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Co-linear, double-uranyl coordination by an expanded Schiff-base polypyrrole macrocycle

Polly L. Arnold,1,* Guy M. Jones,1 Qing-Jiang Pan,2,3 Georg Schreckenbach2 and Jason B. Love1,*

[1] EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.
[3] Key Laboratory of Functional Inorganic Material Chemistry of Education Ministry, School of Chemistry and Materials Science, Heilongjiang University, Harbin, 150080, China.
[1,*] Corresponding authors; P.L.A. e-mail: polly.arnold@ed.ac.uk; J.B.L. e-mail: jason.love@ed.ac.uk

Supporting information:
[†] Electronic supplementary information (ESI) available: full experimental and crystallographic details. CCDC reference number 867432. For ESI and crystallographic data in CIF or other electronic format see http://dx.doi.org/10.1039/C2DT30658A

[‡] Crystallographic details for 2: Single crystals were grown from pyridine solution, C68H58N10O4U2, M 1555.3, monoclinic, P2/n, a = 13.5141 (2), b = 17.9909 (4), c = 23.4778 (5) Å, β = 92.443 (3), V = 5702.99(19) Å³, Temp 100 K, Z = 4, 12 703 independent reflections, R(int) 0.074, R(F² > 2σ(F²)) 0.051, CCDC 867432.

Graphical abstract:
Abstract

Expansion of a Schiff-base polypyrrolic macrocycle allows the formation of a binuclear uranyl complex with co-linear uranyl ions and a very short oxo-oxo distance.

Introduction

The actinyl ions, [AnO$_2$]$^{n+}$, (An = U, Np, Pu, n = 1,2) have metal dioxo motifs in which linear MO$_2$ geometries are dominant due to strong covalent multiple M-O bonding and relativistic effects.$^1$ Of these, the hexavalent uranyl is the best-known and arguably the most important, due to its natural occurrence in the environment and the fact that it makes up approximately 95% of the dissolved metal ions in standard civil nuclear waste.$^2,3$ The uranyl dication has the least basic oxo groups compared to the other actinyl ions, including the reduced, pentavalent uranyl mono-cation, and exhibits little chemistry.$^4$ This is a significant property as the interaction of actinyl ions through oxo-bridge formation to other cations, known as cation-cation interactions (CCIs),$^5$ is important to nuclear waste processing since it can lead to undesirable precipitation of clusters. Furthermore, proton and oxo group exchange reactions that occur during the reductive precipitation of uranyl under anaerobic conditions are facilitated by oxo-bridging between the actinyl centres.$^6-9$ Well-understood cluster formation reactions have also been used in recent years to direct the formation of actinide dimers and oligomers that display interesting electronic coupling, and that help elucidate the fundamental bonding behaviour of f-electrons.$^{10}$ This is still a poorly-understood area, and one made difficult for theoretical studies by relativistic effects.

We have been studying uranyl [UO$_2$]$^{2+}$ oxo-group hydrogen-bonding,$^{11}$ transition-metal coordination,$^{12}$, and reduction through the formation of covalent O-Si and O-H bonds,$^{13-15}$ or lanthanide metallation,$^{16}$ in a Pacman-shaped, polypyrrolic macrocyclic framework, which both equatorially coordinates, and desymmetrises the uranyl ion (Chart 1, A). While under normal conditions only one uranyl cation can fit into the cavity of H$_4$L, we have shown recently that a new binuclear diuranium dioxo geometry can occur in which both reductive silylation and the migration of one oxo group to a mutually cis position are apparent (Chart 1, B).$^{17}$ In related work we have shown that binuclear transition metal complexes of the expanded Pacman ligand H$_4$L$^A$ exhibit greater metal-metal separation and afford superior performance in oxygen reduction catalysis (Chart 1, C).$^{18-20}$ Computational studies by us suggested that this latter ligand should allow the coordination of two actinyl ions, albeit with close oxo-oxo distances.$^{21}$ Herein, we report experimental evidence for the formation of binuclear uranyl complexes of H$_4$L$^A$ and confirm the theoretical predictions.
Chart 1. The desymmetrisation of the uranyl ion upon coordination in the Pacman macrocycle (H₄L) A, the oxo-rearranged product B that allows two uranyl ions to coordinate, and the dicobalt catalyst for O₂ reduction of the expanded polypyrrolic macrocycle with anthracenyl (H₄Lᴬ) hinge C. S = donor solvent molecule.

The reaction between the free base anthracenyl macrocycle H₄Lᴬ and one equivalent of the uranyl bis(silylamido) complex [UO₂{N(SiMe₃)₂}₂(py)₂] (py = pyridine) in pyridine solution was not as straightforward as that of the analogous ligand H₄L, affording a mixture of the brown mono and binuclear uranyl complexes [UO₂(py)(H₂Lᴬ)] 1 and [{UO₂(py)}₂(Lᴬ)] 2 in addition to unreacted ligand in 70:15:15 ratio respectively, even at elevated temperatures. Although the reaction between H₄Lᴬ and two equivalents of [UO₂{N(SiMe₃)₂}₂(py)₂] also yields a mixture of 1 and 2, the latter is formed in much greater yield of 50 %, alongside nearly the same amount (46 %) of compound 1. Both 1 and 2 have similar solubilities, being insoluble in non-polar organic solvents and poorly soluble in pyridine, a property which causes unwanted precipitation of both products over the course of the reaction inhibiting the formation of 2 as a single product. Despite this, fractional crystallisation from the crude mixture did allow isolation of pure samples of 2, albeit in low yields. The binuclear complex 2 represents the first example of a simple bis-uranyl Pacman molecular compound and incorporates a highly unusual co-facial coordination environment for two uranyl ions (see later). In the ¹H NMR spectrum of 1, an asymmetric ligand arrangement is seen, consistent with only one of the two N₄ donor sets being occupied by the uranyl cation. This is evidenced by the presence of two sets of four resonances each for the CH₂ (2.71, 2.54, 2.17 and 1.60 ppm) and CH₃ protons (1.47, 1.05, 0.97 and 0.54 ppm) of the ethyl meso-groups. The magnetic non-equivalence of all four alkyl groups reinforces the
assignment of an asymmetric Pacman geometry to the molecule in solution, with the four sets of resonances due to distinct inner- and outer-cleft ethyl groups. In contrast, the $^1$H NMR spectrum of 2 displays a symmetrical set of ligand resonances consistent with both N$_4$ donor sets being occupied, with four, as opposed to eight, meso-ethyl resonances at 0.90, 1.09, (CH$_3$) and 2.48 (two overlapping CH$_2$ resonances) ppm (see SI).

Scheme 1. Synthesis of mono and di(uranyl) Pacman complexes of L$^A$

The difficulty experienced in the synthesis and isolation of 1 and 2 contrasts with the calculated relative thermodynamic stabilities of the products. In the gas-phase calculations, the mono(actinyl) complexes [AnO$_2$(H$_2$L$^A$)] An = U, Np, Pu were found to be more stable than the binuclear complexes [{AnO$_2$}$_2$(L$^A$)] by 40-50 kcal mol$^{-1}$, a considerable margin presumably arising from the steric clash between the oxo-groups resulting upon complexation of a second uranyl cation. However, the calculated structures omitted the donor solvent molecule in the fifth equatorial site, and calculations that incorporated a continuum solvent model were found to stabilise the formation energy of the binuclear complex by 11 kcal mol$^{-1}$, so reducing the barrier to its formation.$^{21}$

Single crystals suitable for an X-ray structure determination of 2 were grown from pyridine and the solid state
Structure is shown in Figure 1, along with selected distances and angles. Both uranyl cations display pentagonal bipyramidal geometries with the macrocyclic N₄-donor set and the pyridine N-donor atom comprising the equatorial donor ligands and the two oxo atoms, which are mutually \emph{trans} (O-U-O angles 174.0(2) and 176.0(2)°) comprising the axial ligands. The U-O bond distances are short (range = 1.747(4) to 1.779(4) Å) and support the presence of the U(VI) oxidation state; the absorption at 912 cm⁻¹ in the IR spectrum of 2 is also consistent with [UO₂]²⁺. The most notable feature is the short separation of the two oxo groups, O1···O3 2.709(6) Å within the molecular cleft. The two uranyl cations are evidently coordinated with ease in the macrocyclic cavity generated by the anthracenyl groups of L; the N₄-donor sets remain approximately coplanar, subtending an angle of 16.8° due to the steric demand of the \emph{meso}-ethyl groups. However, the two N₄ donor planes are slipped laterally relative to the \emph{meso}-carbons, by rotation around all four N-C anthracenyl bonds. Thus, the perpendicular distance between U₁ and the plane described by U₂, O₃, O₄, and the pyridine nitrogen N₁₀ is 1.957 Å. This lateral twist also allows for favourable π-stacking interactions between the pyridine molecules located in the fifth equatorial coordination site and anthracenyl hinge groups. This contrasts to the complexes of the parent phenylenediamine-derived macrocycle L, in which the inhibition of lateral twisting does not allow favourable aromatic π-stacking interactions.

\textit{Figure 1.} Solid state structure of 2. For clarity, all hydrogen atoms are omitted (displacement ellipsoids are drawn at 50% probability). Selected distances (Å) and angles (°): U₁-O₁ 1.747(4), U₁-O₂ 1.779(4), U₁-O₃ 1.764(4), U₁-O₄ 1.778(4), U₁-N₁ 2.558(6), U₁-N₂ 2.417(6), U₁-N₃ 2.430(6), U₁-N₄ 2.595(6), O₁-U₁-O₂ 174.0(2), 176.0(2).

Attempts to crystallise the mono-uranyl complex 1 from mixtures of 1 and 2 were unsuccessful. However, its structure was verified by analysis of the crude mixture by MALDI-MS in which the ion at 1128 amu was
attributed to $[\text{UO}_2(\text{H}_2\text{L}^\text{A})]^+$, a fragment resulting from desolvation of 1 upon ionisation. Also, a peak at 1528 amu was ascribed to the loss of a single ethyl group from the binuclear complex 2, with further ions at 1452 and 1370 corresponding to mono- and unsolvated fragments.

Examples of complexes which contain a similarly close uranyl oxo contact in the solid state are relatively rare. The uranyl oxalates $[\text{NH}_4]_2[(\text{U}^{\text{VI}}\text{O}_2)(\mu_4-\text{C}_2\text{O}_4)]_3$, $[\text{Rb}]_2[(\text{U}^{\text{VI}}\text{O}_2)(\mu_4-\text{C}_2\text{O}_4)(\text{NO}_3)_3]$, and $[\text{alkyl- imidazolium}]_2[(\text{U}^{\text{VI}}\text{O}_2)(\mu_4-\text{C}_2\text{O}_4)(\text{NO}_3)_3]$ have similarly short oxo-oxo distances of 2.434, 2.702, and 2.703 Å, respectively; all other close O⋯O separations are > 2.8 Å and result from crystal packing in the solid state (39 examples up to 3.0 Å). To our knowledge, none of these contacts persist in solution, whereas a solution of 2 survives unchanged in boiling pyridine over 24 h.

The proximity of the two hexavalent uranyl oxo groups suggests that (electro)chemical reduction by one or more electrons might yield a bimetallic complex with an interesting electronic structure. We have shown previously that magnetic superexchange is facilitated in the binuclear uranium dioxo complex B, and single-electron reduction has been shown to enhance significantly the magnetic properties of lanthanide dinitrogen complexes. Preliminary cyclic voltammetry of 2 in THF (0.2 M Bu$_4$NBF$_4$,Fc$/\text{Fc}$) displayed only an irreversible reduction at $E_{\text{pc}}$ = –2.46 V. If this is assigned to a reduction of the two non-communicating U$^{\text{VI}}$ centres, it represents a significantly more difficult reduction than that of the mononuclear complex $[\text{UO}_2(\text{THF})(\text{H}_2\text{L})]$ A which shows a clear, quasi-reversible U$^{\text{VI}}$/U$^{\text{V}}$ couple at –1.17 V and an irreversible feature, presumed to be U$^{\text{V}}$ to U$^{\text{IV}}$ at –2.88 V. On first inspection, it is a surprise that the redox chemistry of these complexes should be so different, as each uranyl centre contains the same macrocyclic donor set in the equatorial plane. However, the proximity of the oxo atoms within the macrocyclic cleft may be destabilising the reduced states as the Lewis basicity of the oxo groups would be expected to increase considerably on reduction from $[\text{UO}_2]^{2+}$ to $[\text{UO}_2]^+$. Also, the parallel orientation of the uranyl groups within the macrocyclic cleft hinders the formation of diamond or T-shaped CCIs. In support of this, the CV of the mixture of 1 and 2 (since 1 cannot be isolated pure) showed extra, irreversible reductions at $E_{\text{pc}}$ = –1.45 and –2.6 V, potentials similar to those seen for the U$^{\text{VI}}$/U$^{\text{V}}$ and U$^{\text{V}}$/U$^{\text{IV}}$ couples respectively in A, indicating that the pentavalent oxidation state should be almost as readily accessible for mononuclear 1 as it is for A. Furthermore, binuclear complexes of L$^\text{A}$ without ancillary ligands in the molecular cleft such as the Co complex $[\text{Co}_2(L^\text{A})]$ display more straightforward reduction chemistry, with a quasi-reversible reduction at $E_{\text{pc}}$ = –2.32 V (Fc$/\text{Fc}$, PhCN, PT WE) for the Co$^{\text{II}}$/Co$^{\text{I}}$ couple.

We have shown that the computationally-predicted binuclear uranyl complex of L$^\text{A}$, 2, can be synthesised, albeit in low yield due to the difficulties in its isolation from the mononuclear complex 1. The structure of 2 reveals a close oxo-oxo distance within the molecular cleft which considerably affects the reduction chemistry exhibited by these complexes. The computational work also predicted the existence and stability of mixed uranyl-transition metal complexes, so it will be of interest to determine whether these mixed-metal compounds can be prepared and their oxo group chemistry evaluated.
Notes and references


