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Uranyl Complexation by a Schiff-Base, Polypyrrolic Macrocycle

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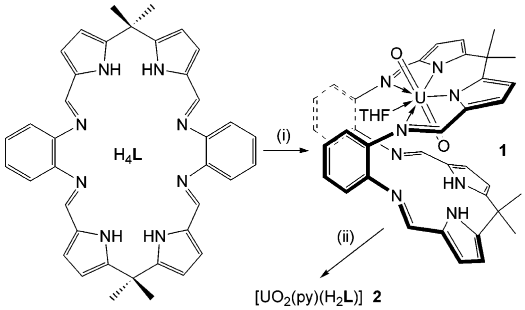
Mononuclear uranyl (UO_2^{2+}) complexes supported by the polypyrrolic macrocycle L have been synthesized and exhibit hinged macrocyclic structures with an expanded cavity and enforced π-stacking and hydrogen bonding motifs.

Porphyrins, phthalocyanines, and related pyrrole-based macrocycles are used widely to support reaction chemistry and catalysis by transition metal cations. Unlike transition metals, however, the uranyl UO_2^{2+} ion neither fits in the cavity of such macrocycles nor is capable of sitting above the plane of these ligands due to its obstinate linearity. While some lower-valent U^{IV} monoporphyrins and sandwiched diporphyrins are known,[1] complexation of the uranyl ion is only possible for macrocycles with large cavities that permit the *trans*-UO_2 motif.[2−4] Due to the possibilities for selective extraction of radionuclides, uranyl ion coordination by superphthalocyanines and expanded porphyrins has become increasingly popular.[5,6]

We recently reported a polypyrrolic, potentially dinucleating macrocyclic ligand, L, that forms a dinuclear palladium complex $Pd_2[L]$ with a well-defined, molecular cleft, a structure related to those of cofacial, or Pacman, diporphyrins.[7] We reasoned that this large and flexible macrocycle should be able to accommodate the uranyl in a way that dinucleating, cofacial diporphyrin ligands cannot, and that the tendency of this ligand set to promote hinged, Pacman topologies[8] could be exploited to study the chemistry of the uranyl ion. The fundamental reactivity of the uranyl oxo-atom is of interest since this linear cation is present in the majority of naturally occurring uranium minerals, and in nuclear waste reprocessing systems.[9−13] We describe herein the syntheses and structures of monouranyl complexes that are supported by L.

Scheme 1. Synthesis of the Macrocyclic Monouranyl Complexes **1** and **2**[a]



[a] (i) $[UO_2(THF)_2\{N(SiMe_3)_2\}_2]$, THF; (ii) pyridine.

The transamination reaction between the free-base macrocycle H_4L and the uranyl amide $[UO_2(THF)_2\{N(SiMe_3)_2\}_2]$ in THF at low-temperature resulted in the rapid and sole formation of the khaki-green mono-uranyl complex, *trans*-$[UO_2(THF)(H_2L)]$, **1** (Scheme 1); this formulation was confirmed by combustion analysis, and no di-uranyl complex, $[(UO_2)_2(L)]$ was observed, even when the reaction was carried out at elevated temperature.

Crystals of **1** suitable for X-ray diffraction studies were grown by hexane diffusion into a CH_2Cl_2 solution, and the solid state structure was determined (Figure 1).

It is immediately evident that one N_4-donor set of L is sufficiently flexible to accommodate successfully the *trans*-uranyl ion; cavity expansion is observed that renders the

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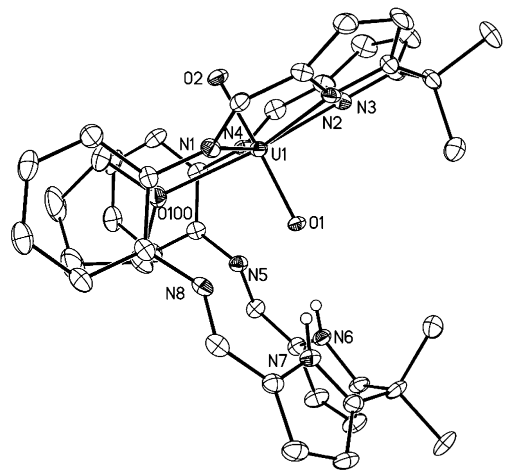

Figure 1. X-ray crystal structure of the mono-uranyl complex **1** (30% ellipsoids). All hydrogens except those on N6 and N7 have been omitted for clarity. Selected bond lengths (Å) and angles (deg): U1−O1 1.790(4), U1−O2 1.766(4), U1−N1 2.593(5), U1−N2 2.442(5), U1−N3 2.444(5), U1−N4 2.578(5), U1−O100 2.442(5), O1−U1−O2 177.6(2), N1−U1−O100 76.59(16), N1−U1−N2 66.75(17), N2−U1−N3 71.12(18), N3−U1−N4 66.73(18), N4−U1−O100 77.52(16).

uranyl ion five-coordinate in the equatorial plane. The second N_4-donor compartment remains metal-free. The expanded coordination site is occupied by THF, which results in approximate pentagonal bipyramidal geometry at the metal in which the U−N and U−O bond distances and angles are standard. The THF molecule adopts a highly unusual, slightly asymmetric sandwiched position between the two aryl rings that bridge the two N_4-donor compartments (aryl centroid−THF centroid = 3.806 and 3.712 Å), and this coordination mode results in both a significantly more obtuse N1−M−N4 angle of 150.74(16)° and more open dihedral angle of 52° between the two bridging aryl rings than seen for $Pd_2[L]$ (110.93(12) Å and 4.9°, respectively). Even though the macrocycle has flexed considerably to accommodate one uranyl ion, the overall molecular topology is still remarkably similar to the Pd_2 and Fe_2O Pacman complexes supported by L.[7,8] The presence of the rigid, bridging aryl groups between the two donor compartments has resulted in a bent structural motif, prescribing a well-defined, monometallic cleft with one oxo group of the linear uranyl ion located within the cleft and the other *exo*. It is also evident that an appreciable hydrogen bonding interaction occurs between the pyrrolic hydrogens H6 and H7 and the uranyl oxygen O1 (N6···O1 3.111(7), N7···O1 3.146(7) Å), of which a consequence may be the fractionally but significantly longer (0.024 Å) U1−O1 bond distance as compared to U1−O2. This slight asymmetry of the uranyl is not reflected in the Raman spectrum of crystalline **1**, in which a resonance is seen at ν_1 823 cm^{-1}. This value is comparable to that of $[UO_2(THF)_2\{N(SiMe_3)_2\}_2]$ (ν_1 819 cm^{-1}) and is significantly lower than that shown by uranyl ions with five equatorial water ligands (ν_1 870 cm^{-1}),[14,15] confirming the π-donor capability of the macrocycle. The solid state structure of **1** is retained in solution as shown by ^1H NMR studies. Here, discrete resonances are seen for both complexed and metal-free N_4-compartments, and also for the asymmetric THF molecule; these latter resonances are significantly shifted from usual values (δ_H 4.80, 3.85, 1.05, and 0.86 ppm, cf. 4.50 and 1.77 ppm for $[UO_2(thf)_2\{N(SiMe_3)_2\}_2]$) which may be a consequence of the geometrically constrained coordination pocket.

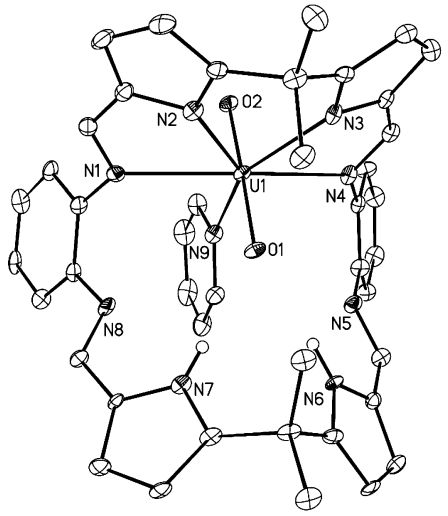

Figure 2. X-ray structure of the monouranyl complex **2** (30% ellipsoids). All hydrogens except those on N6 and N7 and pyridine solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): U1−O1 1.793(6), U1−O2 1.773(6), U1−N1 2.583(8), U1−N2 2.438(7), U1−N3 2.431(7), U1−N4 2.605(7), U1−N9 2.554(2), O1−U1−O2 176.9(3), N1−U1−N9 76.9(2), N1−U1−N2 66.4(3), N2−U1−N3 71.5(2), N3−U1−N4 66.7(2), N4−U1−N9 77.8(2).

The reaction between the THF adduct, **1**, and excess pyridine results in THF substitution and the formation of the mono-pyridine adduct, $[UO_2(py)(H_2L)]$, **2** (Scheme 1); no reaction was observed between **1** and either 2,2-bipyridine or benzophenone. The X-ray crystal structure of **2** was determined (Figure 2) and shows a hinged molecular topology similar to **1**, but with pyridine π-stacked between the aryl-bridged hinge instead of THF. This entrapment of the pyridine molecule between the two aryl rings is reminiscent of the supramolecular interactions exploited to generate motion or switching in molecular machines.[16]

The uranyl coordination geometry, metric parameters, and hydrogen-bonding (N6···O1 3.078(3), N7···O1 3.103(3) Å) motifs in **2** are also similar to those in **1**. In solution, it is again clear that the hinged solid state structure is rigidly maintained. NMR data clearly correlate with the existence of two separate N_4-compartments, and the asymmetric pyridine molecule is readily identified from COSY experiments; as with **1**, these resonances are shifted (δ_H 9.41/8.21 (*o*); 7.38 (*p*); 6.87/6.73 (*m*) ppm) as a consequence of the rigid coordination pocket prescribed by the metallomacrocycle. This is corroborated by NOE measurements, in which through-space interactions are clearly evident between the coordinated pyridine and the bridging aryl rings. Also, exchange correlation spectra indicate that no significant

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exchange occurs between the bound pyridine and pyridine solvent of crystallization at room temperature.

We have shown that the flexible, compartmentalized, polypyrrolic macrocycle L binds a single *trans*-uranyl cation using one N_4 donor set. Hydrogen bonding between the metal-free, N_4-donor compartment and the uranyl ion occurs, and THF or pyridine is ligated within a constrained, equatorial pocket; this results in a unique and asymmetric uranyl coordination environment. Reactivity studies of the oxo atom within the hydrogen-bonding pocket are currently being investigated.

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Supporting Information Available: X-ray crystallographic files for **1** and **2** (CIF) and full experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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