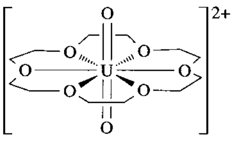
[19] a) Crystal data for **3**: crystal dimensions $0.12 \times 0.20 \times 0.37$ mm, orthorhombic space group $Pbca$ (No. 61), $a = 17.277(5)$, $b = 19.393(7)$, $c = 21.190(8)$ Å, $V = 7100(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.58$ gcm^{-3}, $\mu = 1.90$ mm^{-1}, $F(000) = 3408$; 10912 reflections with $3.7 < 2\theta < 40.0°$. Structure solution and refinement for 3316 independent reflections with $I > 2\sigma(I)$ and 433 parameters, max./min. empirical absorption correction 0.999/0.878; $R = 0.077$; $R_w = 0.168$; max./min. residual electron density $0.64/-1.13$ eÅ^{-3}. b) Nonius CAD4 diffractometer, $Mo_{K\alpha}$ radiation, graphite monochromator. Structure solution and refinement carried out on DEC 3000 and PC computers by using the programs Open MolEN and SHELXTL Version 5.0 and the Patterson–Fourier method. Hydrogen atoms were included in calculated positions (HFIX). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Centre as supplementary publication no. CCDC-100541. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (UK) (fax: int. code + (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

[20] Crystal data for **4**: crystal dimensions $0.07 \times 0.10 \times 0.23$ mm, tetragonal space group $P4_32_12$(No. 96), $a = 16.562(6)$, $c = 26.637(11)$ Å, $V = 7307(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.66$ gcm^{-3}, $\mu = 1.86$ mm^{-1}, $F(000) = 3664$; 9927 reflections with $2.9 < 2\theta < 35.0°$. The crystal was mounted in Paratone oil and all measurements were performed at -105°C. Structure solution and isotropic refinement, except Co atoms, for 2469 independent reflections with $I > 2\sigma(I)$ and 227 parameters, no absorption correction, DAMP 1000, $R = 0.104$; $R_w = 0.175$; max./min. residual electron density $0.75/-0.59$ eÅ^{-3}.[19b]

Synthesis and Structure of the First Transuranium Crown Ether Inclusion Complex: $[NpO_2([18]Crown\text{-}6)]ClO_4$**

David L. Clark,* D. Webster Keogh, Phillip D. Palmer, Brian L. Scott, and C. Drew Tait

Crown ether ligands[1, 2] have been studied as potential actinide extractants for many years, and they have been shown to influence the partitioning of actinides in two-phase aqueous systems.[3–5] Although many examples of crown ether ligands that extract actinides in hydrocarbon/water systems are known,[6, 7] relatively few actinide crown ether complexes in which the actinide ion is coordinated by one or more donor atoms of the crown ether have been reported.[8] There are only two inclusion compounds of *trans*-dioxoactinide cations AnO_2^{n+} in which the actinide ion is completely encapsulated by a crown ether ligand and the counterions (perchlorate[9, 10] or triflate[11]) are uncoordinated in the crystal lattice: $[UO_2([18]crown\text{-}6)]^{2+}$ (**I**) and $[UO_2(dicyclohexano[18]\text{-}crown\text{-}6)]^{2+}$. It has been claimed that synthesis of inclusion complexes from uranyl ions UO_2^{2+} and crown ether ligands requires the use of weakly coordinating anions, nonaqueous conditions, and proper choice of cavity size.[8] Indeed, the majority of actinide crown ether complexes exhibit second-sphere hydrogen bonding between the oxygen atoms of the crown ether and water molecules coordinated to the actinide center.[12–19] Well-known examples include $[UO_2(H_2O)_5([18]crown\text{-}6)_2(H_2O)(CH_3CN)_2][ClO_4]_2$ (central unit: **II**)[15] and $[UO_2(H_2O)_5([18]crown\text{-}6)][CF_3SO_3]_2$.[17]



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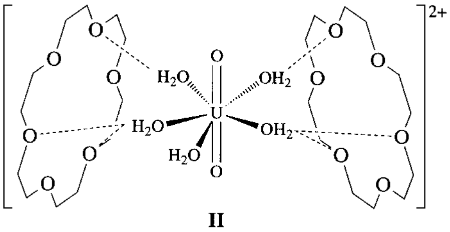

II

Crown ether inclusion complexes of a transuranic ion in any oxidation state are unknown.

On attempting to employ this well-known ability of crown ether ligands to form second-sphere hydrogen-bonded complexes of *trans*-dioxometal ions (as in **II**), we were surprised to observe the complete encapsulation of the NpO_2^+ ion by the [18]crown-6 ligand. Addition of one equivalent of [18]crown-6 to a stirred solution of NpO_2^{2+} in 1M HX ($X = ClO_4^-$, $CF_3SO_3^-$) resulted in reduction of Np^{VI} to Np^V and formation of large turquoise crystals of $[NpO_2([18]crown\text{-}6)][X]$ (**1**[X]) over 12–24 h. The presence of an absorption band at 980 nm ($\varepsilon = 395$ M^{-1}cm^{-1}), characteristic of the NpO_2^+ ion,[20] in the NIR spectra of the crystalline solids dissolved in 1M $HClO_4$ confirms that reduction of Np^{VI} to Np^V has occurred. Even in the presence of O_3, the Np^{VI} was reduced to **1**[X] on addition of [18]crown-6. Finally, solutions of Np^V compounds in 1M HX, which are present as hydrated NpO_2^+ ions, react smoothly with [18]crown-6 to give **1**[X] in almost quantitative yield.

A single-crystal X-ray diffraction study of **1**[ClO_4] revealed an NpO_2^+ ion completely encapsulated by a disordered [18]crown-6 ligand.[21] The Np center of the $[NpO_2([18]crown\text{-}6)]^+$ ion is coordinated by two *trans* oxo ligands and six approximately coplanar crown ether O atoms to give an approximate hexagonal bipyramidal coordination environment (Figure 1). In the crown ether ligand, all C-O-C-C units have an *anti* (a), and the O-C-C-O units a *gauche* conformation (g), and this results in a distorted $g^-g^+g^+g^-g^+g^+$ conformation,[22] similar to that reported for **I**.[11] The Np=O bond length of 1.800(5) Å is unusually short for an NpO_2^+ ion; 1.85 Å is usual.[23, 24] The average equatorial Np–O distance of 2.594(10) Å is unusually long for a neutral oxygen-donor ligand when compared with the U–OH_2 distance of 2.43 Å in $[UO_2(OH_2)_5]^{2+}$ complexes.[15, 17] Coordination of σ-donor ligands in the equatorial plane of an *trans*-dioxo actinide ion generally results in a slight lengthening of the An=O bond, accompanied by decreased intensity of the Raman-active ν_1 O=An=O stretching band.[25] However, in **1**[ClO_4] the Np=O bond is shorter, and presumably stronger, than in the uncomplexed cation. Similar structural changes are observed in the uranyl system, for which encapsulation by [18]crown-6 results in a significant shortening of the U=O bond from 1.758(2) to 1.64(4) Å.[15, 17]

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[**] This work was supported by the Office of Basic Energy Sciences (U.S. DOE, contract no. W-7405-ENG-36 with the University of California) and by the Laboratory Directed Research and Development Program.

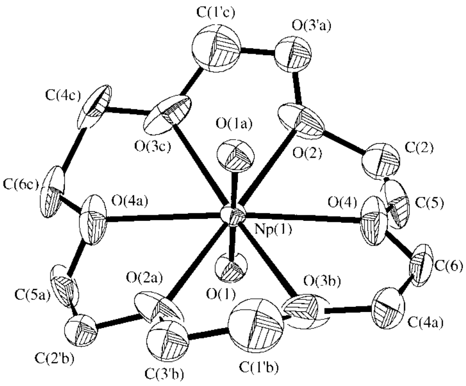

Figure 1. ORTEP plot of the molecular structure of **1** in crystals of **1**[ClO_4] (ellipsoids drawn at the 50 % probability level). Selected bond lengths [Å] and angles [°]: Np(1)-O(1) 1.800(5), Np(1)-O(2) 2.576(9), Np(1)-O(3) 2.604(10), Np(1)-O(4) 2.603(8); O(1)-Np(1)-O(2) 91.7(2), O(1)-Np(1)-O(4) 85.6(2), O(2)-Np(1)-O(4) 59.5(5), O(1)-Np(1)-O(3) 85.6(3).

For *trans*-dioxoactinide ions, the Raman-active ν_1 vibrational mode is a much better indicator of bond strength than bond length. For the $[NpO_2(H_2O)_5]^+$ ion[24] (Np=O 1.85 Å), the ν_1 vibrational mode occurs at 767 cm^{-1}.[26] Raman spectra of **1**[ClO_4] showed an intense band at 778 cm^{-1}, which is consistent with a stronger Np=O bond than in the aquo ion. To confirm this band assignment, ^{18}O was electrochemically incorporated into the Np=O unit [Eqs. (1)-(3); the asterisk

$$[NpO_2(OH_2)_n]^+ \xrightarrow[H_2^{*}O/HClO_4]{-0.2\,V\,(SCE)} [Np(^*OH_2)_n]^{3+}/[Np(^*OH_2)_n]^{4+} \quad (1)$$

$$[Np(^*OH_2)_n]^{3+}/[Np(^*OH_2)_n]^{4+} \xrightarrow[H_2^{*}O/HClO_4]{+1.22\,V\,(SCE)} [Np^*O_2(^*OH_2)_n]^{2+} \quad (2)$$

$$[Np^*O_2(^*OH_2)_n]^{2+} \xrightarrow[HClO_4]{[18]crown\text{-}6} [Np^*O_2([18]crown\text{-}6)][ClO_4] \quad (3)$$

indicates enrichment with ^{18}O]. Water enriched in ^{18}O (98 % ^{18}O) was added to 0.56 M NpO_2^+ (aq) in 1 M $HClO_4$ and reduced electrochemically at −0.2 V to a mixture of hydrated Np^{3+}/Np^{4+}[27] with removal of the oxo ligands. The potential was then reversed, and the mixture was oxidized to hydrated, ^{18}O-enriched $Np^*O_2^{2+}$ ions. The purity of the oxidized compounds was confirmed with NIR spectroscopy by monitoring the absorption band of hydrated NpO_2^{2+} at 1223 nm (ε = 45 $M^{-1}cm^{-1}$).[20] [18]Crown-6 was subsequently added, and turquoise crystals of *__1__[ClO_4] formed after cooling the mixture to 5 °C overnight. The Raman spectra of *__1__[ClO_4] crystals show ν_1 bands for all three isotopomers ^{18}O=Np=^{18}O, ^{18}O=Np=^{16}O, and ^{16}O=Np=^{16}O at 734, 751, and 780 cm^{-1}, respectively, confirming our original assignment.

The complete encapsulation of the NpO_2^+ ion by a crown ether ligand under any conditions is unprecedented, and **1**[ClO_4] represents the first structurally and spectroscopically characterized transuranium crown ether complex. The relative ease of encapsulation in aqueous solution contrasts with the related UO_2^{2+} ion, for which anhydrous conditions are necessary to ensure that the crown ether oxygen atoms bind directly to the metal center.[8] This difference attests to the ability of crown ether ligands to separate ions of almost identical chemical behavior, and the apparent preference for Np^V over Np^{VI} may be related to the differing ionic radii of these ions.[1] Although the mechanism is unknown, dicyclohexano-[18]crown-6 has been shown to separate Pu^{IV} from U^{VI} and fission products more effectively than tributyl phosphate,[3] the extractant used in the well-known Purex process.[20] The potential ability of crown ether ligands to extract actinide ions selectively from radioactive process streams or solutions of nuclear waste is particularly interesting due to its economic and environmental implications. The actinophilic nature of crown ether ligands towards other transuranic ions is under further investigation.

Received: May 26, 1997 [Z10472IE]
German version: *Angew. Chem.* **1998**, *110*, 173-175

Keywords: actinides · crown compounds · host-guest chemistry · neptunium

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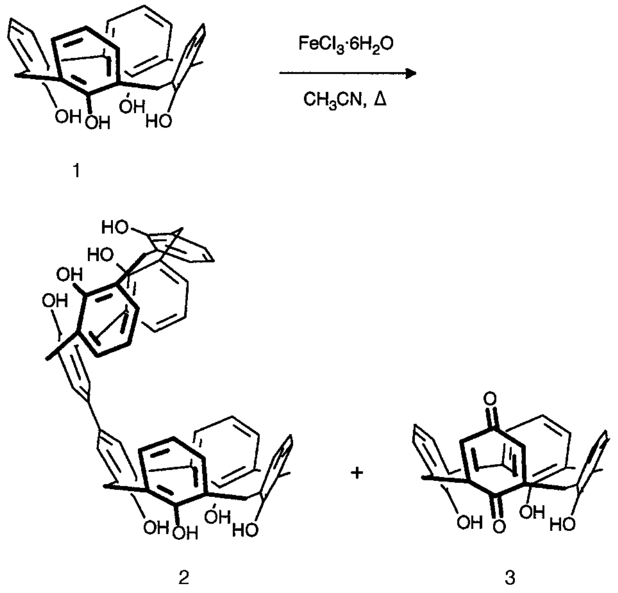
5,5′-Bicalix[4]arene: The Bridgeless Prototype of Double Calix[4]arenes of the "Head-to-Head" Type[**]

Placido Neri,* Alessandra Bottino, Francesca Cunsolo, Mario Piattelli, and Enrico Gavuzzo

In the past decade several double (or multiple) calixarenes[1] have been prepared as examples of higher order molecular architectures with new high-level host properties, such as allostery and cooperativity.[2] In these compounds, two (or more) calixarene units are linked at their upper or lower rims[3, 4] through one or more spacer elements. Various structural motifs have been used as spacers, including alkyl, alkenyl, and alkynyl chains, diesters, diamides, metallocenes, ethers and polyethers, sulfides, and diimines.[1, 2, 5] However, to the best of our knowledge, examples of the prototypal compounds with directly coupled (bridgeless) calixarene units have not been reported so far.[6] Here we describe the synthesis, X-ray crystal structure, and derivatization of the first double calixarene of the "head-to-head" type[7] with direct *para-para* linkage, 5,5′-bicalix[4]arene **2**.[8]

Linkage of the two calix[4]arene units was accomplished by oxidative coupling of the *p*-H-calix[4]arene **1**[9a] under conditions similar to those of Pummerer's classic binaphthol synthesis[10] (Scheme 1). A solution of **1** in hot CH_3CN was treated with solid $FeCl_3\cdot 6H_2O$, and the suspension was heated at reflux for 4 h. Workup of the reaction mixture and column chromatography of the crude product afforded bicalix[4]arene **2** (10%) and calix[4]monoquinone **3** (6%). The dimeric nature of **2** was indicated by a quasi-molecular ion at $m/z = 847$ in the positive-ion fast-atom-bombardment (FAB) mass spectrum. Correspondingly, the ^{13}C NMR spectrum contains two $ArCH_2Ar$ signals, six aromatic CH resonances, three C–OH singlets, and a diagnostic singlet at $\delta = 135.3$ attributable to quaternary carbon atoms involved in bonding of the two halves in **2**.



Scheme 1. Synthesis of 5,5′-bicalix[4]arene **2** by oxidative coupling of *p*-H-calix[4]arene **1**.

Both calixarene moieties are in the *cone* conformation because of the stabilizing cyclic hydrogen bond, as revealed by two broad AX systems for $ArCH_2Ar$ protons in the ^1H NMR spectrum.[1] These systems sharpen at low temperature, and a Gibbs free energy of activation $\Delta G^{\neq} = 14\ \mathrm{kcal\,mol^{-1}}$ was estimated from the coalescence temperature for the *cone*–*cone* conformational interconversion, a value very similar to that reported for the parent monomer **1**.[9b] With respect to the biphenyl moiety, one can presume relatively free rotation around the Ar–Ar bond, with a slight deviation from coplanarity for the two aryl rings. This leads to a *syn* or *anti* orientation of the calix[4]arene units (Figure 1). Energy evaluations (MM2 and MM3) of the two geometries gave very similar values; the *anti* orientation is slightly lower in energy. Therefore, the *syn* and *anti* forms of bicalix[4]arene **2** are expected to be in equilibrium in solution (Figure 1).

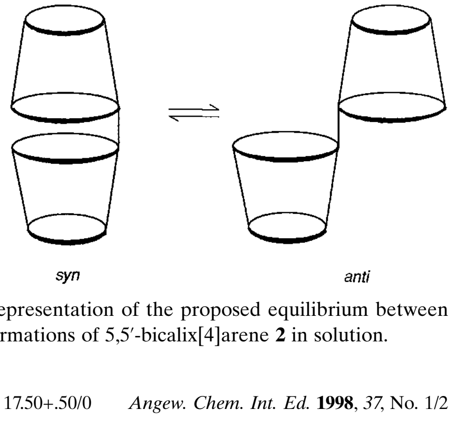


Figure 1. Schematic representation of the proposed equilibrium between the *syn* and *anti* conformations of 5,5′-bicalix[4]arene **2** in solution.

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[**] We wish to thank Mr. R. Rapisardi (ICTMP-CNR, Catania) for FAB-MS measurements and Dr. G. Chessari (University of Sheffield) for evaluation of NMR titration data. The institutes cited are associated with the Istituto Nazionale di Coordinamento per la Chimica dei Sistemi Biologici.