

A metal-organic molecular box obtained from self-assembling around uranyl ions

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We used the peculiar coordination geometry of uranyl ions to build a three-dimensional superstructure of unprecedented architecture. The complexation of uranyl ions by a monoester derivative of the *cis,trans* regioisomer of Kemp's triacid and μ -peroxy bridges leads to a cage-like molecule with a roughly parallelepipedic inner cavity of ca. 700 Å³ able to host four medium-sized organic molecules.

The search for nanometer-sized molecular or supramolecular containers with recognition properties is a subject of wide interest and the design of molecules defining inner cavities able to host organic molecules or ions has received a new impulse in the last years due to the use of self-assembling from non-covalent interactions, in an attempt to mimic biological processes.^{1,2} Among these interactions, hydrogen bonding has been used to build some remarkable supramolecules such as Rebek's 'tennis ball'³ or Atwood's spherical assembly.⁴ The other most useful non-covalent interaction is the metal ion coordination bond, with its specific geometrical requirements, such as the widely used square planar arrangement.² Among the various architectures resulting from self-assembling around metal ions, the box shape is particularly appealing.⁵ We show herein how the unique coordination properties of the uranyl ion UO₂²⁺ can be used to build nanometer-sized molecular boxes of remarkable shape and size.

It is well known that the highly anisotropic linear uranyl ion requires a nearly planar equatorial environment of four to six donor atoms. We recently began to investigate the complexes of uranyl with ligands derived from Kemp's triacid (*cis,cis*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acid) or its *cis,trans* regioisomer. The ligand used in this work is *t*-5-(4-*tert*-butylbenzyloxycarbonyl)-1,3,5-trimethylcyclohexane-*r*-1,*c*-3-dicarboxylic acid, noted H₂L.⁶ Its single-step reaction with uranyl nitrate hexahydrate in the presence of triethylamine and atmospheric oxygen led to complex **1** whose structure has been determined by X-ray crystallography.† As shown in Fig. 1, the ligand assumes a *chair* conformation in the complex, with the two acid groups in equatorial positions. The anionic complex core (Scheme 1 and Fig. 2) appears to be built from two macrocycles consisting of four uranyl ions and four L²⁻ molecules each, bonded to each other by four μ -peroxy O₂²⁻ ions. The coordination geometry around the uranyl ion comprises six oxygen donor atoms in the equatorial plane, as is usual for small bite bidentate ligands. Each L²⁻ ligand is found, as expected, to be bridging two uranyl ions by its two acid functions [mean U–O distance 2.47(5) Å]. Four structures with uranyl ions bridged by μ -peroxy ions have been reported⁷ and a reaction mechanism proposed.^{7b} The O–O [mean value 1.48(5) Å] and U–O [2.33(3) Å] distances in **1** are in perfect agreement with the values already reported.

The most striking point in this structure is the remarkable

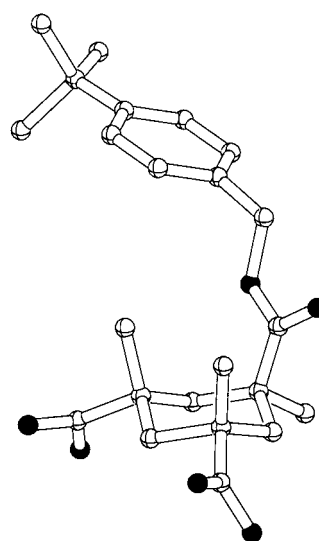
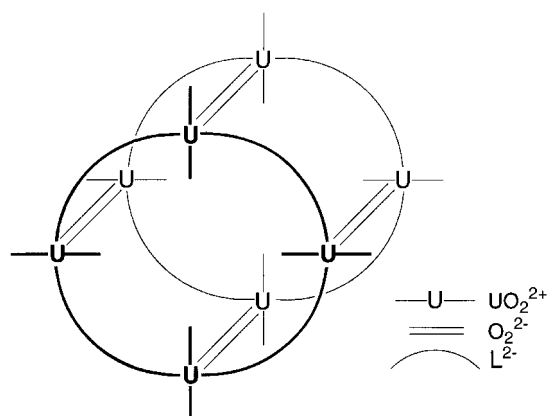


Fig. 1 View of the ligand L²⁻ in the uranyl complex **1**. Oxygen atoms in black.

ability of the ligand L²⁻ to give rise to a four-membered ring of nearly perfect rectangular shape. This can only be achieved because the angle between the two binding 'pincers' is not far from right angle [mean value 83(5)°]. The most striking examples of metal-organic rings with right angles up to now are based on the combination of linear ligands and 'protected' metal ions such as Pt^{II}en or Pd^{II}en (where en is ethylenediamine) which require square planar environments.² The present work illustrates the possibility of another methodology, with the metal ion defining the plane of the parallelepiped faces and the ligand providing the right angle. An example of such a methodology using *trans* coordination of Pd^{II} ions to build large square arrays of porphyrins has recently been reported.⁸

The volume of the inner cavity in **1** can be estimated from the distance between two facing uranyl oxygen atoms, 10.8(3) and 7.6(5) Å in the smaller and larger dimensions respectively, and, in the third direction, which is largely open to the outside, the length of the rigid 'channel' defined by the ligands without their 'tail', which is about 12.6 Å. The resulting value, when taking into account the oxygen ionic radius, is about 700 Å³, which is a low estimation since the distance between facing oxygen atoms defines the 'bottleneck' of the channel. Even more than its size, the internal organization of the cavity is notable since it displays eight bonding sites, comprised of the uranyl oxygen atoms pointing inwards. The propensity of uranyl ions to behave as hydrogen bond acceptors is well documented and has been used in the stereognostic coordination concept,⁹ which consists in designing uranyl-specific ligands able to provide the required



Scheme 1 Schematic representation of the anionic complex core in **1**.

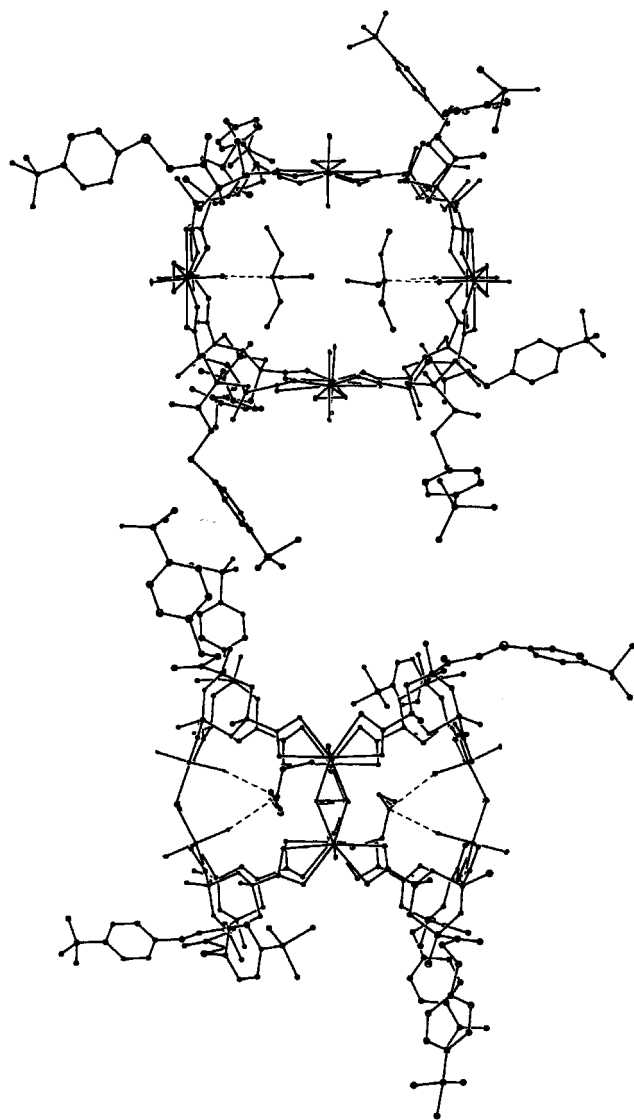


Fig. 2 Two orthogonal views of the structure of **1**. All counter ions and solvent molecules omitted other than the two triethylammonium ions included in the cavity. Hydrogen bonds between nitrogen and uranyl oxygen atoms in dashed lines. Top view parallel to the larger face defined by a $(\text{UO}_2\text{L})_4$ macrocoring. Lower view showing the coordination geometry around uranyl ions and the bridging μ -peroxo ions.

equatorial electron pair donor atoms array plus a hydrogen bonding site. Molecule **1** illustrates the reverse approach: the eight uranyl ions provide inner hydrogen bonding sites able, in principle, to recognize any donor moiety of suitable size and assume in this way a double role, structural and functional. The synthetic procedure adopted led to the inclusion of two triethyl-

ammonium ions which occupy a central position in the cavity, each of them hydrogen bonded to two uranyl oxygen atoms {mean value of $\text{N}\cdots\text{O}$ distances 2.9(1) Å, slightly larger than those previously reported for the same ions [mean value 2.76(6) Å]¹⁰}. The presence of these triethylammonium ions is necessary for the complex to be formed, which is an infrequent phenomenon referred to as 'guest-induced organization' or 'induced fit molecular recognition'.¹¹ These two cations do not fill all the available space and two chloroform molecules (not represented on the drawing for clarity) are also included in the cavity, near its openings. The inclusion of multiple guests is obviously a requisite if one wants to make chemical use of such container molecules, for example in catalysis or to study endohedral micro-environmental chemical processes.

Notes and references

† Preparation of **1**. When a solution of uranyl nitrate hexahydrate (0.5 mmol) in 10 ml of methanol–chloroform (1:1) is added to a solution of H_2L (0.5 mmol) in 15 ml of methanol, no reaction occurs and crystals of H_2L are deposited. When the same procedure is followed by addition of a large excess of triethylamine (1 ml), the solution, initially light yellow, becomes intensely yellow and, under convenient slow evaporation conditions, yields crystals of **1** suitable for X-ray crystallography. ES-MS. Spectra recorded on a QUATTRO II system (Micromass, UK). m/z 1479, $[(\text{L}^{2-})_2(\text{UO}_2^{2+})_2(\text{O}_2^{2-})(\text{HNEt}_3^+)]^-$, $[(\text{L}^{2-})_4(\text{UO}_2^{2+})_4(\text{O}_2^{2-})_2(\text{HNEt}_3^+)]^{2-}$ and $\{[(\text{L}^{2-})_8(\text{UO}_2^{2+})_8(\text{O}_2^{2-})_4(\text{HNEt}_3^+)_2] \cdot [(\text{HNEt}_3^+)_2]\}^{4-}$; m/z 1093, $\{[(\text{L}^{2-})_8(\text{UO}_2^{2+})_8(\text{O}_2^{2-})_4(\text{HNEt}_3^+)_2](\text{CHCl}_3)_2(\text{NEt}_3)_6\}^{6-}$; m/z 1095, $[(\text{L}^{2-})_8(\text{UO}_2^{2+})_8(\text{O}_2^{2-})_3 + \text{H}^+]^{5-}$.

Crystal data: $[(\text{UO}_2^{2+})_8(\text{L}^{2-})_8(\text{O}_2^{2-})_4(\text{HNEt}_3^+)_8] \cdot 5\text{CHCl}_3 \cdot 16\text{H}_2\text{O} \cdot 6\text{CH}_3\text{OH}$, $\text{C}_{243}\text{H}_{429}\text{Cl}_{15}\text{N}_8\text{O}_{64}\text{U}_8$, $M = 7402.93$, monoclinic, space group $P2(1)/n$, $a = 28.2861(13)$, $b = 40.881(3)$, $c = 29.318(2)$ Å, $\beta = 96.882(4)^\circ$, $V = 33657(4)$ Å³, $Z = 4$, $D_c = 1.461$ g cm⁻³, $\mu = 4.027$ mm⁻¹, $F(000) = 14744$, $T = 123(2)$ K. Data collected on a Nonius Kappa-CCD area-detector diffractometer with Mo-K α radiation. Absorption effects empirically corrected. Structure solved by direct methods. Hydrogen atoms not included. Owing to the presence of 368 non-hydrogen atoms in the asymmetric unit and many disordered counter ions and solvent molecules, many restraints and constraints on geometrical and displacement parameters had to be applied. Refinement of 1393 parameters by full-matrix least-squares on F^2 based on 29482 unique reflections (out of 91745 measured reflections), $R_1 = 0.146$ ($wR_2 = 0.282$). CCDC reference number 186/1361. See <http://www.rsc.org/suppdata/dt/1999/1047> for crystallographic files in .cif format.

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