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Actinide expanded porphyrin complexes

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Abstract

In this article the uranyl cation (UO_2^{2+}) coordination chemistry of several prototypic expanded porphyrins is reviewed. The ability of certain expanded porphyrins, large polypyrrolic ligands, to stabilize complexes containing the uranyl cation is contrasted to that of the porphyrins. These latter systems, well-recognized for their ability to stabilize a range of transition metal complexes, among others, have hitherto been shown to form structurally characterized complexes with only uranium(IV) and thorium(IV) cations among cations of

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the actinide series. Possible reasons for these differences in cation complexation behavior are discussed.

Keywords: Porphyrin; Expanded porphyrin; Macrocycle; Coordination chemistry; Actinide; Uranyl cation

1. Introduction

The scientific and technological significance of the discovery of the actinides cannot be underestimated. It led, for instance, to the Manhattan Project and the world's first nuclear weapons. Though actinide production for defense purposes has helped preserve an uneasy peace between 1946 and the present, a legacy of environmental problems are the byproduct of this age. At the same time, the peaceful application of nuclear energy for the production of electricity, while attractive, is plagued with waste management risks that must be addressed [1,2]. In both cases, much of the problem involves cations of the actinide series (abbreviated An).

All isotopes of the actinide elements are radioactive. The half-lives of the most stable isotopes decrease across the series, with the heaviest members of the series being so unstable they can only be created and isolated a few atoms at a time [3]. By contrast, 50 years of nuclear weapons production has generated more than 100 metric tons of purified plutonium in the USA and a similar amount in Russia. The production of plutonium from power reactors amounts to perhaps as much as 7000 metric tons worldwide, most of which is dilute and contained in spent reactor fuel [4]. This large quantity is increasing daily.

As the result of 50 + years of research, it is now known that the actinides are easily hydrolyzed acidic metal ions that form strong complexes with common chelating agents [5,6]. They prefer interactions with hard acid donor atoms like O and F, but demonstrate some covalency in their interactions with softer donor atoms such as Cl^-, N, and S, a key factor in their separation science. The actinides between U and Am have a moderately diverse redox chemistry, with four principal oxidation states (III, IV, V, VI and a heptavalent state for Np and possibly Pu). The penta- and hexavalent oxidation states exist as linear dioxocations, or 'yl' cations, in most solutions and many solid media [5]. This diverse redox chemistry is utilized in their chemical separation from reactor fuels. The transplutonium actinides have fewer oxidation states and generally behave quite similarly to the trivalent lanthanides (abbreviated Ln).

Because actinide production in reactors is accompanied by fission, the ability to isolate the transuranic actinides from the matrix that includes both fission products and uranium, remains a separation problem central to An production. Accordingly, efficient separation processes continue to be sought [7–14]. The use of a $BiPO_4$ precipitation process, better than the original ether extraction/lanthanum fluoride precipitation first used to isolate plutonium, proved suitable for the rapid production of pure Pu demanded by the Manhattan project [3,15]. This process suffered from the drawback of allowing valuable purified uranium to enter the process waste stream. It also only achieved 97–98% recovery of Pu.

The development of solvent extraction processes, first the REDOX process (based on extraction by methyl(isobutyl)ketone) and subsequently the PUREX process (relying on tributylphosphate as a selective extractant for uranium and plutonium) overcame these limitations to a considerable extent [3,15]. They both rely on extraction of the Pu and subsequent reduction to the trivalent state, leaving the excess uranium in the extractant phase for subsequent recovery and recycle. Though the industry standard at present, the PUREX process remains far from perfect. It also does not address the isolation of other An cations.

One solution to the problem of trying to dispose of the actinides long-term is to transmute these elements into shorter-lived fission products, which become less hazardous in a shorter period of time. Transmutation can be accomplished either by incorporating the actinides in reactor fuels or through the use of accelerator-based techniques. Both approaches result in actinide fission and allow at least some of the energy released during the fission process to be extracted for power production. Unfortunately, the neutron physics of the processes are such that they require some processing of the actinide targets or fuel rods to remove neutron poisons that build up and decrease the efficiency of the process. Most problematic are the lanthanides between lanthanum and dysprosium. These are produced in ca. 40% of the fission events and have chemical properties nearly identical to the transplutonium actinides. This similarity makes the separation of actinide from lanthanide cations one of the most difficult known in the generalized field of separation science [6].

It was observed first by Diamond et al. [16], that trivalent actinide cations interact somewhat more strongly with chloride ion than the lanthanides, thus enabling a cation exchange resin-based separation of moderate efficiency. This effect was attributed to f-electron covalency in the actinide–chloride complex that is essentially absent in the lanthanides. While this rationale remains subject to debate, subsequent research demonstrated a similar effect in both ion exchange and solvent extraction separations based on thiocyanate [17]. All known An(III) | Ln(III) group separations are based on the stronger interactions of actinide with soft donor atoms like Cl^-, S, or N [18].

The above historical background, helps highlight some of the benefit that could come from the preparation of new actinide complexing agents [19]. Key elements that merit particular attention include:

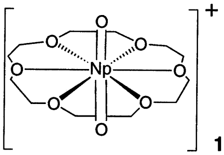
1. Identifying more selective extractants;
2. Decreasing the number of steps required to achieve the required separation;
3. Exploring methods that do not require specific pH or adjusting the eluent pH;
4. Alleviating the need for specialized equipment;
5. Limiting the quantities of solvent required.

Within each of these elements, there exists room for advancement in our understanding of fundamental f-element chemistry, while concurrently addressing one of the great environmental challenges of our time. This combination of understanding and need has stimulated a desire to produce, among other approaches being explored, macrocyclic complexes that are capable of coordinating actinide cations with high specificity.

2. Actinide macrocyclic complexes

While the focus of this review is on expanded porphyrin-based approaches to actinide coordination, specifically uranyl cation complexation, and with it a brief review of related studies made using porphyrins, some mention of other approaches to the problem is warranted [20–22]. Unfortunately, limitations of space preclude all but the most cursory of treatments. For more detailed reviews, the reader is referred to other literature featuring macrocyclic based studies of uranium complexation [20–25].

One seminal contribution to the field came from the group of Clark et al. at Los Alamos National Laboratory (LANL). These researchers recently demonstrated that crown ethers (e.g. **1**) may be used to effect the complexation of neptunyl cations [26]. In related work, it was reported by Deshayes and coworkers [27] that appropriate crown ethers are able to complex uranyl (UO_2^{2+}) cations within their 'pockets'. Many others have put forward evidence that crown ethers are capable of coordinating UCl_3 or uranyl cations in the solid state, albeit not always via an in-cavity mode of interaction [28–32].



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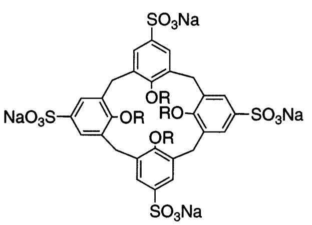
In work that parallels that in the crown ether area, researchers have sought for many years to use calixarenes to complex actinide cations. The first such example was reported by Shinkai in the late 1980s [33]. Inspired by the prior polyketone-based systems of Tabushi [34], he sought to design a calixarene optimized in terms of size and structure for the UO_2^{2+} cation, studying in particular compounds **2**–**4**. Atwood later disputed Shinkai's proposed mode of binding for the system that showed the most favorable complexation characteristics, namely the calix[6]arene 4, because of its preferred 'cone-up–cone-down' conformation [35]. This incipient controversy did not, however, slow the growth of the field, as Thuéry [36] and Leverd [37,38] have continued to study the uranyl complexation characteristics of calix[6]arenes [36], calix[7]arenes [38], and even a double pocket calix[12]arene [37].



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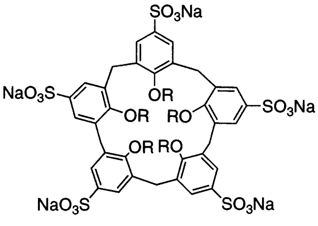

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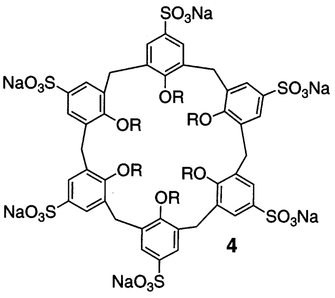

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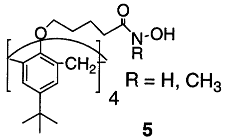
R = - H, - CH2COOH

Other researchers have also sought to apply calixarenes as actinide extractants, and have found success with a variety of substituted calix[4]arenes [39–46]. For instance, Dasaradhi et al. [39], reported using 4-*tert*-butylcalix[4]arene tetrahydroxamate (**5**) for selective solvent extractions of thorium(IV), a model for plutonium, from solutions containing iron, copper, and uranyl cations. Barboso et al. [40], reported that carbamoylmethylphosphine oxide (CMPO) substituted calix[4]arenes might be useful as extractants for actinides, especially thorium and americium. These elaborated receptors combine the CMPO actinide-binding capabilities applied in the TRUEX processes with the complexation features of the calix[4]arenes, species that have been shown to be useful as selective extractants for cations in other instances. Lambert et al. [41], synthesized several 3-hydroxy-2-pyridinone derivatives of 4-*tert*-butylcalix[4]arenes and found them not to require the high concentration of nitric acid required by the other CMPO substituted systems [19,40]. On the other hand, in this latter case, as in other instances [42], the actinide cations were found as having to compete with Fe(III) for the presumed metal coordination sites. Finally, in work of particular note, Beer and coworkers [43–45], found unique extraction properties in a 1-carboxylic acid 3-diethyl amide substituted calix[4]arene ligand. This compound (**6**) was found to make a 2:2 UO_2^{2+} complex when exposed to uranyl cations; in this complex, the amide-linked carboxylic acid 'arms' were found to hold the cation within the calix[4]arene cavity. Beer and his group were also able to attach an analogue of compound **6** to Tentagel beads, an important first step in generating a system suitable for use in real life lanthanide and actinide separations [43].



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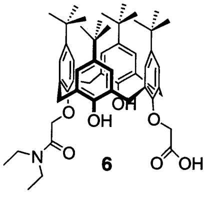

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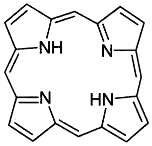
3. Porphyrin actinide complexes

Often considered chemical cousins of the calix[4]arenes, the porphyrins (**7**) [47] are recognized as being cation complexing agents par excellence, particularly as far as cations of the late transition series are concerned. As a result, there is a natural interest in applying them to the coordination of actinides cations as well. Unfortunately, relatively little success in this area has actually been enjoyed. Although success with coordination of transition metals to porphyrin has led to volumes of work, examples of actinide porphyrin complexes are limited. Indeed, only complexes involving the coordination of uranium(IV) and thorium(IV) have so far been characterized by structural means [48–51]. Interestingly, as detailed below, two types of complexes have been observed in the context of this work, namely 1:1 coordination systems [48], and 2:1 sandwich complexes [49–51]. These latter systems can be further subdivided into heterolyptic and homolyptic complexes, or so-called 'mixed' and 'mirrored' systems.



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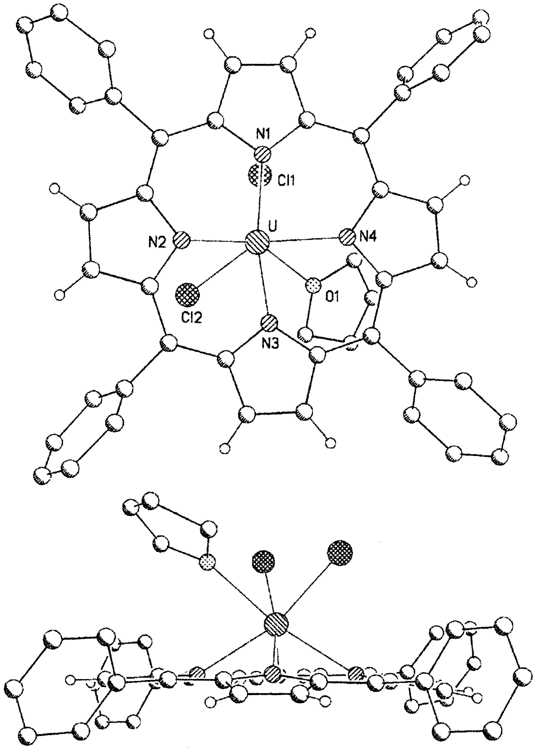


Fig. 1. Molecular structure of (top and side views) U(tetraphenylporphyrin)Cl_2(THF). This figure was generated from data downloaded from the Cambridge Crystallographic Database as published originally in Ref. [48].

Shown in Fig. 1 is an image of the X-ray diffraction crystal structure of a 1:1 porphryin uranium complex, in this case a structure of U(TPP)Cl_2–THF [48] (TPP = tetraphenylporphyrin). This image is based on work done by Girolami et al. [48], which was reported in 1987. In this structure, the uranyl cation sits 1.29 Å above the plane of the ring. The coordination geometry is similar to that of other U(IV) complexes (obtained with other ligand systems) as are the bond distances of the stabilizing anion (2.624 Å) and solvent (2.496 Å) molecule. On the other hand, the U–N distances (averaging at 2.41 Å) are notably longer than those typically seen in amido (NR_2) complexes. It has been theorized that the location of the metal in this complex is due to the size of the binding pocket of the ligand. The limited size of the pocket requires that the cation sit well above the tetraaza porphyrin-derived ligating pocket. While such an above plane placement is clearly destabilizing, the dianionic charge of the porphyrin ring is sufficient to coordinate and stabilize the metal complex through what are likely to be largely electrostatic interactions. Additional studies with thorium(IV) cation (often used as a model for plutonium), including tests involving the specific nature and reactivity of the complex, were also reported by these authors, but not detailed extensively [48]. In any event, it is important to appreciate that the heat and air sensitive complex formed between U(IV) and this particular porphyrin (as well as presumably others) is of interest more from the point of fundamental science than in terms of putative utility in separation or remediation-type applications.

Sandwich-type thorium(IV) and uranium(IV) porphyrin complexes were reported by Suslick and Girolami [49,50] as well as by Kadish and his coworkers [51], both in 1993. Like their 1:1 counterparts (vide supra), these systems were also found to have the metal cation seated out of the plane of the slightly ruffled tetraaza ligand [50]. The homolyptic complexes were complemented in the Kadish studies via the preparation of the corresponding heterolyptic porphyrin–phthalocyanine complex [51]. With the additional coordinating macrocycle helping to provide stabilizing energy for the coordinated metal cation, the bond distances from the actinide to the ligand are unusually long (2.531–2.554 Å). It is not surprising that the crystal structure reported by Girolami et al. (Fig. 2) [50], details the increased distances for the ligands, and also reveals some ruffling away from planarity. This would imply, as above, that the porphyrin-derived binding pocket available to the metal is adequate to stabilize complex formation but is far from ideal in terms of size and shape.

A variety of porphyrins, bearing various substitution patterns (e.g. tetraphenyl porphryin (TPP), octaethyl porphyrin (OEP), etc.) have been investigated extensively in the context of actinide complexation [50,51], but the basic cation coordination properties of the tetraaza coordinating core remained largely unaffected by these changes. No dramatic developments in terms of structurally characterized actinide complexes were forthcoming as the result of these modest structural explorations. On the other hand, a host of other double decker phthalocyanine complexes have been reported. Examples with coordinated neptunium [52], tho-

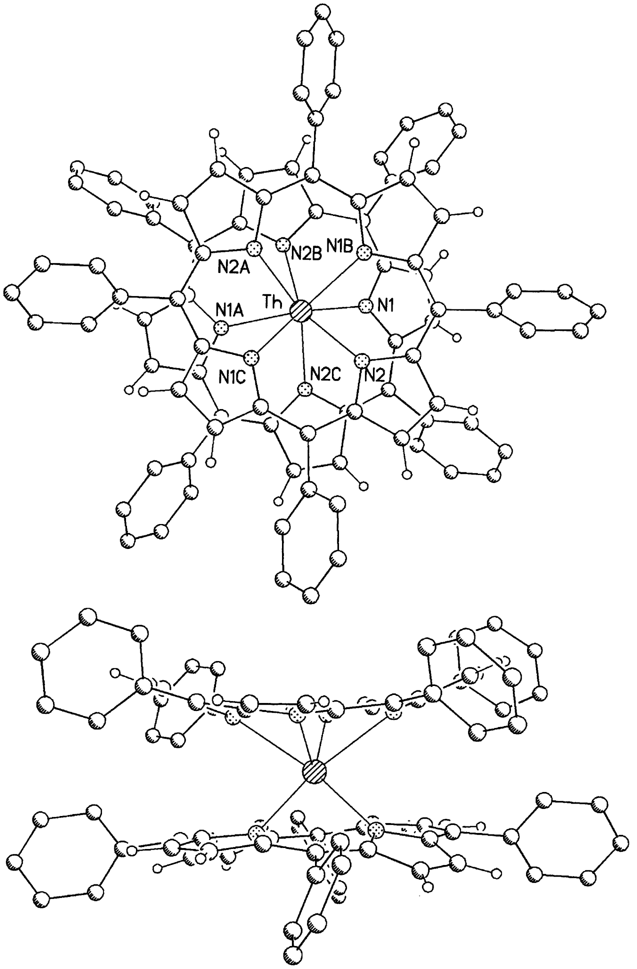
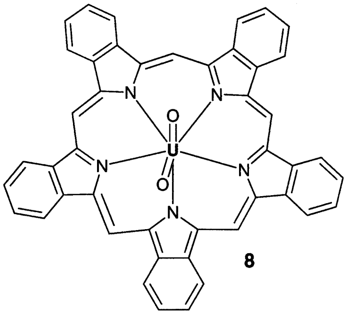


Fig. 2. Molecular structure of (top and side views) Th(tetraphenylporphyrin)$_2$. This figure was generated from data downloaded from the Cambridge Crystallographic Database as published originally in Ref. [50].

rium, and uranium [53] have been reported. Plutonium phthalocyanine complexes have also been prepared and investigated in the context of energy production [54], while an americium phthalocyanine complex has been applied to the problem of isotope separation [55]. Unfortunately, these phthalocyanine-based designs, while elegant, suffer from the drawback that the requisite syntheses are often quite difficult, especially when the functionalized systems, required for application, are considered.

4. Superphthalocyanine

In 1975, more than twenty years before the first characterized structurally actinide porphyrin complex was reported, the X-ray diffraction structure of a uranyl complex of an expanded phthalocyanine, so-called superphthalolcyanine (**8**), was reported by Marks and Day [57]. This structural work helped explain a previously recognized anomaly observed when standard phthalocyanine preparations were carried out in the presence of UO_2^{2+} [56]. Instead of obtaining a macrocycle with four isoindoline-type subunits, one obtains a system with a different stoichiometry that the work of Marks and Day confirmed as representing a macrocyclic structure containing five pyrrole-type subunits for every uranyl cation. Based on their results, Marks and Day concluded that the superphthalocyanine–UO_2 complex was formed as the result of the uranyl metal cation serving as template for the formation of the expanded, pentaaza ligand [57–61].



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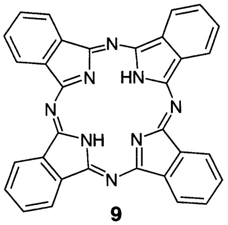
While the results of Marks and Day remain seminal in the field and were very exciting at the time of publication, it is important to appreciate that all efforts to obtain a superphthalocyanine using a different templating cation failed. Also, all attempts to remove the coordinated UO_2^{2+} cation from superphthalocyanine resulted in decomposition of the ligand and production of normal phthalocyanine [62]. While the origin of this chemistry remains subject to debate, it could be explained in terms of inherent strain present in the ligand itself. This is apparent upon inspection of a side view of the uranyl complex (Fig. 3). There is clearly a mis-match between the ligand and the cation. Although the central core of the pentaaza superphthalocyanine complex is more than 30% larger than the corresponding tetraaza core of phthalocyanine, the pocket of superphthalocyanine still does not provide a perfect fit. Thus, it is safe to infer that in the absence of the uranyl cation and the electrostatic stabilization it provides, the ligand itself would be subject to considerable strain. Apparently, this strain is sufficient to induce decomposition under the conditions associated with demetallation. Independent of this rationale, the fact that decomposition occurs obviously limits the use of superphthalocyanine-based processes in extraction or other separation-related applications.

More than a decade after Marks and Day, 1987 to be precise, the first 1:1 actinide phthalocyanine (Pc, **9**) complexes were reported by Guilard et al. [63]. Formed by coordination to a preformed macrocycle, rather than through the use of a template-mediated condensation process, complexes were obtained using thorium(IV) and uranium(IV). While not subject to X-ray diffraction-based structural analyses, evidence was put forward to suggest that the (Pc)Th(acac)$_2$ and (Pc)U(acac)$_2$ complexes prepared in this way, like their double decker counterparts discussed in the previous section, feature out-of-plane cation coordination. Not inconsistent with this out-of-plane coordination mode and the lability it might imply, a temperature of -20°C proved necessary to enforce complex stability. Needless to say, this has limited the use of these systems in real-world applications [63].



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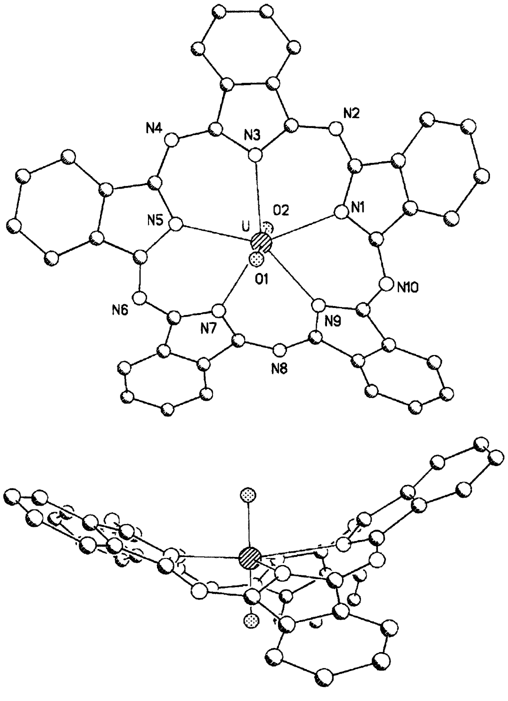
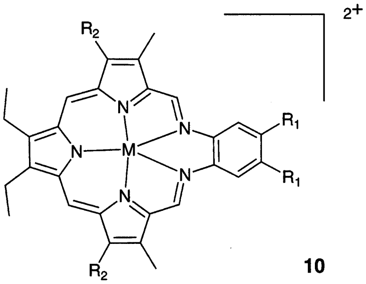


Fig. 3. Molecular structure of the uranyl superphthalocyanine complex (top and side views). This figure was generated from data downloaded from the Cambridge Crystallographic Database as published originally in Ref. [57].

5. Pentadentate systems: pentaphyrin and the sapphyrins

Research in the Sessler group has focused on the synthesis and characterization of expanded porphyrin and porphyrin-type macrocycles and the study of their use in various applications. One notable success in this area has been texaphyrin (**10**) [64]. This class of aromatic porphyrin analogue has a unique ability to form stable, nonlabile, 1:1 complexes with cations of the trivalent lanthanide series [65–67]. This has led to the consideration that the texaphyrins, or suitably modified analogues, might also serve as highly effective ligands for trivalent transuranic elements (e.g. Am(III) cations). Incorporation of trivalent actinide cations into such structures could provide an opportunity to investigate the contribution of covalency to actinide bonding in polyaza ligand systems and might lead to new approaches in waste remediation. Because of technical limitations associated with working with these highly radioactive species, this possibility remains to be tested at present. It has been found that, at least in the authors' hands, the texaphyrins fail to stabilize nonlabile complexes with either thorium(IV) or uranium(VI) (UO_2^{2+}) cations.



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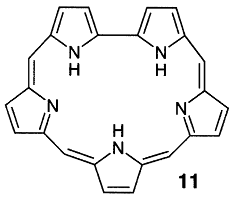
R_1 = H, $[O(CH_2)_2]_3OH$
R_2 = - CH_2CH_3, $(CH_2)_3OH$
M = Ln(III)



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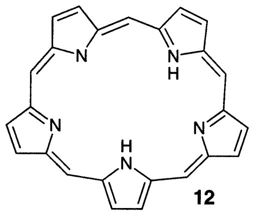
Prior to the advent of the texaphyrins, Bauer et al. proposed that another prototypical expanded porphyrin, sapphyrin (**11**) ([22]-pentaphyrin(1.1.1.1.0)) [68], an aromatic 22 p-electron system first prepared by Woodward in 1966 [69], might be useful as a uranyl cation coordinating ligand. Here, the idea, successfully developed in the case of the texaphyrins and the trivalent lanthanides [65], was that the larger core size would translate into the coordination of larger cations. Unfortunately, as reported by Bauer et al., sapphyrin failed to form a stable uranyl complex [68]. Intrigued by this apparent failure, we decided to reinvestigate the reaction of sapphyrin with salts of UO_2^{2+} as well as the associated reaction chemistry of pentaphyrin (**12**) ([22]-pentaphyrin (1.1.1.1.1)), a system first reported by Gossauer in 1983 [70].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We were pleased to find that pentaphyrin (**12**) acts as a highly effective uranyl cation coordinating ligand. In the initial studies of Gossauer, hints of reactivity with the uranyl cation were found, but these studies were lacking in supporting structural evidence [70]. The system prepared in that instance suffered from difficulties in preparation and inappropriate solubility. Modifications to the three- and four- (beta) positions of the pyrrole subunits rendered the system more soluble in organic solvents, easier to prepare, and hence, easier to study. As a consequence, a crystalline uranyl complex could be prepared [71]. Shown in Fig. 4 is the resulting X-ray diffraction crystal structure. As can be seen from an inspection of this figure, pentaphyrin, like superphthalocyanine [57], stabilizes a uranyl complex in which the ligand itself is distorted in a bowl-like fashion. The uranyl-to-nitrogen distances are long when compared with those seen in uranyl amide complexes but are similar to those seen in uranyl superphthalocyanine (2.494–2.566 Å). In marked contradistinction to superphthalocyanine [57], pentaphyrin may be made in the absence of a uranyl or other templating cation. Further, once prepared, the metal may be removed from the uranyl complex via protonation. This makes pentaphyrin potentially useful for extraction and recovery applications. Unfortunately, pentaphyrin is not all that stable, and this could limit its utility except in certain specialty situations [71].

The behavior of sapphyrin, under conditions of putative uranyl cation insertion, stands in marked contrast to what was observed with pentaphyrin [72]. Unexpectedly, numerous attempts to produce a pentacoordinate sapphyrin UO_2 complex with this potentially trianionic ligand, failed to produce the expected aromatic product. Rather, under forcing conditions, involving treatment with HCl in hot methanol, an unprecedented pentacoordinate uranyl complex was produced that contained a methoxy group 'added in' to one of the *meso*-like bridging postions. The resulting rehybridization of the methene bridge, from sp^2 to sp^3, serves to destroy the aromaticity of the ligand, something that was confirmed both by spectroscopic analyses and by a single crystal X-ray diffraction analysis (Fig. 5) [72].

Given the superficial resemblance between sapphyrin and pentaphyrin, the obvious and perplexing question is why sapphyrin fails to stabilize a bon fide uranyl complex. Two explanations, that are not necessarily mutually exclusive, have been put forward. First, the decreased size and flexibility of sapphyrin compared to

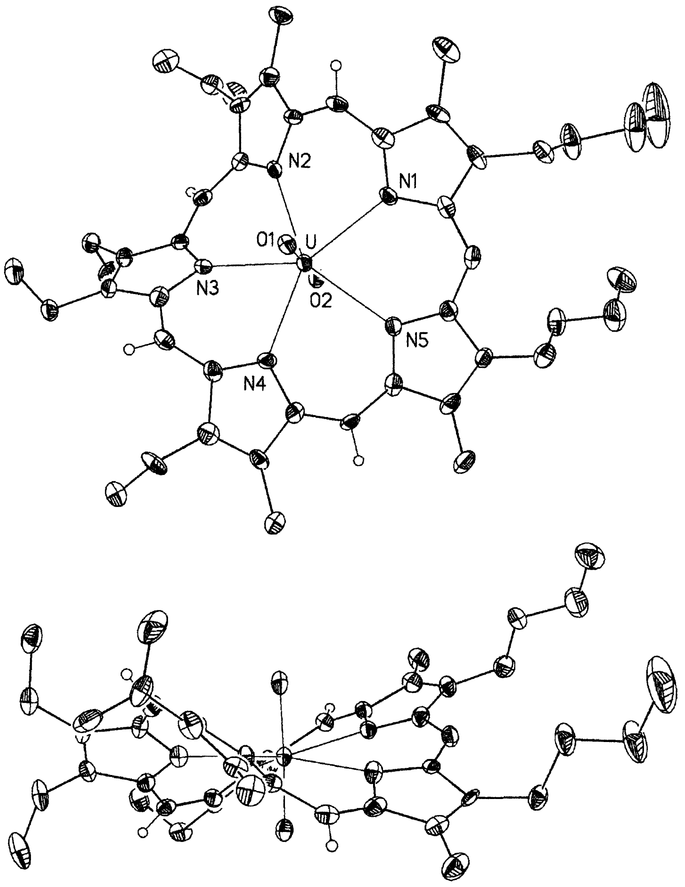
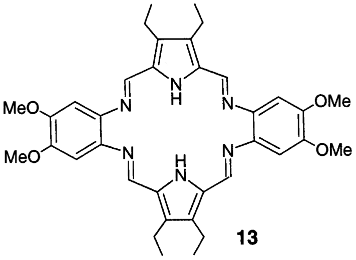


Fig. 4. Molecular structure of the uranyl complex of pentaphyrin (top and side views). This figure is generated from data reported originally in Ref. [71].

pentaphyrin (one *meso*-like carbon is 'missing' in the case of sapphyrin) could render the core size incommensurate for uranyl cation complexation. Second, the higher charge density of fully deprotonated sapphyrin, as compared fully deprotonated pentaphyrin (3^- vs. 2^-), might render it unsuitable for complexation of a dicationic cation such as UO_2^{2+}. Currently, this latter explanation is preferred, in part because it would account for the incipient stabilization of coordinated uranium intermediates of lower valence but higher charge that, in turn, might facilitate the addition of a nucleophile. A mechanism based on the latter assumptions has been put forward; it is reproduced as Scheme 1 [72].

Recently, chemical support for the proposed mechanism has been put forward by the Sessler group. As the result of work devoted to the production of expanded porphyrins containing heteroatoms other than nitrogen (in the form of pyrrolic NH substituents), a monoxasapphyrin (**13**) was synthesized [73,74]. On heating with uranyl diacetate in acetonitrile, a uranyl complex was produced. In contrast to what proved true for sapphyrin, the ligand was unaltered (except for the replacement of two pyrrolic protons by the UO_2^{2+} metal center). Further, the cation itself was found to reside within the mean plane of the five coordinating donor atoms. The conformation of the ligand was twisted from planarity, presumably as the result of a need to conform to the size of the cation. While the nature of this distortion is different from what is seen in the case of pentaphyrin, the uranyl-to-nitrogen bond lengths are almost exactly the same in these two expanded porphyrin uranyl cation complexes. While drawbacks associated with the use of monoxasapphyrin in waste remediation applications could include difficulties associated with its synthesis, as well as a need to apply heat to form the complex, it is important to appreciate that, once formed, the uranyl complex is remarkably stable [75] (Fig. 6).



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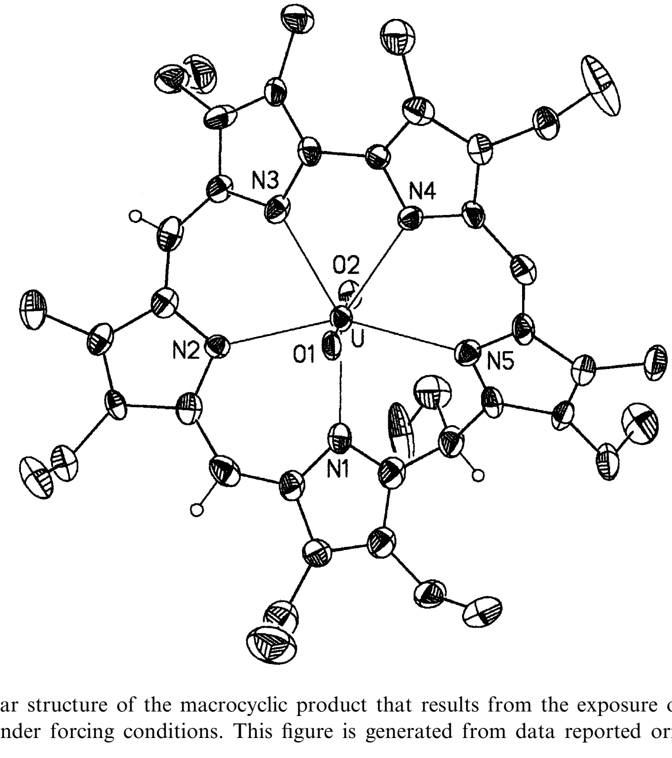
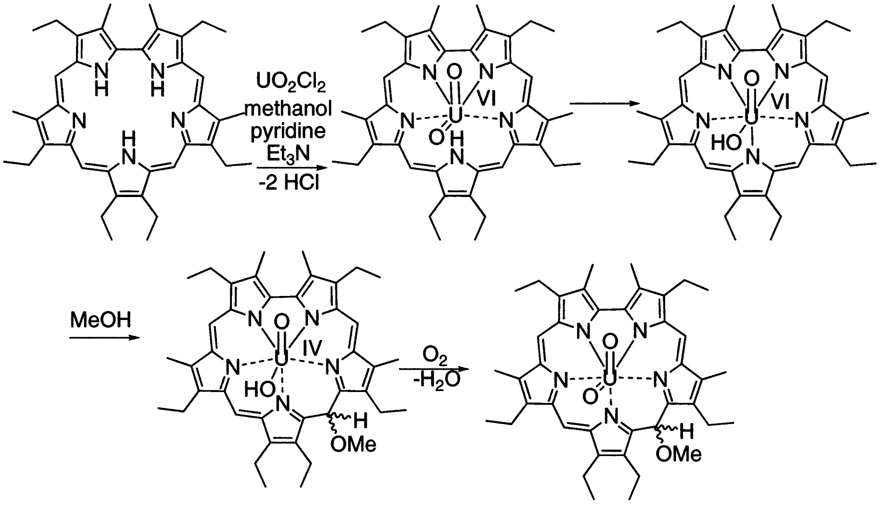


Fig. 5. Molecular structure of the macrocyclic product that results from the exposure of sapphyrin to uranyl cation under forcing conditions. This figure is generated from data reported originally in Ref. [72].

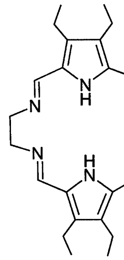


Scheme 1. A proposed mechanism for the insertion of a methoxy group into the 22 π-electron aromatic conjugated system of the outer ring of sapphyrin upon metallation with uranyl after heating in MeOH with HCl [72].

6. Schiff base complexes: alaskaphyrin

The key step associated with the synthesis of the lanthanide texaphyrin complexes involves the oxidative insertion of the metal cation to a non-aromatic pentaaza precursor [64]. The success of this step, and a realization that the non-aromatic precursor could itself be assembled readily from appropriate subunits (a diformyl tripyrrane and an *o*-phenylenediamine), led to the consideration that other polypyrrolic uranyl complexes could be produced using appropriate pyrrolic Schiff base systems, either with or without the benefit of uranyl cation templation. In 1996, these musings culminated in the synthesis of the uranyl complex of a dipyrrolic, hexaaza system now affectionately referred to as alaskaphyrin (**14**) (Fig. 7) [76]. In fact, it proved possible to prepare this complex using one of two strategies. First, by employing a diformyl pyrrole and an *o*-phenylenediamine derivative, it proved possible to prepare metal-free alaskaphyrin, a ligand system first prepared in unsubstituted form by Fenton [77–79]. Subsequent exposure to the uranyl cation then led to complex formation without destruction of the ligand. Alternatively, it was found that the uranyl complex could be made directly by mixing the two precursors in the presence of a uranyl cation template. Interestingly, the metal-free species could also be produced by using NO_3^- as a template, something that at the time, a bona fide anion template effect, was almost without precedence in the literature. Unfortunately, as proved true for superphthalocyanine

[57], once formed, the uranyl complex of alaskaphyrin could not be demetallated without destruction of the ligand [76].



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Subsequent to the initial synthesis of the uranyl complex of alaskaphyrin, several related macrocycles were produced using diamines other than *o*-phenylenediamine [80]. Like the original system, many of these were characterized by X-ray diffraction analysis (e.g. **15** and **16**). Not surprisingly, given the diamines used, these complexes proved less stable than the original alaskaphyrin complex as well as less planar in the solid state (Fig. 8) [80]. On a different level, the substitution of various

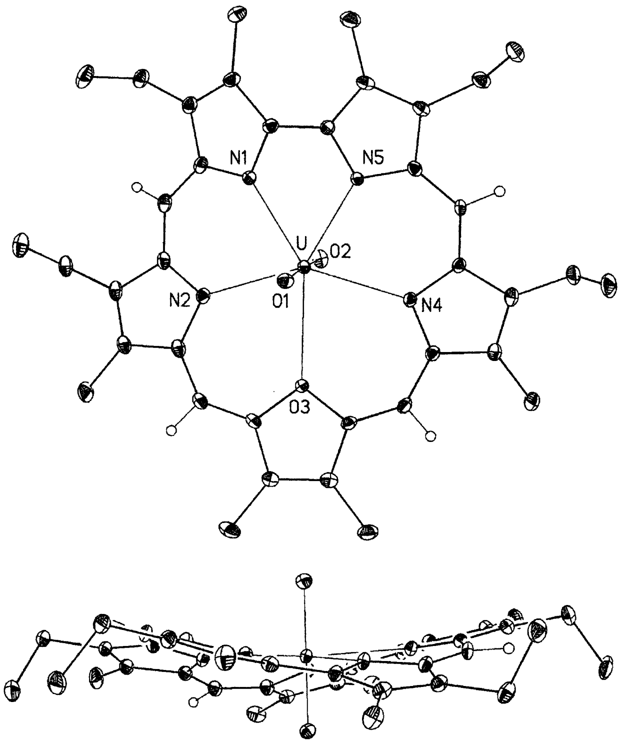


Fig. 6. Molecular structure (top and side views) of the uranyl complex of oxasapphyrin. This figure is generated from data reported originally in Ref. [75].

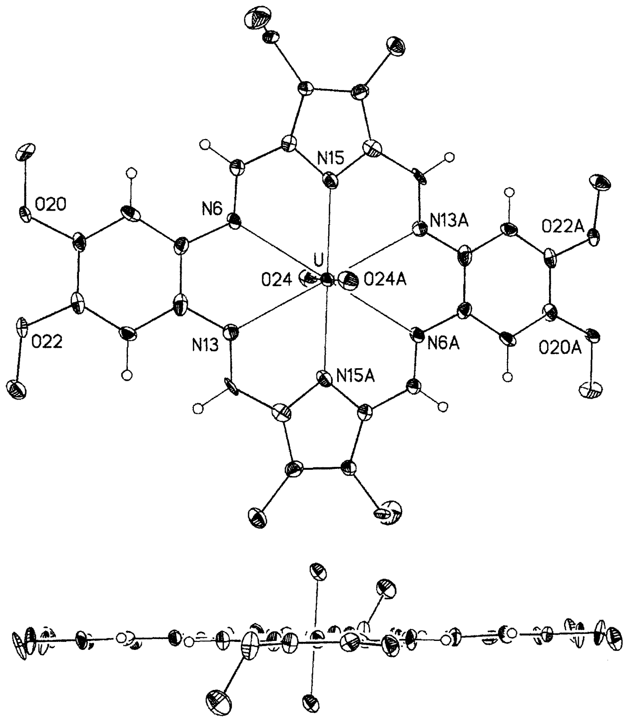
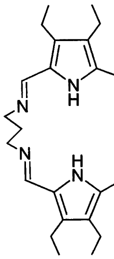


Fig. 7. Molecular structure (top and side views) of the uranyl complex of alaskaphryin. This figure is generated from data reported originally in Ref. [76].

diamines, including aliphatic ones, was found to affect the key uranium(VI)-to-nitrogen distances somewhat. For instance, average distances of 2.456 and 2.656 Å, respectively, were observed for the U–$N_{pyrrole}$ and the U–N_{imine} distances in compound **15**, while the U–$N_{pyrrole}$ and the U–N_{imine} average distances were reported to be 2.444 and 2.660 Å, respectively, for compound **16**. These compare to the analogous U–$N_{pyrrole}$ and U–N_{imine} average bond lengths found for the alaskaphyrin complex, 2.418 and 2.740 Å, respectively. These modest differences most likely reflect obvious difference in overall macrocycle flexability [80].



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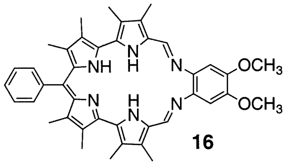

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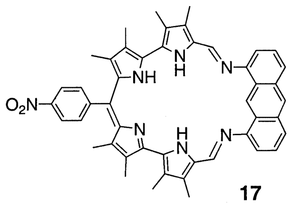
Recently, a number of other Schiff base polypyrrolic macrocycles (e.g. **17** and **18**) were prepared in the Austin laboratories [81]. While not yet tested as actinide complexing agents, it is possible they will prove useful in this regard in as much as they may display improved stability or faster rates of coordinated cation exchange than alaskaphyrin and its analogues. Improvements along these lines would be useful for certain applications, with the exact choice of the latter being dependent, of course, on the specific properties of the system. For instance, highly labile systems would be useful for extractions, whereas more stable systems could prove advantageous in direct remediation-type applications [7,19].



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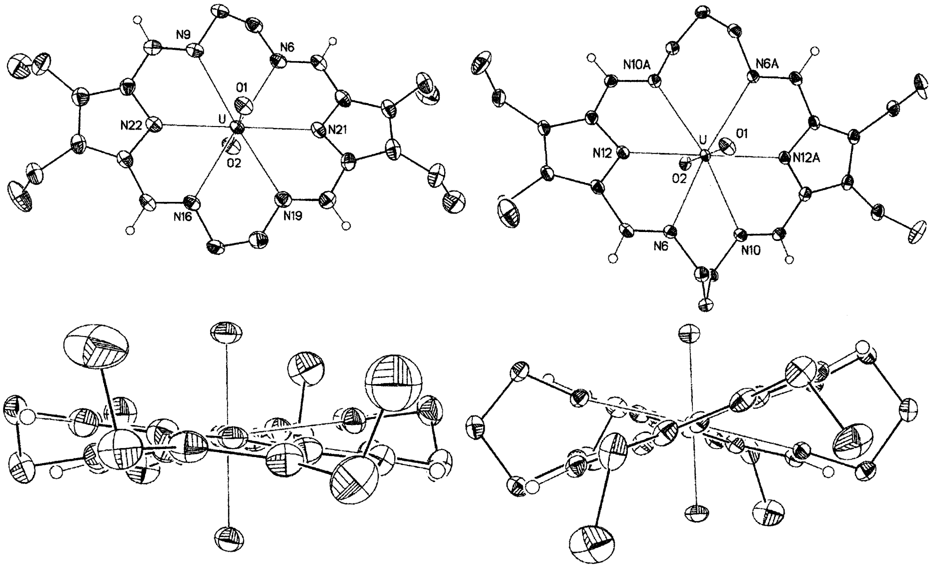
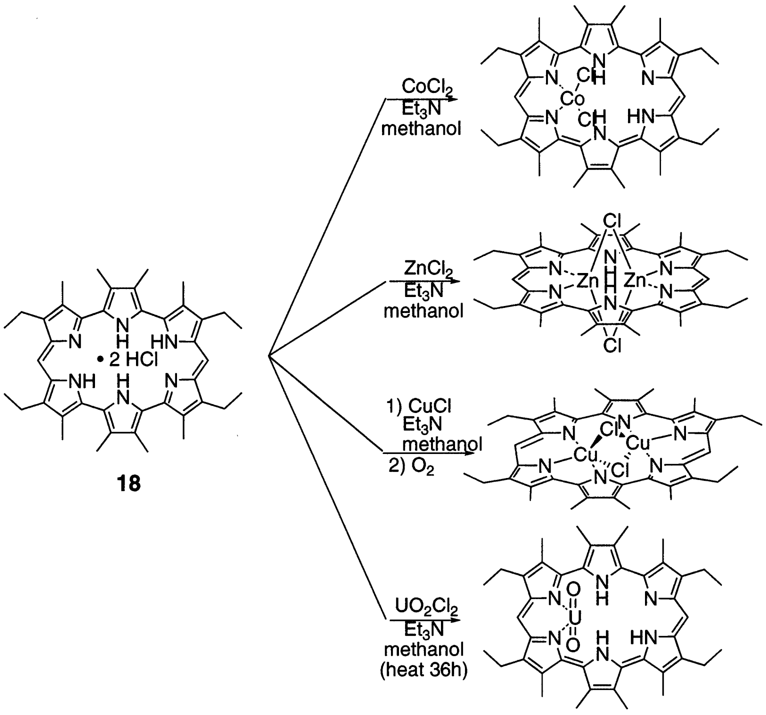
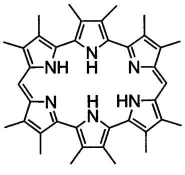


Fig. 8. Molecular structure (top and side views) of the uranyl complexes of the alaskaphyrin analogues **14** and **15**. The side views shown feature the diamine subunits on either side. This figure is generated from data reported originally in Ref. [80].



Scheme 2. Metal complexes of amethryin [82].



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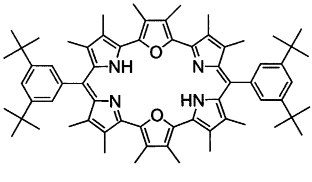
7. The amethyrins

In 1995, the first synthesis of a hexapyrrolic macrocycle containing terpyrrolic subunits was reported by our group [82]. This 24 π-electron system, [24]hexaphyrin(1.0.0.1.0.0), was assigned the trivial name amethyrin (**19**) in light of the deep amethyst color displayed by its HCl salt. So far, it has proved rather unique among non-Schiff base expanded porphyrins in that it displays a rich metallation chemistry. For instance, as summarized in Scheme 2, a cobalt, a bis zinc, a bis copper, and a mono uranyl complex have all been stabilized using this ligand. Unfortunately, the uranyl complex, formed after more than a day of heating, was never characterized structurally. On the basis of spectroscopic and mass specroscopic analyses, however, this complex is believed to bear a net plus one charge with the dicationic uranyl center occupying two of the possible six amethyrin-derived ligation sites. To the extent this proves true, this complex should bear structural analogy to the corresponding cobalt dichloride complex, a product characterized by single crystal X-ray diffraction analysis [82].

From the same terpyrrolic subunits, other macrocycles have been prepared. One of these, [40]-decaphyrin(1.0.1.0.0.1.0.1.0.0), or turcasarin (**20**; Scheme 3), was found to produce a bis-uranyl complex [83]. This large decapyrrolic system is believed to be capable of coordinating these two 'yl' metal centers concurrently in a helical type structure (Scheme 3). Spectroscopic data are consistent with this hypothesis. Unfortunately, at present, it still remains to be confirmed by X-ray diffraction methods [84].

Quite recently, two other macrocycles were prepared and studied as uranyl complexing agents. The first of these is dioxamethyrin (**21**), an amethyrin-like system that contains two furan subunits within the macrocyclic framework. Dioxamethyrin contains a core comparable to that of the alaskaphyrin in terms of both size and shape, and exposure to uranyl salts produces a uranyl complex within minutes. This system is also quite unusual in terms of its color in methanol solution; it is a dark orange when protonated (as its metal-free HCl salt), yellow as its free base, and deep red when coordinated to the uranyl cation. These latter complexes, interestingly, are green when isolated as microcrystals. Unfortunately, this system has not, as yet, yielded to complete characterization via single crystal X-ray diffraction analysis [85].



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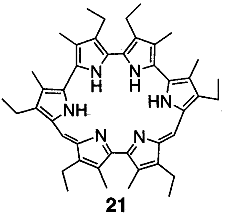

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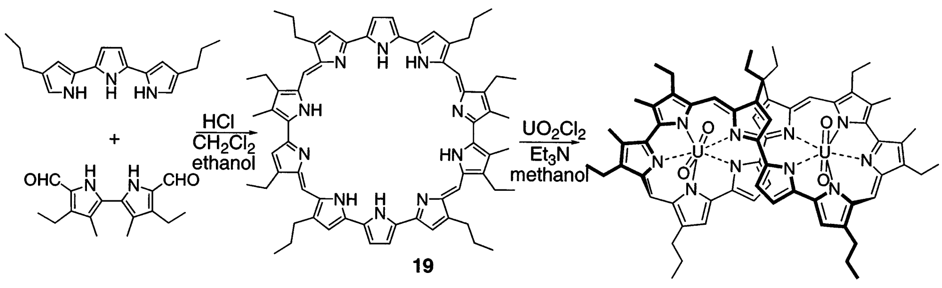
The second system generated of late is called isoamethyrin ([24]hexaphyrin-(1.0.1.0.0.0)]; **22**). It is not as colorful as its amethyrin and dioxamethryin cousins, but it complexes uranyl just as readily and interestingly, becomes aromatic upon



Scheme 3. Synthetic reaction scheme and proposed structure of a turcasarin bis-uranyl complex [83].

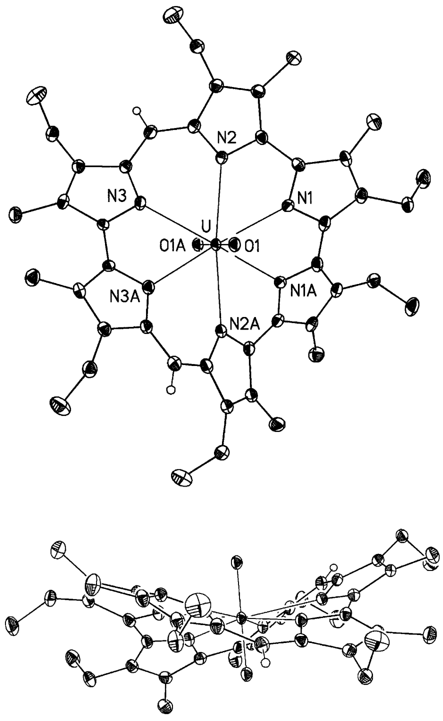
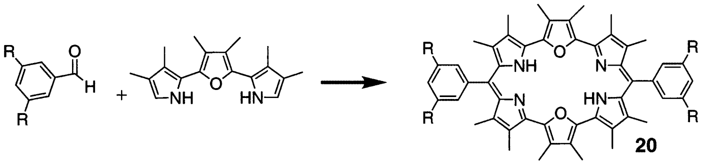


Fig. 9. Molecular structure (top and side views) of the uranyl complex of isoamethyrin. See Ref. [85].

doing so. While further explorations of this latter, rather unprecedented, change in electronic structure are in progress, it is important to appreciate that, upon metal complexation, the isoamethyrin ligand retains a fair degree of planarity as judged from X-ray diffraction analysis (Fig. 9). This could reflect the fact, as proved true for alaskaphyrin, the uranyl cation center is coordinated through six nitrogen-to-UO_2 interactions [85].

Unlike previous systems, the uranyl complexes formed from these new amethyrin derivatives are formed within minutes, do not require the application of heat, or the use of an inert atmosphere to be generated. Further, the ligands themeselves are relatively easy to produce, requiring only one-third of the synthetic steps required to produce sapphyrin [83–85]. This makes them potentially attractive in actinide coordination-based applications. Abetting this conclusion, is the realization that there are several options that would allow these systems to be functionalized readily. Perhaps the easiest of these functionalization strategies would involve modification of the *meso*-like bridges, as shown in Scheme 4. All that would be required is reaction with an appropriate chosen aldehyde in the final synthetic step. Needless to say, this possibility has us quite excited about the prospect of using these new expanded porphyrins as actinide sensors or extractants.



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Scheme 4. Depicted is the synthetic reaction scheme for the final step in the synthesis of dioxamethryin (**21**). Incorporation into polymer or resins and the construction of water soluble analogues could be accomplished through modification of the ligand using benzaldehydes substituted at R with any of a variety of amines or alcohols [85].

8. Future directions

While previous work using extractants and resins may present the problem of An(III) recognition as solved, there remain areas where further research is warranted. As detailed in this review, several expanded porphyrin-type systems have been demonstrated as coordinating the uranyl cation well and thus show considerable promise as complexing agents for related actinide species, such as NpO_2^+ and PuO_2^{2+}. It is thus deemed worthwhile to continue the study of these systems, while likewise working to generate other, further improved expanded porphyrin systems. Also of interest would be various open-chain analogues of expanded porphyrins since these might form complexes that are more labile than their macrocyclic congeners. This would make them of use for effecting extraction based purifications of trivalent actinides from trivalent lanthanides.

While it remains an open question as to whether some or all of the above promise will be achieved, work devoted towards its realization is currently in progress in collaboration with researchers at Los Alamos National Laboratory and Argonne National Laboratory, including Drs D. Webster Keogh and Kenneth Nash, among others. Appropriate results from these investigations, which have just recently produced a stable NpO_2^+ complex of isoamethyrin (**22**) [85], will be published in due course.

Acknowledgements

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