

Two-dimensional assemblies in f-element ion (UO_2^{2+} , Yb^{3+}) complexes with two cyclohexyl-based polycarboxylates



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ABSTRACT

Three complexes of f-element metal cations, uranyl and ytterbium(III), with either Kemp's triacid (H_3L^1) or 1,2,3,4,5,6-cyclohexanhexacarboxylic acid (H_6L^2) were obtained under solvo-hydrothermal conditions. The trianionic ligand in $[\text{H}_2\text{NMe}_2][\text{UO}_2(\text{L}^1)]$ (**1**) is in the very unusual boat conformation, with two equatorial and one axial carboxylate groups. In contrast to the all-axial chair conformation, this ligand geometry is not conducive to the formation of a closed species, and a honeycomb 2D network is formed instead. Adopting the chair conformation, this ligand reacts with ytterbium(III) to give the complex $[\text{Yb}(\text{L}^1)(\text{H}_2\text{O})_2]$ (**2**), which crystallizes as a 2D network. All-*cis* H_6L^2 undergoes isomerization into its all-*trans* form under the conditions used, with all functional groups equatorial. In the presence of additional nickel(II) nitrate, the complex $[\text{Ni}(\text{H}_2\text{O})_6][(\text{UO}_2)_2(\text{L}^2)] \cdot 1.5\text{H}_2\text{O}$ (**3**) is obtained, in which the unusual coordination mode of the hexa-anionic ligand leads to the formation of a 2D assembly.

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1. Introduction

In recent years, cyclohexyl-based polycarboxylates have proven to be a valuable addition to the already wide range of ligands used in the synthesis of uranyl–organic coordination polymers or frameworks (UOFs) [1]. While the simplest member of this family, cyclohexane-1,3-dicarboxylate, gives unsurprising 1D or 2D assemblies [2], the more complex members, with three to six functional groups and, in some cases, additional substituents (resulting in different conformational preferences), yield more original architectures such as polynuclear rings or cages [3–5], and nanotubular arrangements [4,6], as well as 3D frameworks [6,7], some of them including d-block metal cations. An interesting aspect of this series, which differentiates it from that involving the planar aromatic polycarboxylates, is the influence of the ring conformation and the position, axial or equatorial, of the carboxylate groups, on the geometry of the species formed. A striking example is provided by Kemp's triacid (*cis,cis*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acid, H_3L^1), where the most stable conformation, with three axial, and thus convergent, carboxylic groups, favors the formation of closed species [4,5]. In contrast, the equatorial positioning of these groups, also found in the unsubstituted 1,3,5-cyclohexanetricarboxylic acid, favors quasi-planar arrangements [6]. This

apparently simple situation is however subject to exceptions, the most notable being the formation of a nanotubular architecture with the all-equatorial 1,3,5-cyclohexanetricarboxylate [6]. In all these complexes, the cyclohexyl ring is in the chair conformation, the boat being present only in the uranyl ion complex with the geometrically constrained, all-equatorial bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid, which gives a 2D assembly [8]. In the course of the present study, we obtained a novel uranyl ion complex with Kemp's triacid in which the ring is in the boat conformation, a rare case among the structures with this molecule reported in the Cambridge Structural Database (CSD, Version 5.35) [9], and its crystal structure and luminescence properties are described herein. The behavior of this acid with an f-element devoid of the geometrical constraints of uranyl is also of interest, and the crystal structure of its first lanthanide ion complex (apart from that of a mixed uranyl–terbium complex [5]) is also described. Finally, the first crystal structure of a complex formed by all-*trans* 1,2,3,4,5,6-cyclohexanhexacarboxylic acid (H_6L^2) and uranyl ions is described (only uranyl–lanthanide heterometallic species with the all-*cis* form of this ligand having been obtained previously [10]).

2. Results and discussion

2.1. Syntheses

All three complexes were synthesized under solvo-hydrothermal conditions, a modification of the usual hydrothermal method

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which has been found to be useful in uranyl chemistry, enabling in particular the generation of different species through variation of the organic solvent, and to avoid in a fair measure the common uranyl oligomerization through hydrolysis [4–7,11]. While the thermally stable acetonitrile and *N*-methyl-2-pyrrolidone (NMP) were used in the syntheses of **2** and **3**, respectively, *N,N*-dimethylacetamide (DMA) behaves like *N,N*-dimethylformamide (DMF) [7,12] and is hydrolyzed to give dimethylamine and acetic acid under the reaction conditions, resulting in dimethylammonium counter-ions being present in **1**. Whereas crystals of **1** are readily obtained during the heating phase, crystals of **3**, with the hexacarboxylate ligand (L^2)⁶⁻, were only obtained in very low yield after prolonged heating at 140 °C and upon subsequent cooling of the solution. As previously observed, the ligand undergoes isomerization from the all-*cis* to the all-*trans* form under these conditions [13]. This ligand is quite averse to crystallizing in the presence of uranyl ions, and the present conditions are the only ones which led to an exploitable crystalline material, among the many which have been tried, either without additional species, or in the presence of other 3d block metal cations (Mn²⁺, Co²⁺, Cu²⁺), alkali or alkaline-earth cations (Cs⁺, Mg²⁺, Sr²⁺), and under purely hydrothermal or solvo-hydrothermal conditions (with CH₃CN, NMP, DMA or THF). These conditions generally yield precipitates, and in some cases crystals of uranyl oxalate species. These difficulties may be due to the large number of coordinating sites and coordination modes of (L^2)⁶⁻, and the resulting possible presence of mixtures of different species in solution (as well as possibly incomplete isomerization). Crystallization of lanthanide complexes of Kemp's triacid appeared capricious also, and the experiment reported here is the only one which gave any crystalline complex of sufficient quality for structure determination, albeit in low yield, among many others involving combinations of different lanthanide cations (La³⁺, Ce³⁺, Eu³⁺, Tb³⁺ and Lu³⁺), solvents (CH₃CN, NMP, DMA, THF or methanol), temperatures (140 and 180 °C) and additives (bases such as 2,2'-bipyridine, pyridine, pyrazine or DABCO). A common outcome of these reactions is the formation of precipitates which were not further characterized, with crystals of Kemp's triacid or its acetonitrile solvate formed in some cases. Only with Lu³⁺ were crystals isomorphous to those of complex **2** obtained, but of too low a quality for structure refinement.

2.2. Crystal structures

The complex [H₂NMe₂][UO₂(L¹)] (**1**) crystallizes in the orthorhombic space group *Pnma*, with the uranium atom and its two oxo atoms located on the mirror plane perpendicular to the *b* axis (Wyckoff position 4c), which also bisects the trianionic ligand (Fig. 1). The metal atom is chelated by three carboxylate groups from three ligands, with U–O bond lengths in the range 2.452(5)–2.493(7) Å [average 2.468(18) Å], the shortest bond being with O5 and the longest with O3. The hexagonal bipyramidal coordination geometry is unexceptional. The conformation of the ligand is more interesting and unusual. The most frequent conformation of Kemp's triacid (as well as its ester derivatives) is of the chair type, with all carboxylic/ate or ester groups axial [14], due to the 1,3-diaxial repulsions being larger for the methyl groups. However, electrostatic repulsion in the trianionic form favors the equatorial positioning of the carboxylate groups [15], a trend which can be altered by complexation, resulting in a half-chair conformation with two axial carboxylate groups (which was however not definitely established by a crystal structure determination) [16], or even the chair conformation with all three carboxylate groups axial, as frequently observed in uranyl complexes [4,5]. Among the 45 compounds including Kemp's triacid and its ester derivatives which have been crystallographically characterized, only two display a twist-boat conformation

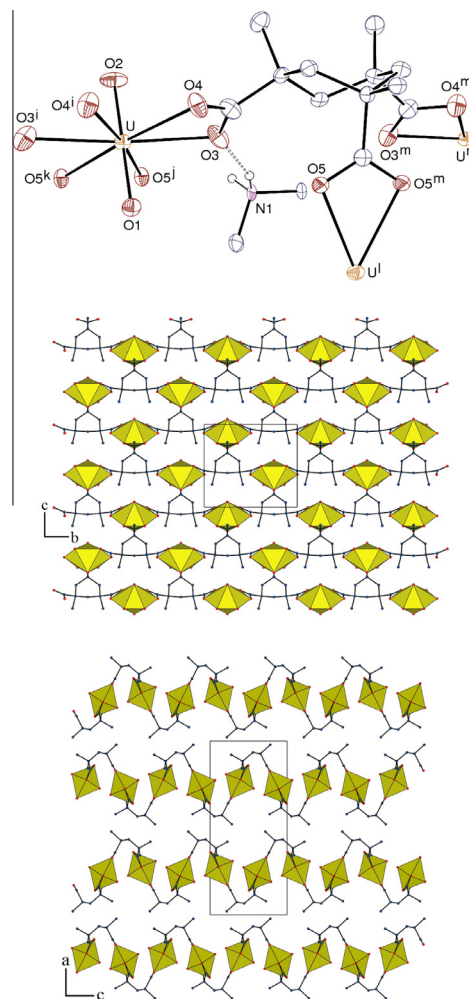


Fig. 1. Top: View of complex **1**. Displacement ellipsoids are drawn at the 30% probability level. Only one position of the disordered ammonium cation is represented. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Symmetry codes: $i = x, 3/2 - y, z$; $j = 1/2 - x, 2 - y, z + 1/2$; $k = 1/2 - x, y - 1/2, z + 1/2$; $l = 1/2 - x, 2 - y, z - 1/2$; $m = x, 5/2 - y, z$. Middle: View of the 2D assembly. Bottom: View of the packing with the layers viewed edge-on. The uranium coordination polyhedra are shown and the counter-ions and hydrogen atoms are omitted in the last two views.

[17,18]. Both compounds contain the trianionic form of the molecule crystallized with ammonium counter-ions, so that electrostatic repulsion may be viewed as the main reason for the conformation change. The conformations in these two species are not identical, since either one carboxylate group is axial and two equatorial [17], or the reverse [18]. The (L^1)³⁻ ligand in complex **1** displays a quite regular boat conformation (the first ever observed for this molecule), with the sequence of C–C–C torsion angles (starting from the atom bearing the O3/O4 carboxylate group) 56.6°, –56.6°, 6.1°, 46.7°, –46.7° and –6.1° (to be compared with $\pm 60^\circ$ for the chair conformation). Two carboxylate groups (O3/O4 and its image by the mirror plane) are equatorial, while the third (O5/O5^m), in the flagpole position, is axial. Obviously, the three carboxylate groups being no longer convergent, this geometry is not favorable to the formation of closed or cyclic species. A honeycomb 2D assembly parallel to (100) is formed instead, in which both metal ion and ligand are 3-fold nodes, thus giving the total point (Schläfli) symbol {6³}. A similar topology was observed in [Hbipy][UO₂(L¹)]·0.5H₂O·0.25THF, in which the trianionic, tris-chelating ligand is in the chair conformation with all carboxylate groups equatorial [5]. The change in the ligand shape

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