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Uranyl Binding by a Novel Bis-Calix[4]arene Receptor

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Abstract

A new bis-calix[4]arene receptor **3** has been synthesized which complexes and extracts the uranyl cation in organic media.

Keywords: *calixarene; uranyl; complexation; extraction.*

Introduction

Because of its great potential as an energy source, the selective extraction of uranium dissolved in seawater in the form of the uranyl cation (UO_2^{2+}) has attracted the attention of many chemists [1,2]. Many tailor-made ligands (uranophiles) have been designed to perform this operation at the molecular level, some of which have utilised the calixarene framework [2]. In order to achieve the desired commercial viability, the ideal receptor must display a remarkable specificity and this may be achieved by taking into consideration as many of the coordinating particularities of the uranyl cation as possible. One of these key-features is the ability of the UO_2^{2+} ion to accommodate from four to six oxygen donor ligands in an equatorial pseudo-planar arrangement [3,4]. In order to enhance the recognition in favour of a linear di-oxo species such as uranyl the incorporation of receptor-linked H-bond donors in a suitable geometry to interact with the target's oxo group would also be beneficial [4]. This last approach involving second-sphere coordination has been named 'stereognostic coordination' [5].

Taking these coordinating features into account, we have synthesized a new bis-calix[4]arene-based uranophile designed to bind and ultimately extract uranyl into organic solvent media. Fashioned to provide a planar tetradentate coordinating platform for the uranium(VI) atom, **3** also contains four hydrogen-bond donor groups that can interact with uranyl oxygen atoms (Figure 1).

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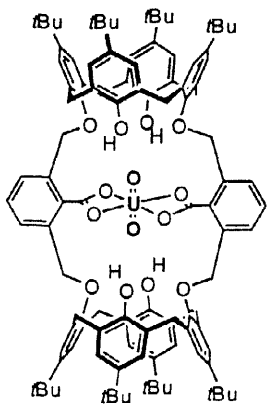
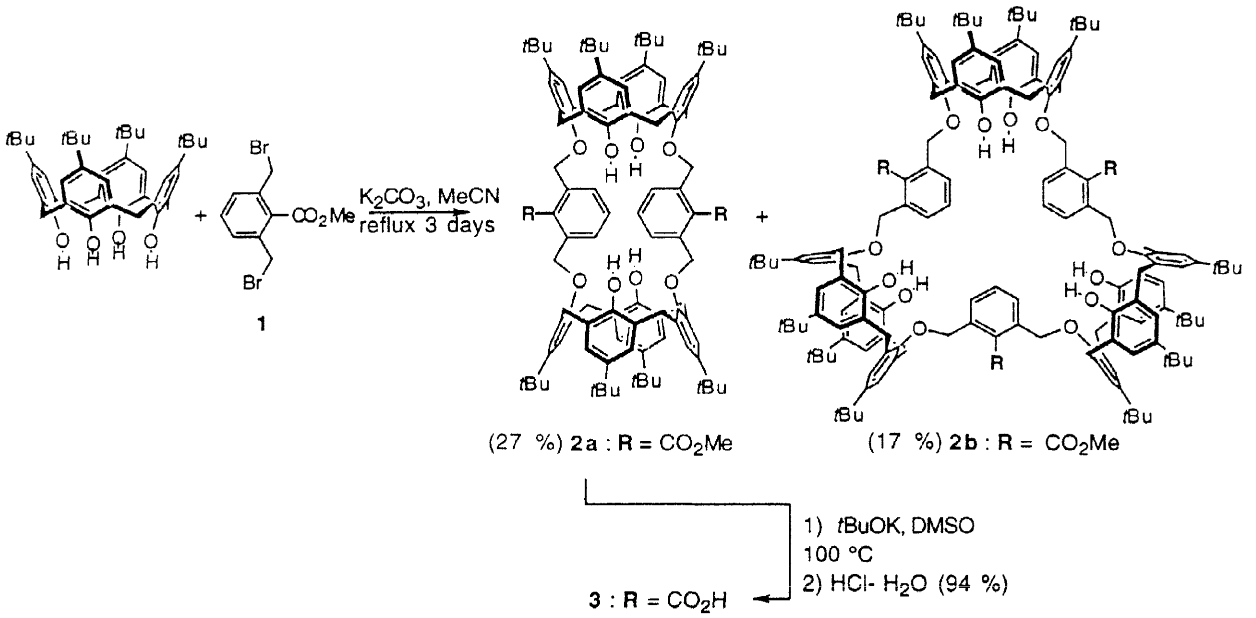


Fig. 1

Synthesis and Solid State Structure

The condensation of *p-tert*-butyl-calix-calix[4]arene with one equivalent of methyl 2,6-bis-(bromomethyl)benzoate [6] (**1**) in refluxing acetonitrile furnished both dimeric (**2a**) and trimeric (**2b**) species in 27% and 17% yields respectively (Scheme 1).[1]



Scheme 1

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[1] Characterization data for: **2a**, ^{1}H NMR (CDCl$_3$, 500 MHz), 8.55 (d, 4H, *J* 8Hz), 7.46 (s, 4H), 7.07 (s, 8H), 6.92 (t, 2H, *J* 8Hz), 6.89 (s, 8H), 5.18 (s, 8H), 4.37 (d, 8H, *J* 8Hz), 3.84 (s, 6H), 3.36 (d, 8H, *J* 8Hz), 1.26 (s, 36H), 0.97 (s, 36H). ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz), 168.7, 151.1, 159.7, 147.4, 141.5, 136.0, 133.0, 132.2, 129.1, 128.5, 127.6, 125.9, 125.2, 75.3, 52.2, 34.0, 33.9, 32.2, 31.8, 31.1. (FAB$^+$)MS : 1641 (M+Na).

2b, ^{1}H NMR (CDCl$_3$, 500 MHz), 8.41 (d, 6H, *J* 8Hz), 7.95 (t, 3H, *J* 8Hz), 7.06 (s, 6H), 7.04 (s, 12H), 6.79 (s, 12H), 5.17 (s, 12H), 4.25 (d, 12H, *J* 8Hz), 3.69 (s, 9H), 3.31 (d, 12H, *J* 8Hz), 1.28 (s, 54H), 0.95 (s, 54H). ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz), 168.4, 150.7, 150.3, 146.9, 141.3, 135.8, 132.4, 131.3, 129.0, 127.7, 127.5, 125.6, 125.0, 75.4, 52.2, 33.9, 33.8, 31.8, 31.7, 31.0. (FAB$^+$)MS : 2450 (M+Na).

The diacid derivative **3** was obtained by treatment of **2a** with potassium *tert*-butoxide in DMSO at 100 °C and subsequent addition of aqueous hydrochloric acid.[2]

The X-ray crystal structure of **3** exhibits a solid state 'closed structure' characterized by the two benzoic acid groups being directed away from the cavity defined by the two calix[4]arene moieties (Figure 2).[3]

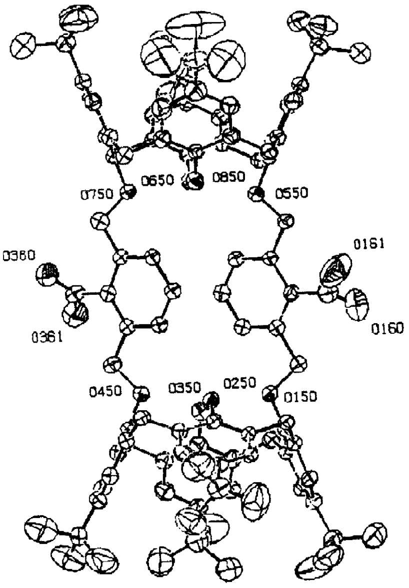

Fig. 2

Uranyl Binding Studies

The preliminary binding capabilities of **3** towards uranyl were initially explored by ^{1}H-NMR. In a 8:2 deuterated chloroform-methanol solvent mixture the addition of $UO_2(OAc)_2(H_2O)_2$ to **3** produced substantial downfield shifts of the carboxylate ortho-related benzylic and meta-related aromatic protons (+ 0.32 and + 0.25 ppm respectively) which is indicative of a conformational rearrangement consistent with the opening of the binding cavity. A simple 1:1 complexation model was shown to satisfactorily fit the binding curve (Figure 3) and an apparent binding constant of 5×10^3 M^{-1} was estimated. A mononuclear uranyl complex was also

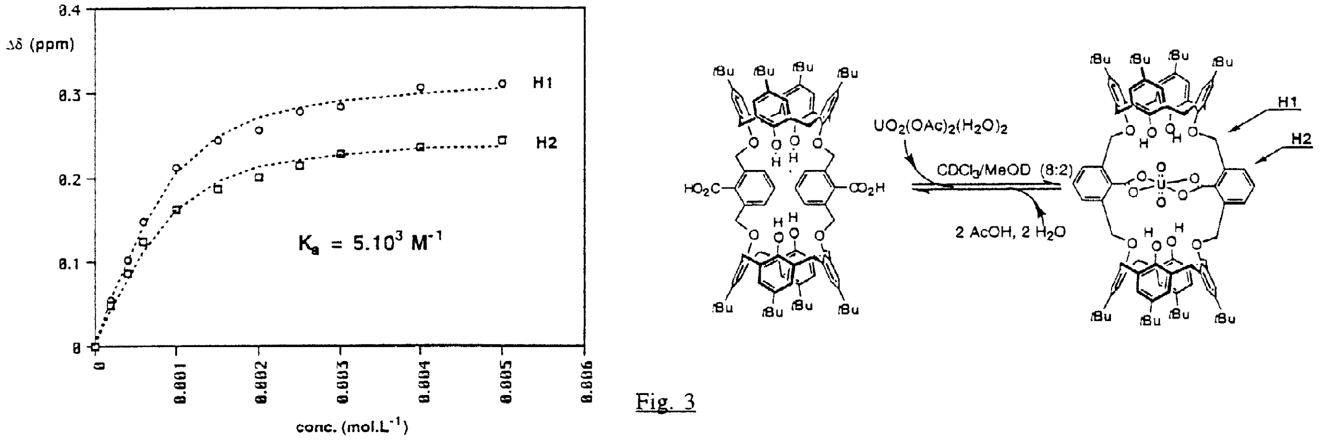

Fig. 3

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[2] **3** : ^{1}H NMR ($CDCl_3$, 500 MHz), 7.28 (t br, 2H), 7.22 (d br, 4H), 7.01 (s, 8H), 6.66 (s, 8H), 6.41 (s, 4H), 5.46 (s, 8H), 4.23 (d, 8H, *J* 8Hz), 3.15 (d, 8H, *J* 8Hz), 1.27 (s, 36H), 0.84 (s, 36H). (ES$^+$)MS : 1612.9 (M+Na). (ES$^-$)MS : 1688.9 (M-H).
3 · 3MeOH Found: C, 77.78; H, 7.99. Requires: C, 77.64; H, 8.13).

[3] Crystal data for: **3** : $C_{112}H_{138}O_{12}$, M = 1920.88, monoclinic, spacegroup $P2_1/n$, Z = 4, a = 23.40(2), b = 23.11(2), c = 23.37(2) Å, β = 110.71(1)°, U = 11821 Å^3, dcalc = 1.079 Mgm^{-3}, μ = 0.20 mm^{-1}, F(000) = 4096, 14438 independent reflections.

isolated as the sole product from the reaction of an excess of $UO_2(OAc)_2(H_2O)_2$ with **3** in 95:5 THF-methanol mixture.[4] Preliminary extraction experiments were carried out using an aqueous phase containing uranyl nitrate (0.4×10^{-3} mol. dm^{-3}) at pH = 9 and the extractant dichloromethane solvent phase containing **3** at a concentration of 9.6×10^{-3} mol.dm^{-3}. After one hour of rapid mixing of solutions, inductively coupled plasma atomic emission spectral (ICP-AES) analysis revealed 30% extraction of uranyl.

In summary, a new chelating bis-carboxylate calix[4]arene has been prepared which displays binding and extraction capabilities towards the uranyl cation.

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References

[1] Thuery P, Keller N, Lange M, Vignier J-D, Nierlich M. New J. Chem. 1995;19:619 and references cited therein.

[2] (a) Thuery P, Nierlich M. J. Incl. Phenom. 1997;27:13; (b) Thuery P, Lance M, Nierlich M. Supramolecular Chemistry. 1996;7:183; Kubo Y, Maeda S, Nakamura M, Tokita, S. J. Chem. Soc., Chem. Commun. 1994:1725; Nagasaki T, Shinkai S. J. Chem. Soc., Perkin Trans. 1991:1063; Shinkai S, Koreishi H, Ueda K, Arimura T, Manabe O. J. Am. Chem. Soc. 1987;109:6371.

[3] Van der Sluys WG, Sattleberger AP. Chem. Rev. 1990;90:1027.

[4] Guilbaud P, Wipff G. J. Phys. Chem. 1993;97:5685; Muzet N, Wipff G, Casnati A, Domiano L, Ungaro R, Ugozzoli JF. J. Chem. Soc., Perkin Trans., 2. 1996:1065.

[5] Walton PH, Raymond KN. Inorg. Chim. Acta. 1995;240:593; Franczyk TS, Czerwinski KR, Raymond KN. J. Am. Chem. Soc. 1992;114:8138; Kobuke Y, Tabushi I, Oh K, Aoki T. J. Org. Chem. 1988;53:5933.

[6] Moore SS, Tarnowski TL, Newcomb M, Cram DJ. J. Am. Chem. Soc. 1977;99:6398.

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[4] **3**UO_2 : (FAB+)MS : 1880 (M+Na). (**3** $\cdot$ UO_2 $\cdot$ $6H_2O$ Found: C, 64.85; H, 6.62; U, 12.18. Requires: C, 64.75; H, 6.87; U, 12.11).