Synthesis and characterization of an oxasapphyrin-uranyl complex

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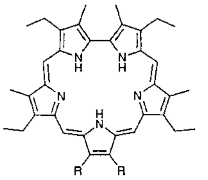
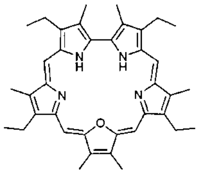
Reaction of monooxasapphyrin with uranyl diacetate in the presence of triethylamine leads to the formation of a stable, in-plane aromatic uranyl complex.

Sapphyrin (*e.g.* **1**) is an aromatic 22 π-electron expanded porphyrin that has been known for more than 30 years.[1,2] Its pioneering role in expanded porphyrin research[2a–c] and the more recent finding that it[2d] and other related materials[3] bind anions in their protonated forms continues to inspire interest in these pentapyrrolic systems. In spite of this increased attention, the metal coordination chemistry of sapphyrin remains woefully underdeveloped.[2] At first blush this seems surprising since one of the most intuitively appealing aspects of sapphyrin[2a] is that it should act to stabilize complexes with larger cations than those normally coordinated by porphyrins (*e.g.* Gd^{3+}, UO_2^{2+}, *etc.*).



1a R = Me
1b R = Et



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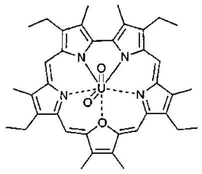

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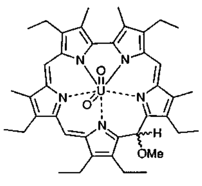
However, efforts to obtain such complexes have so far failed.[2a,4]† Recently, we prepared an organic-soluble, furan-containing analogue of sapphyrin, system **2**,[8] and now wish to report that this monooxa species supports the formation of a stable, in-plane uranyl complex (**3**).

The rationale for using **2** as a possible uranyl chelating ligand derived from an appreciation of what happens when sapphyrin **1b** is treated with UO_2^{2+}. Under most reaction conditions the macrocycle is either returned unchanged or suffers decomposition. However, in the presence of methanol a uranyl complex (**4**) of what is a formally a reduced form of sapphyrin may be isolated.[4] This finding was rationalized in terms of intermediates **I**, **II** and **III** (Scheme 1) playing a critical role in mediating the key nucleophilic attack step leading to the formation of the reduced, methoxy-functionalized product **4**.



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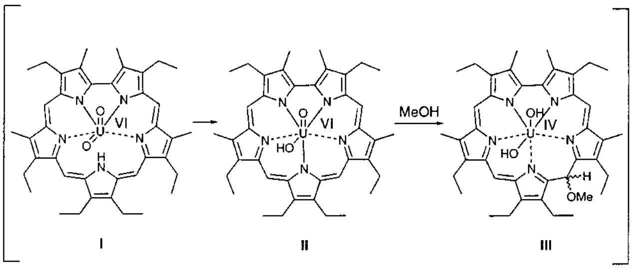
This led us to consider that a stable, aromatic uranyl complex might be obtainable were the central pyrrole of the tripyrrane 'replaced' by a furan. Such a replacement would also create a ligand that, once deprotonated, would be dianionic and hence well suited to coordinate the uranyl cation on a charge matching basis.

As it transpired, treatment of the bis-hydrochloride salt of **2**, but not **1**·2HCl,[4] with uranyl diacetate dihydrate in acetonitrile containing triethylamine led, after column chromatographic purification, to the formation of a green metallic solid. This material displays a UV–VIS spectrum typical of a sapphyrin species with one strong Soret band at 483 nm and three weaker Q-type absorption bands at 624, 647 and 708 nm (Fig. 1). The significant bathochromic shift (29 nm) of the Soret band compared to the starting oxasapphyrin bis-HCl salt (Soret band at 454 nm, Q-type bands at 625, 633, 669 and 689 nm), together with the bathochromic shift and different aspect of the Q-type bands (Fig. 1), provided a preliminary 'hint' that (i) the metal insertion process was successful and (ii) the monooxasapphyrin skeleton was still intact.



Scheme 1 Proposed intermediates in the formation of **4**

Proton NMR spectroscopic studies revealed the presence of two sets of peaks at the low field frequencies (*i.e.* 10.37 and 10.78 ppm, respectively) typical of aromatic sapphyrin *meso* protons.[9] On the other hand, no signals ascribable to internal NH protons were observed. Since sapphyrins such as **1** and **2** are known to be quite basic (*i.e.* easily protonated),[2,10] this finding is interpreted as being consistent with the formation of a metal complex wherein the key metal-to-ligand contacts involve, at a minimum, all four of the nitrogens present in the macrocyclic core (*i.e.* structure **3**). The presence of a uranyl moiety was also implied by the identification of a ν(O=U=O) band in the IR spectrum at 936 cm^{-1}. Final proof for the formation of the proposed 1 : 1 uranyl complex then came from an X-ray crystallographic analysis.

Crystals of **3** were grown by allowing a dichloromethane solution of the complex to diffuse slowly into hexanes.‡ As illustrated in Fig. 2(*a*) the uranyl cation is located almost in the center of the sapphyrin. The uranyl-to-nitrogen distances of 2.449(4) Å (U–N1), 2.470(3) Å (U–N5), 2.582(4) Å (U–N2), and 2.587(3) Å (U–N4) are all very similar to one another. By contrast, the oxygen of the sole furan subunit, at a distance of 2.791(3) Å (U–O3), is significantly further away. The ur-

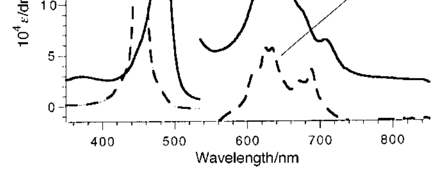


Fig. 1 UV–VIS spectrum of the monooxasapphyrin-uranyl complex **3** (—) as recorded in CH_2Cl_2. Also shown for comparison is the spectrum (---) of the starting monooxasapphyrin macrocycle (**2**·2HCl).

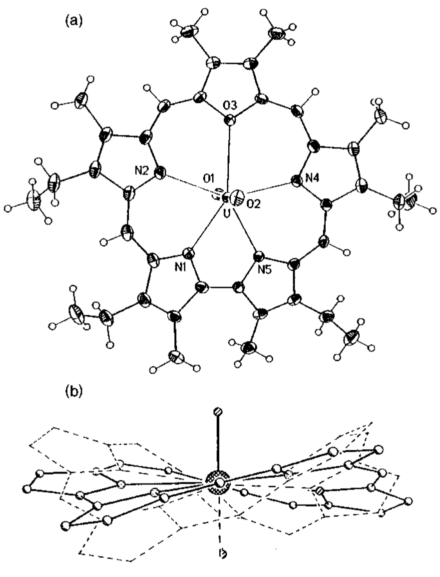
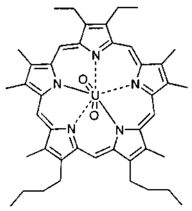


Fig. 2 (*a*) Front view of $C_{38}H_{42}N_4O_3U$ (**3**) showing the heteroatom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. H atoms are scaled to an arbitrary size. (*b*) Overlay of the side views of **3** (ball-and-stick model) and the pentaphyrin–uranyl complex **5** (dashed lines). The β-substituents of both have been omitted for clarity.

anium(VI) cation is found to sit within a distorted pentagonal bipyramidal ligand environment (the relevant angles are: 75.00(11)° (N1–U–N2), 72.97(10)° (N2–U–O3), 74.18(10)° (O3–U–N4), 74.75(11)° (N4–U–N5), 64.11(12) (N1–U–N5) and 176.29(13) (O1–U–O2), respectively.

Complex **3** possesses a saddle-shaped conformation as illustrated in Fig. 2(*b*). However, the distortion found is much less than that observed in the case of an earlier reported pentaphyrin uranyl complex **5** (*cf.* Fig. 2).[6b] To the extent that the binding core of pentaphyrin is expected to be larger than that of sapphyrin, this comparative finding lead us to suggest that the saddle-shaped distortion of the uranyl pentaphyrin **5**, and to a lesser extent that of the oxasapphyrin complex **3**, is caused by a macrocyclic core that is too big (as opposed to too small) for the uranyl cation. This is reflected in the average $N–UO_2{}^{2+}$ bond distances; these are 2.522 and 2.541 Å, in the case of **3** and **5**, respectively.



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Complex **3** was also studied by cyclic voltammetry.§ Here, one quasi-reversible reduction wave was observed at 0.62 V (100 mV s^{-1}) that most likely belongs to the $UO_2{}^{2+}–UO_2{}^{+}$ couple. In addition, one irreversible reduction wave at 1.58 V (100 mV s^{-1}), assignable to a $UO_2{}^{2+}$ to U^{4+} reduction process, and one irreversible oxidation wave at 0.64 V (100 mV s^{-1}), ascribed to the oxasapphyrin ligand, are also observed. The quasi-reversible wave of the $UO_2{}^{2+}–UO_2{}^{+}$ couple is found to fall at a significantly more positive potential than the corresponding uncomplexed $UO_2{}^{2+}–UO_2{}^{+}$ couple (E_0 = 0.163 V),[11] as would be expected in light of the favorable bonding interactions present in complex **3**.

Complex **3** was found to be very stable when stored as a solid or in CH_2Cl_2 solution over long periods of time at room temp. in the presence of air. It was also found to be stable, as a CH_2Cl_2 solution, when exposed briefly to aqueous solutions of pH = 2 (70% decomposition after 72 h), or when treated with those of pH = 11 for longer periods (no apparent decomposition after 72 h). By contrast, almost complete decomplexation was observed within a few min when HOAc (10% v/v) was added to a solution of **3** in $CHCl_3$.

In summary, we have described the first example of a stable in-plane metal cation complex of a sapphyrin derivative. It provides a further cogent demonstration of how small changes in ligand structure (in the present instance an O for NH 'replacement') can influence significantly the metal chelation chemistry of a given system.

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Notes and References

† Uranyl complexes of two other pentapyrrolic systems, namely superphthalocyanine[5] and pentaphyrin[6] are known. Also known are sitting-atop η^2-Rh^I and -Ir^I complexes as well as 1 : 1 Zn^{II} and Co^{II} derivatives.[2a,e,7]

‡ *Crystal data* for **3**: dark green crystals, monoclinic, $P2_1/n$, Z = 4, a = 11.990(1), b = 15.351(1), c = 18.954(1) Å, β = 104.53(1)°, V = 3377.1(5) Å^3, D_c = 1.65 g cm^{-3}, μ = 48.49 cm^{-1}. 11 387 reflections were measured, of which 9466 were unique [R_{int} (F^2) = 0.021]. The structure was refined on F^2 to a $R_w(F^2)$ = 0.0857 with a goodness of fit = 1.074 for 416 parameters, while the conventinal $R(F)$ = 0.0358. CCDC 182/945.

§ Cyclic voltammetry was carried out (25 ± 2 °C) under dry argon using a Bioanalytic Systems Inc. (BAS) CV-59W version 2 MF9093 voltammetric analyzer. Dry MeCN was the solvent, 0.1 M $NBu^n{}_4PF_6$ the electrolyte, a 1.6 mm Pt disk the working electrode, and a Pt wire the auxilary electrode. A Ag–AgCl couple, separated from the bulk solution by means of a porous Vycor plug, was used as the reference electrode.

¶ Determined by recording the change in absorption at 455 nm as a function of time.

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