

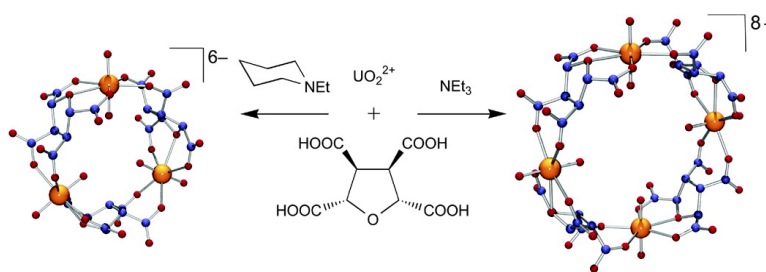
Communication

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Uranyl-Based Metallamacrocycles: Tri- and Tetranuclear Complexes with (2*R*,3*R*,4*S*,5*S*)-Tetrahydrofuran-2,3,4,5-tetracarboxylic Acid

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The use of highly directional coordination bonds in the design of nanometric supramolecules has attracted much attention in recent years, and self-assembly of selected ligands around d transition metal ions is now a widespread method for obtaining polynuclear species displaying a wide range of geometries in an often predictable manner.¹ In contrast, the potential of f-elements, more flexible in their coordination behavior, seems at first less promising. The linear uranyl [dioxouranium(VI)] ion, however, appears as an exception among actinides, owing to its peculiar requirement of tetra-, penta-, or hexa-coordinated planar equatorial environments.

We reported some years ago a first serendipitous example of a large box-shaped assembly including eight uranyl ions, four μ -peroxo ions, and eight monoester derivatives of the *cis,trans* epimer of Kemp's triacid as bridging ligands,² and we later succeeded in obtaining a second molecular cage comprising eight uranyl ions, eight μ -peroxo ions, and four bis(catecholate) ligands.³ However, these syntheses suffered, the first from an unduly elaborated ligand, the second from a quite unstable one (in a basic medium), and both from very low yields and uncontrolled experimental conditions. In our search of other suitable molecules for the design of supramolecular assemblies including uranyl ions, we considered the (2*R*,3*R*,4*S*,5*S*)-tetrahydrofuran-2,3,4,5-tetracarboxylic acid (H₄L), which has never been used in this context but was considered as an extractant in selective partitioning of uranyl from transuranic and lanthanide ions in nuclear waste reprocessing.⁴ Although, in the previous studies, the complexes of H₄L with uranyl in acidic media appeared to be rather weak and the nature of the bonding could not be ascertained, the potentially mirror-symmetric and pentadentate nature of this ligand suggested the design of a macrocyclic tetranuclear species that could actually be obtained along with the corresponding trinuclear one. We describe herein simple routes leading to the quantitative formation, in a basic medium, of the trinuclear [UO₂L]₃⁶⁻ and tetranuclear [UO₂L]₄⁸⁻ complexes which, to the best of our knowledge, are the first uranyl-based metallamacrocycles and provide a rare example (the first with f-element ions) of easy triangle/square size-tailoring in supramolecular assemblies.⁵ Crystallization of one complex or the other is simply determined by the base used to deprotonate the tetraacid, *N*-ethylpiperidine or triethylamine, respectively.

The crystal structures⁶ of the hexa- and octa-anionic supramolecular assemblies are represented in Figure 1. Compounds **1** and **2** crystallize in the hexagonal *P*6₃/*m* and tetragonal *I*4/*m* space groups, respectively, and the asymmetric unit in both cases contains one uranyl ion located on a symmetry plane and half a tetraacid (with the ether atom O3 on the symmetry plane). The uranyl ion in both **1** and **2** is bound to the tridentate site of one ligand and to

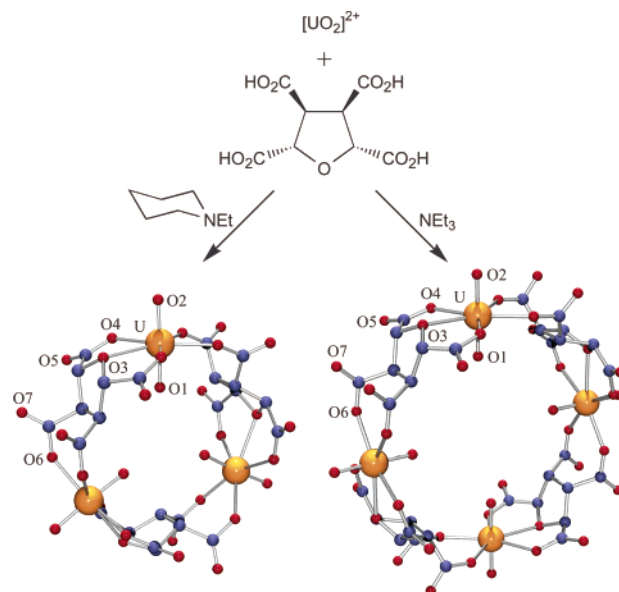


Figure 1. Schematic reaction pathways and ball-and-stick representation of the metallamacrocycles [UO₂L]₃⁶⁻ in **1** (left) and [UO₂L]₄⁸⁻ in **2** (right).

the bidentate site of another, thus defining two five- and one seven-membered chelate rings. The resulting metal environment is pentagonal bipyramidal with mean U–O(oxo), U–O(carboxylate), and U–O(ether) bond lengths of 1.787(10), 2.33(2) and 2.546(2) Å, respectively. As far as we know, these are unique examples of triangular or square assemblies exploiting planar penta-coordination in place of the usual square planar or octahedral ones. The uranium atom and the ether oxygen atom O3 are at distances of 0.026(6) and –0.236(16) Å (**1**) or 0.014(7) and –0.077(19) Å (**2**), respectively, from the plane defined by the four metal-bound carboxylic donor atoms. This equatorial geometry defines the planar parts of the macro-ring, the corners being provided by the rigidly angular ligand, which results in dihedral angles of 60° (**1**) or 90° (**2**) between the mean equatorial planes of adjacent uranyl ions. Three or four uranyl oxo groups are directed toward the cavity center (Figure 2). The distance between the uranium atoms in **1** is 6.9018(15) Å, and the separation between the inner oxo groups is 3.791(19) Å only, leaving little space for inclusion of a guest, whereas in **2**, the distances between adjacent uranium atoms and between two diametrically located oxo groups are 7.4494(12) and 6.98(2) Å, respectively, and the inner oxo groups represent four potential binding sites. The geometries of both uranyl environment and ligand are nearly identical in both compounds, the difference in curvature being essentially due to the rotation of the ligand with respect to the uranyl ions along the O4O4' and O6O6' lines (perpendicular to the symmetry plane), with, as a consequence, the

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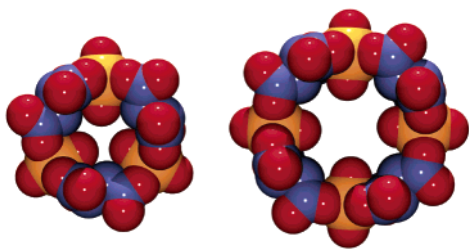


Figure 2. CPK representation of the metallamacrocycles $[\text{UO}_2\text{L}]_3^{6-}$ in **1** (left) and $[\text{UO}_2\text{L}]_4^{8-}$ in **2** (right). Yellow: U, red: O, blue: C.

larger out-of-plane displacement of atom O3 in **1** (vide supra). The possibly more strained nature of the trinuclear complex is reflected in the distances between the oxo atom O1 and the proximal hydrogen atoms, much smaller than in the tetranuclear complex [2.61 Å in **1**, slightly shorter than the sum of van der Waals radii (2.72 Å) and 3.10 Å in **2**]. In contrast with the previous cases of triangle/square coexistence,⁵ the flexibility of the ligand does not seem to be an important parameter in these complexes.

L^{4-} can be viewed as composed of two parts, one including the ether and the two adjoining carboxylate groups and the other comprising the remaining ethylenediacetate group, these two parts being analogous to the oxydiacetate and succinate ligands, respectively.^{4,7} The geometry of uranyl complexes with tridentate oxydiacetate ligands matches that in **1** and **2**.⁸ On the other hand, succinic acid, which is not rigidified as its counterpart in H_4L , is known to react with uranyl to give a polymeric species.⁹ The crystal structures of H_4L , H_3L^- , and H_2L^{2-} and some of their complexes have been reported.⁷ In contrast with all these cases, L^{4-} in **1** displays an ideal mirror symmetry, with the four cyclic carbon atoms perfectly planar and an out-of-plane displacement of 0.54(2) (**1**) or 0.52(2) Å (**2**) for the ether oxygen atom. The six *N*-ethylpiperidinium (**1**) or eight triethylammonium (**2**) counterions are located around the complex and are hydrogen bonded to six or eight carboxylate oxygen atoms [O4 (uranium-bound) in **1** or O7 (uncomplexed) in **2**, and their symmetry equivalents]. Each complex molecule is thus separated from its neighbors by a sheet of hydrogen-bonded cations. Despite the differences in cation/anion association, the crystal structures do not provide any obvious clue about the effect of the cation on the formation of one or the other complex.

ES-MS analysis reveals the presence of both cyclic tri- and tetranuclear complexes in dilute methanol solution of either **1** or **2**.¹⁰ It is likely that the two species are in equilibrium in solution and that the role of the different bases could be limited to promote crystallization of one or the other complex, as observed in other systems.^{5f} The ¹H NMR signals corresponding to the two polyanions in methanol are nearly identical, the small shifts observed being likely due to differences in the association with counterions, and only some line broadening is observed on lowering the temperature down to 181 K.

It has been shown that uranyl complexes with H_4L , in an acidic medium {p[H] 2.5 to 5, dominant species $[\text{UO}_2(\text{H}_2\text{L})]$ with minor amounts of $[\text{UO}_2(\text{HL})]^-$ }, are anomalously weak with respect to those of trivalent or tetravalent lanthanides or actinides, which permits the selective removal of the latter ones.⁴ Steric conflicts between the uranyl oxo groups and some parts of the ligand were predicted by simple molecular mechanics modeling calculations,^{4b}

whatever the coordination site involved, but the structures of **1** and **2** show that complexation of two uranyl ions through the tridentate and bidentate coordination sites to give quite stable cyclic species is possible, which is to be taken into account in further investigations of this molecule as an extracting agent.

We have shown previously that the uranyl ion, owing in particular to the basic nature of the oxo groups, can be used to build supramolecular assemblies involving homooxalixarenes as ligands.¹¹ The ready synthesis of the metallamacrocycles **1** and **2**, which exploits the planar equatorial coordination of this ion, further evidences its potential as a building block in supramolecular chemistry, which has been little investigated hitherto. No protection or blocking step (i.e. no extra ligand on the metal ion) is necessary with this ion since the presence of the two oxo groups ensures planar, and hence side-defining, divergent coordination convenient for ring closure with a preoriented angular ligand. A new family of metallamacrocycles based on this much stereochemically constrained actinide ion is thus open to investigation.

Supporting Information Available: Experimental details and X-ray crystallographic files in CIF format for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) ES-MS data for **1**: m/z 515 $([\text{UO}_2\text{L}]_3 + 3\text{H})^{3-}$; 773 $([\text{UO}_2\text{L}]_3 + 4\text{H})^{2-}$; 830 $([\text{UO}_2\text{L}]_3 + 4\text{H} + \text{pip})^{2-}$; 1031 $([\text{UO}_2\text{L}]_4 + 6\text{H})^{2-}$; 1547 $([\text{UO}_2\text{L}]_3 + 5\text{H})^-$. ES-MS data for **2**: m/z 386 $([\text{UO}_2\text{L}]_3 + 2\text{H})^{4-}$; 515 $([\text{UO}_2\text{L}]_3 + 3\text{H})^{3-}$; 773 $([\text{UO}_2\text{L}]_3 + 4\text{H})^{2-}$; 824 $([\text{UO}_2\text{L}]_3 + 4\text{H} + \text{NET}_3)^{2-}$; 874 $([\text{UO}_2\text{L}]_3 + 4\text{H} + 2\text{NET}_3)^{2-}$; 1031 $([\text{UO}_2\text{L}]_4 + 6\text{H})^{2-}$; 1547 $([\text{UO}_2\text{L}]_3 + 5\text{H})^-$.
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