{\max} (KBr)/cm⁻¹ 1605 (N=CH); δ_{H} [250 MHz; (CD₃)₂SO] 9.53 (2 H, s, N=CH), 7.70 (4 H, s, ArH), 7.61 (2 H, s, ArH), 7.41 (2 H, d, *J* 7.1, ArH), 7.28 (4 H, d, *J* 8.3, ArH), 6.71 (2 H, d, *J* 8.4, ArH), 6.61 (2 H, t, *J* 7.8, ArH), 5.76 (4 H, s, CH₂) and 1.36 (18 H, s, CH₃); δ_{C} [62.5 MHz; (CD₃)₂SO] 164.4 (N=CH), 160.2, 159.5, 150.0, 141.3, 138.6, 137.5, 128.4, 127.6, 125.7, 125.1, 118.2, 115.2, 113.6 (ArC), 70.1 (CH₂), 33.9 (CCH₃) and 31.8 (CH₃); *m/z* (FAB) 1207.2 ([M – H]⁻).

μ -[8,11,14,22,25,28-Hexaoxa-3,5,17,19-tetraaza- κ^4 -N-1(1,3), 4(1,2),7(1,3),15(1,3),18(1,2),21(1,3)-hexabenzencyclooctacosaphane-3,5,16,19-tetraene-1²,7²,15²,21²-tetraolato- κ^4 -O]-tetraoxoduranium(vi) 1·2Bu₄NH₂PO₄(**6**).—A mixture of **1** (275 mg, 0.2 mmol) and NBu₄H₂PO₄ (136 mg, 0.4 mmol) in MeCN (25 cm³) was stirred at room temperature for 12 h under argon by which time an orange–red solution had formed with complete dissolution of the diuranyl host. The solvent was evaporated off and the residue was dried *in vacuo* to give **6** as an orange solid; m.p. 257–258 °C (Found: C, 45.5; H, 5.7; N, 3.9. C₈₀H₁₁₆N₆O₂₂P₂U₂·3H₂O requires C, 45.63; H, 5.84; N, 3.99%); Karl Fischer titration: Found: 2.6. Calc. for 3H₂O: 2.58; ν_{\max} (KBr)/cm⁻¹ 1603 (N=CH); δ_{H} [250 MHz; (CD₃)₂SO] 9.55 (4 H, s, N=CH), 7.8–7.7 (4 H, m, ArH), 7.6–7.5 (4 H, m, ArH), 7.42 (4 H, d, *J* 7.0, ArH), 7.29 (4 H, d, *J* 7.7, ArH), 6.60 (4 H, t, *J* 7.7, ArH), 4.46 (8 H, t, *J* 5.2, CH₂), 4.36 (8 H, t, *J* 5.0, CH₂), 3.3–3.1 (16 H, m, NCH₂), 1.7–1.5 (16 H, m, NCH₂CH₂), 1.4–1.2 (16 H, m, CH₂CH₃) and 0.95 (24 H, t, *J* 7.2, CH₃); δ_{C} [62.5 MHz; (CD₃)₂SO] 166.7 (N=CH), 161.8, 150.6, 147.4, 128.5, 124.7, 120.5, 120.2, 115.3 (ArC), 69.6, 69.3 (OCH₂), 57.5 (NCH₂), 23.0 (NCH₂CH₂), 19.2 (CH₂CH₃) and 13.5 (CH₃); *m/z* (FAB, +ve) 1712.4 ([1 + NBu₄H₂PO₄]⁺); *m/z* (FAB, –ve) 1468.9 ([1 + H₂PO₄]⁻).

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