Nucleophilic Attack at the *meso* Position of a Uranyl Sapphyrin Complex

Anthony K. Burrell, Michael J. Cyr, Vincent Lynch and Jonathan L. Sessler*

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712, USA

Contrary to previous reports sapphyrin does react with uranyl cation to give a stable complex, which is no longer aromatic, having undergone attack by methoxide to give a new neutral complex; the synthesis, characterisation and X-ray structure of the new compound are described.
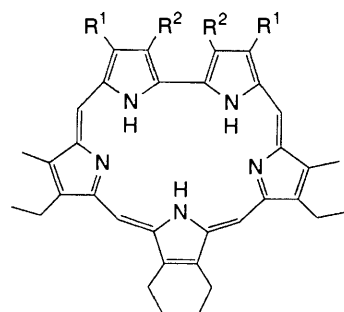
The sapphyrin macrocycle, of which 1 is an example, was first described over 20 years ago.[1] Despite being known for this considerable time and in spite of its obvious potential as a ligand, few well characterized examples of metal complexes of sapphyrin have been reported.[2] Indeed, the full report from the Woodward group detailing the complete, stepwise synthesis of sapphyrin included an account of its failure to form any coordination complexes with the uranyl cation.[1] Recently, however, we have found that a related macrocycle, pentaphyrin 2, gives an extremely stable uranyl complex.[3] The ease with which the uranyl complex of 2 was formed, along with its high stability, led us to reexamine the reaction of the uranyl cation with sapphyrin.

To our surprise and contrary to the previous report,[1] sapphyrin undergoes a rapid reaction with the uranyl cation, as the chloride salt, in a mixture of methanol, pyridine and triethylamine. The reaction proceeds from the initial green colour of sapphyrin to give, finally, a deep-red solution. This complex behaves as a neutral compound, and has spectral properties unlike those of any previously described sapphyrin or sapphyrin complex.[2,4] The presence of the uranyl moiety was confirmed by the identification of the ν(OUO) band in the

IR spectrum at 919 cm^{-1}.† The visible spectrum of the red uranyl complex, however, did not display the usual Soret-like absorption, characteristic of the sapphyrins and their complexes. Instead two broad bands at 479 and 508 nm were observed. In addition the proton and ^{13}C NMR spectra of the uranyl compound were unusually complex. Finally and most importantly the mass spectrum indicated that the uranyl complex was 31 m/z units heavier than would be expected for a simple UO$_2$ complex of sapphyrin.
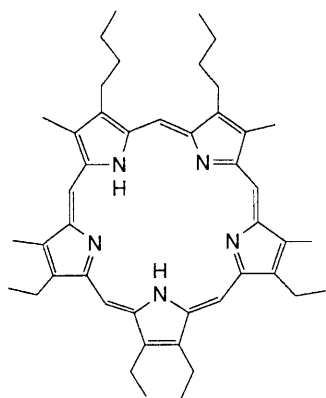
At this point, a close examination of the ^{13}C NMR spectrum enabled the identification of carbon signals at a chemical shift associated with methyl ethers as well as a 'doubling' of the peaks as would be expected for the presence of two unsymmetrical isomers in solution. All the available evidence thus pointed to a complex that had somehow incorporated methanol, and which, by virtue of doing so, became diastereoisomeric in nature.

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† Satisfactory spectroscopic and mass spectrometric data were obtained for all new compounds.

1; R^1 = Et, R^2 = Me
5; R^1 = Pr^n, R^2 = H

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Fig. 1 (a) View of **3** showing the nearly pentagonal bipyramidal coordination around uranium. The thermal ellipsoids are scaled to the 30% probability level while the hydrogen atoms are scaled to an arbitrary size. The hydrogen atoms of the alkyl portion of the macrocycle have been omitted for clarity. Only the major diastereo-isomer [71(1)%] is shown. Some relevant bond lengths (Å) are: U(1)–O(1) 1.727(10); U(1)–O(2) 1.747(10); U(1)–N(1) 2.477(11); U(1)–N(2) 2.515(12); U(1)–N(3) 2.466(10); U(1)–N(4) 2.492(10); U(1)–N(5) 2.548(11). The N–U–N angle for adjacent nitrogens is 72.3(2)°av which is equivalent to the ideal value of 72° for an exact pentagonal arrangement around uranium. (b) View of **3** showing the distorted conformation assumed by the macrocycle to accommodate the coordination to the uranyl group. The uranium lies in the plane of the nitrogen donors. The maximum deviation from the plane is −0.232(11)Å for N(3).

The precise formulation of the uranyl complex was determined by a single crystal X-ray analysis.‡ The structure is shown as in Fig. 1 and pictorially in Scheme 1 as structure **3**. Formally the sapphyrin ring has undergone attack by methoxide anion at the meso-carbon C(1), resulting in a disruption of the inherent two-fold symmetry of the sapphyrin macrocycle. The result is a severely distorted solid-state structure for this macrocycle. There are two diastereoisomers present in the lattice in a ca. 70 : 30 ratio.‡

This structure provides an explanation for the unusual spectral properties mentioned above. The addition of methoxide results in the loss of overall aromaticity and results in the lack of a Soret-like transition in the optical spectrum. It also

accounts for the complex nature of the ¹H NMR spectrum. Complex **3** is produced as a mixture of four different stereoisomers: an enantiomeric set of diastereoisomers. Here, however it is important to appreciate that these two sets of diastereoisomers can be interconverted by simple conformational flips involving overall inversion of the 'bowl-like' macrocycle (Fig. 2). Interestingly, this inversion is slow on the NMR time-scale. Nonetheless, it does take place; dissolving the crystalline sample, from which the single crystal structure was determined, in CDCl₃ gives rise to the 1 : 1 'doubled' spectra consistent with an equimolar mixture of diastereo-isomers **3**.

To determine the criterion for the formation of **3** a series of reactions were carried out varying the conditions and substrates. Firstly, if sapphyrin **1** is heated in a mixture of methanol, pyridine and triethylamine for 72 h no reaction

‡ Crystal data for **3**: $C_{41}H_{49}N_5O_3U$, M = 897.90, monoclinic, space group C2/c (no. 15), a = 23.066(8), b = 20.344(5), c = 16.715(4) Å, β = 106.07(2)°, V = 7537(4)Å³, Z = 8, D_c = 1.58 g cm⁻³ (198 K), $F(000)$ = 3568, μ(Mo-Kα) = 41.26 cm⁻¹, λ = 0.7107 Å, Nicolet R3 diffractometer, 15 433 reflections collected (2θ range 4–50°) at 198 K, using a Nicolet LT-2 low-temperature device, 7643 unique reflections, R for averaging symmetry-equivalent data = 0.038. The structure was solved by the heavy atom method and refined by full-matrix least-squares using SHELXTL-Plus.⁶ The methanol addition at C(1) results in the formation of two possible diastereoisomers. Both are present in the lattice but in unequal amounts. The major diastereo-isomer, with site occupancy factor = 71(1)%, assumes the axial conformation. All non-H atoms were refined anisotropically except the methoxy group with the lower occupancy. All H atoms were idealized with U set to 1.2 × U_{eq} of the relevant atom. Owing to the partial occupancy, no H atoms were calculated for methoxy C carbon atoms or for the methine carbon atom of the macrocycle. 459 parameters were refined to a final R = 0.0570, R_w = 0.0588 and a goodness-of-fit = 1.483 using 4124 reflections having $F > 6\sigma(F)$. Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.
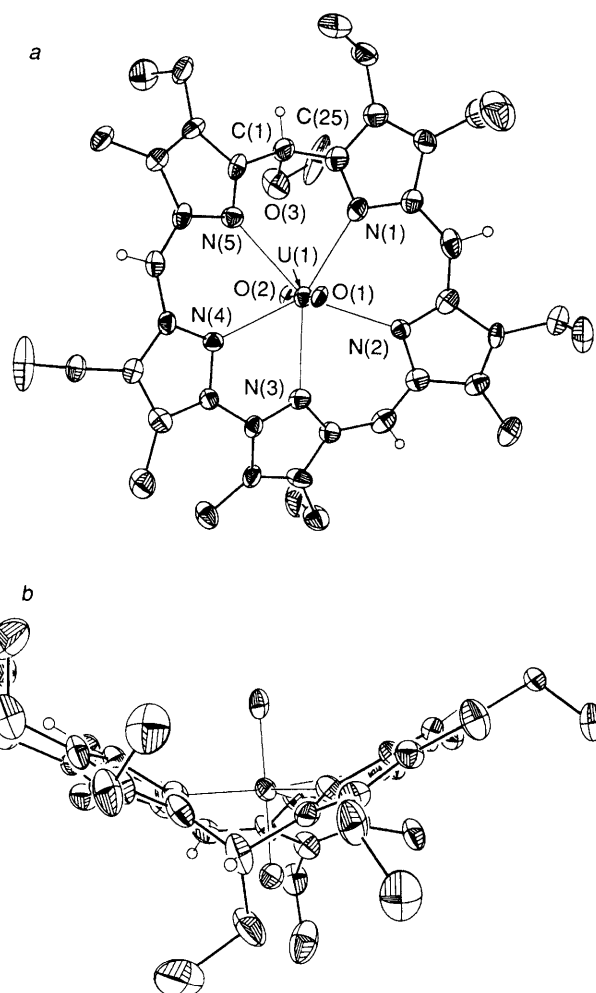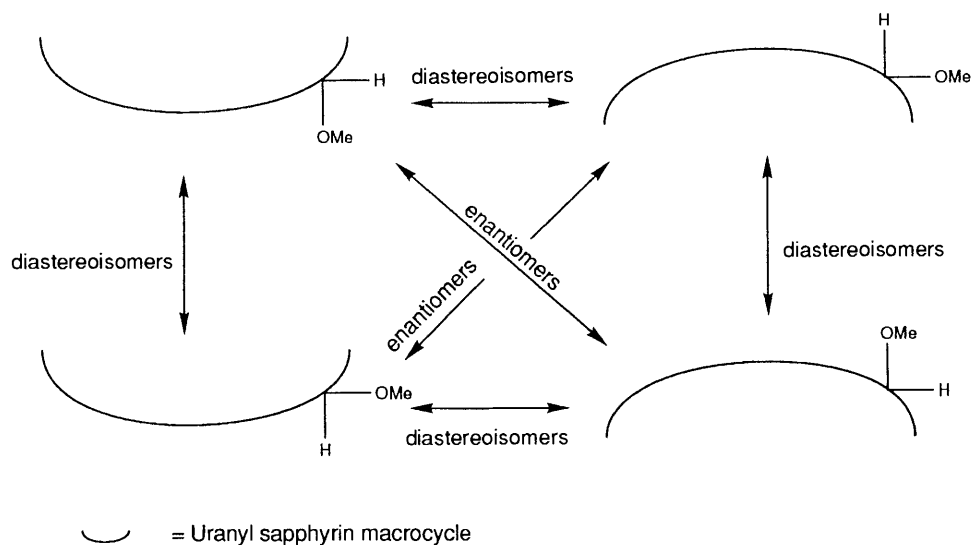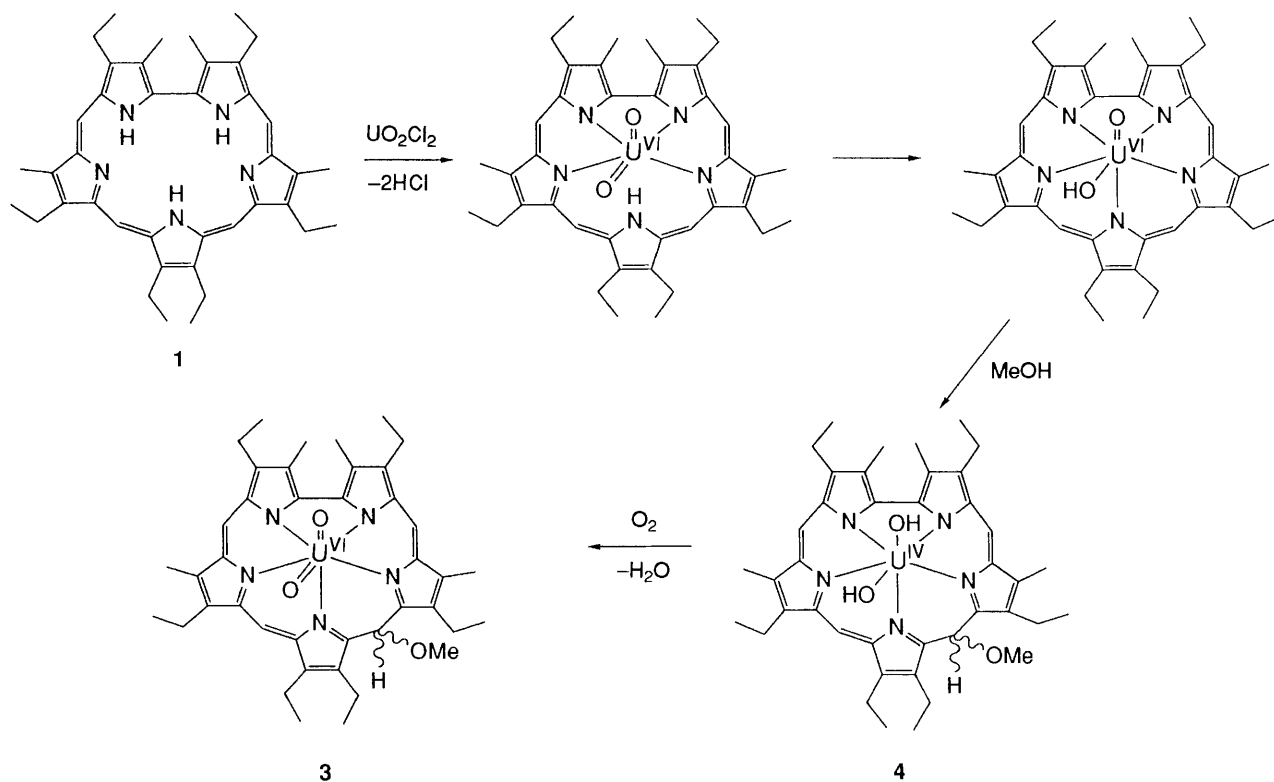
= Uranyl sapphyrin macrocycle

Fig. 2 Pictorial representation of the two enantiometric sets of diastereoisomers formed upon dissolution of **3**

Scheme 1

occurs. However, upon the addition of uranyl chloride, the formation of **3** is complete within 2 h. It would, therefore, appear that the coordination of the uranyl cation by sapphyrin, in some manner, is an important step. Secondly, if the reaction of sapphyrin with uranyl chloride is carried out in a solvent mixture that does not contain methanol, the result is complete decomposition of the sapphyrin. It would also appear that atack by methanol (or methoxide anion) plays a vital role in stabilizing a macrocyclic uranyl complex. Finally, when all oxygen is excluded the reaction proceeds to give a different, but nonaromatic, complex assigned the structure **4** on the basis of NMR evidence. This complex, which has resulted from the formal reduction of U^{VI}, may be handled in the absence of oxygen. Under these conditions, all the solvent

may be removed, and the residue redissolved in methylene chloride (with no methanol present) and filtered. If the resulting filtrate is then exposed to oxygen conversion to **3** is rapid. Thus, complex **4** must already contain both the coordinated uranium and the methoxide group. A possible mechanism that is consistent with these facts is shown in Scheme 1.

The reaction of sapphyrin with the uranyl cation in a mixture of methanol, pyridine and triethylamine thus gives a new macrocyclic uranyl complex in which methoxide has attacked the sapphyrin ring. This reaction is significant in that only a small number of reactions involving nucleophilic attack at the exterior of porphyrins have been described.[7] In all cases these have resulted from prior activation of the macrocycle by

the presence of electron-withdrawing substituents on the porphyrin periphery. This is the first example of such a reaction being promoted by metal complexation alone, and the first example of modification of the *meso*-position of an expanded porphyrin.[8]

This reaction is sensitive to both the conditions and the nature of the sapphyrin used. Other sapphyrins such as **5** give much smaller yields of the methoxide–sapphyrin–uranyl complex. The reaction of sapphyrin with uranyl chloride in the presence of other potential nucleophiles is currently being investigated,§ and may provide a route to *meso*-functionalised expanded porphyrins.

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§ Preliminary reactions with nucleophiles such as cyanide anion give the expected cyanide-functionalized products but in very poor yields.

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