Uranyl ion complexation by citric and tricarballylic acids: hydrothermal synthesis and structure of two- and three-dimensional uranium–organic frameworks

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The first crystal structure of uranyl citrate is reported, as well as that of uranyl sodium tricarballylate; both compounds are polymeric, with all acid groups coordinated, but they differ strongly in their coordination modes; the resulting assembly architecture is either three-dimensional with $[(UO_2)_2(Hcit)_2]^{2-}$ metallacycle subunits with citrate or two-dimensional with tricarballylate.

The uranyl-complexing properties of citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) have been extensively studied from the early '50s.[1,2] Recent work has been triggered by the multi-facetted interest in this natural triacid for decontamination technology. Several studies have shown its potential for uranium extraction from soils contaminated by radionuclides or wastes generated by the nuclear industry, giving complexes which can later be subjected to bio- or photodegradation,[3] and its effect on toxic metal mobility has been assessed.[4] Citric acid also dramatically increases uranium accumulation in plants and may thus be an important agent in phytoremediation strategies for contaminated soils.[5] A wealth of data relating to the behaviour of the uranyl–citric acid system in solution is available[1,2,6] and structural information has been obtained by such methods as EXAFS[7] or Energy-Dispersive X-ray Diffraction.[8] However, up to now, the crystal structures of the complexes formed have remained elusive.

Following the investigation of (2*R*,3*R*,4*S*,5*S*)-tetrahydrofuran-tetracarboxylic acid in the synthesis of uranyl-based metallamacrocycles,[9] it also appeared worthwhile to extend this study to the uranyl complexes of triacids, which are likely candidates for the synthesis of uranium–organic polymers, a rapidly developing research field.[10] Single crystals of complexes with citric acid (H_4cit) and the related tricarballylic acid (1,2,3-propanetricarboxylic acid, H_3tca) could not be obtained in organic solvents, but grew readily under mild hydrothermal conditions,† and their structures could be determined.‡ To the best of our knowledge, these results are the first solid state structural contributions to the old problem of the uranyl–citrate interaction.

Both compounds were obtained from reaction between uranyl nitrate hexahydrate and the triacid, in the presence of aqueous NaOH. The asymmetric unit in compound **1**, $[(UO_2)_3(Hcit)_2(H_2O)_3]\cdot 2H_2O$, comprises three uranyl ions and two citrate ligands (Fig. 1a). The uranium atoms U1 and U2 are both bound to one chelating citrate through the hydroxyl (not deprotonated) and α-carboxylate groups, the coordination sphere being completed by three oxygen atoms pertaining to β-carboxylate groups of neighbouring molecules (α and β with respect to the central carbon atom). The third uranium atom, U3, is bound to two oxygen atoms from α-carboxylate groups and three water molecules (Scheme 1a). In all cases, the metal environment is pentagonal bipyramidal, with the oxo groups in axial positions. The mean U–O(hydroxyl) bond length, 2.496(10) Å, is larger than the mean U–O(α-carboxylate) and U–O(β-carboxylate) bond lengths, 2.40(2) and 2.36(3) Å, respectively, which is at variance with the order proposed from EXAFS data.[7a]

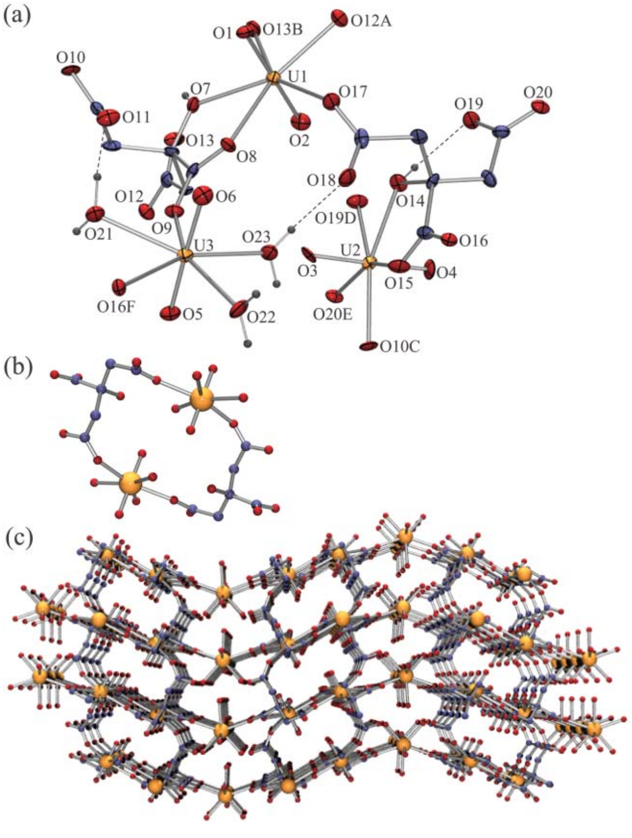

Fig. 1 Crystal structure of **1**. (a) Environment of the uranium atoms with hydrogen bonds shown as dashed lines. Ellipsoids are drawn at the 50% probability level. Symmetry codes: A = *x* − 1, *y*, *z*; B = *x* − ½, ½ − *y*, −*z*; C = *x*, *y* + 1, *z*; D = *x* + ½, 3/2 − *y*, −*z*; E = *x* + 1, *y*, *z*; F = 1 − *x*, *y* − ½, ½ − *z*. (b) 2 : 2 Metallacycle viewed down the *a* axis. (c) View of the packing (*c* axis horizontal, *b* axis vertical). Water solvent molecules are omitted.

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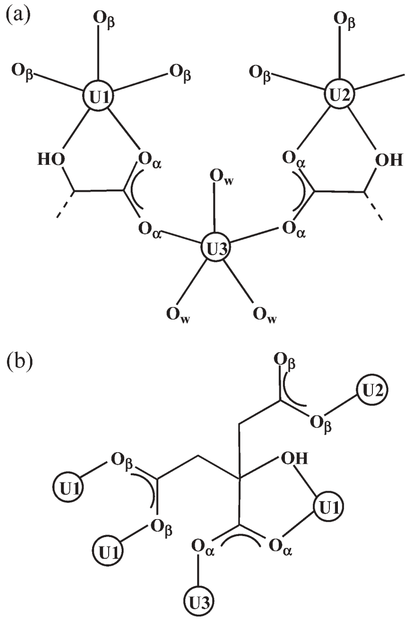

Scheme 1 (a) The uranyl ions' coordination sphere in **1**. The oxo groups are omitted. (b) Citrate coordination in **1** (U1 and U2 are permuted for the second citrate ligand). OH, O_α, O_β and O_w stand for hydroxyl, α-carboxylate, β-carboxylate and water oxygen atoms, respectively. U*n* represents the uranium atom labelled *n* or one of its equivalents by symmetry.

Two of the U3–O(water) bond lengths are short [mean value 2.367(13) Å] and the third one longer [2.495(6) Å]. Each citrate molecule, apart from chelating one uranyl ion, is bound to four uranium atoms, *i.e.* U3 through one oxygen atom of the α-carboxylate group and three atoms equivalent to U1 or U2 through the β-carboxylate groups, with no metal-bridging oxygen atom and no chelating bidentate carboxylate group (Scheme 1b). Each citrate is thus bound to five metal centres, with a conformation in which one of the β-carboxylate groups is swung away with respect to the extended conformation (one *anti* and one *gauche* angles are defined by these two groups around the central carbon atom).[11] The part of both citrates defined by the central carbon atom and the hydroxyl and α-carboxylate groups is nearly planar [torsion angles around the C–C bond 7.2(12) and 9.7(12)°]. Due to the twisted citrate conformation, $[(UO_2)_2(Hcit)_2]^{2-}$ 2 : 2 metallacycles are formed (Fig. 1b),[12] which are further bound to neighbouring ones to form adjacent very narrow channels directed along the *a* axis. These channels are arranged in layers parallel to the *ab* plane and are bridged by $[UO_2(H_2O)_3]^{2+}$ units to give a three-dimensional polymer (Fig. 1c). An extended hydrogen bonding network links the coordinated and solvent water molecules and the hydroxyl and acid groups of the citrate ligands.

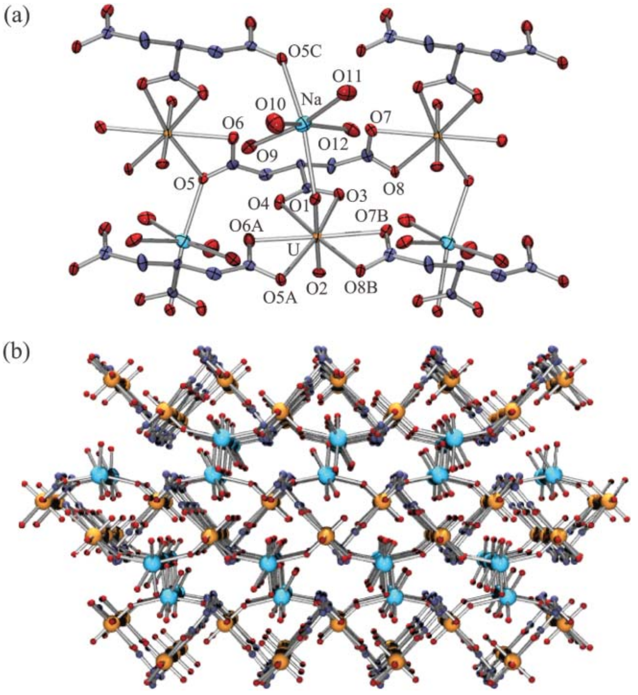

Fig. 2 Crystal structure of **2**. (a) The asymmetric unit and its surroundings. Hydrogen atoms omitted. Ellipsoids are drawn at the 50% probability level. Symmetry codes: $A = x + \frac{1}{2}, \frac{3}{2} - y, 1 - z$; $B = x + \frac{1}{2}, \frac{3}{2} - y, 1 - z$; $C = x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$. (b) View of the packing (*a* axis horizontal, *c* axis vertical). The sheets parallel to the *ab* plane are viewed edge on.

Compound **2**, $[(UO_2)Na(tca)(H_2O)_4]$, by contrast with **1**, includes both uranium and sodium ions. The uranium atom is bound to three chelating carboxylate groups pertaining to three different molecules, which gives a hexagonal bipyramidal environment with the oxo atoms in axial positions (Fig. 2a). The mean U–O(acid) bond length, 2.47(3) Å, is larger than in **1** due to the larger equatorial coordination number. Each tca molecule, in extended conformation (the torsion angles defined around the central carbon atom by the β-carboxylate groups are *anti*) is thus bound to three uranium atoms. The plane defined by the α-carboxylate group being nearly orthogonal to that defined by the two β groups, bidimensional zigzag uranium–organic polymers parallel to the *ab* plane are formed. The $[Na(H_2O)_4]^+$ group occupies the vacant space in the triangular grooves thus created. The Na atom is bonded to the uranyl oxo atom O1 [Na–O1 2.715(9) Å, larger than usual[13]], the acid oxygen atom O5 (which is bridging the two cations) and four water molecules, in a distorted octahedral environment. The $[Na(H_2O)_4]^+$ moieties are thus located on both surfaces of the layers, the surfaces of adjacent layers along the *c* axis facing each other with extended hydrogen bonding as inferred from the O···O distances. Surprisingly, no water is incorporated as solvent in the interlayer space, as it is often the case in analogous clay-like structures.

Comparison of the structures of compounds **1** and **2**, obtained under similar conditions, but differing in every respect both at the metal environment and polymeric arrangement levels, is evidence for the remarkable effect of the hydroxyl group in citrate. The variability in metal complexation, with the possible coexistence of different environments in the same species and extensive water coordination as observed in **1**, points to the difficulty of generalizing these observations or using such simple organic polyacids as models for uranyl complexation by natural organic matter such as humic or fulvic acids.

The structure of **1** is representative of the insoluble uranyl complexes which could form at high temperatures with naturally occurring citrates but, of course, it can only provide indirect clues to the solution behaviour of the uranyl–citrate system. Following much controversy, it is presently admitted that, in the pH range

~2–4, the predominant species in solution is the dimer $[(UO_2)_2(Hcit)_2]^{2-}$, with coordination through both hydroxyl and carboxylate groups.[1b,2,7a,c] Indeed, complexation by the hydroxyl oxygen, which has been shown to prevent biodegradation,[4a] is evidenced in **1**. Although the overall metal : citrate stoichiometry in **1** is 3 : 2 (observed in solution for pH > 6.5[2]), the basic unit is also a dimer, but it differs from the models previously proposed in that each uranium is bonded to each citrate in monodentate fashion. The shortest U···U distance, ~3.9 Å in solution[7a,8] and 5.8 Å in **1** evidences further difference. The absence of chelating bidentate carboxylate and bridging hydroxyl groups accounts for this much less compact uranium arrangement in the crystal.

From the solid state chemistry viewpoint, the present results add to the current wide use of dicarboxylic acids to synthesize microporous uranyl–organic species[10] and demonstrate the unexplored potential and versatility of triacids as multifunctional uranium assemblers.

Notes and references

† Synthesis of **1**. $UO_2(NO_3)_2 \cdot 6H_2O$ (200 mg, 0.40 mmol), citric acid (77 mg, 0.40 mmol) and NaOH (32 mg, 0.80 mmol) in demineralized water (3 mL) were placed in a 20 mL tightly closed vessel and heated at 180 °C under autogenous pressure (pH ~1.8). Yellow crystals of **1** appeared in 24 h. After a week, the product was filtered and washed with water, giving a yellow crystalline powder in 77% yield. Anal. calcd. for $C_{12}H_{20}O_{25}U_3$: C, 11.28; H, 1.58. Found: C, 11.21; H, 1.61%. The same compound was obtained with a 3 : 2 : 4 U : acid : Na stoichiometry. Synthesis of **2**. Analogous as for **1**, with a 1 : 1 : 2 U : acid : Na stoichiometry (pH ~1.4). Yellow crystals appeared in 48 h. After two weeks, the product was filtered and washed with water, giving a yellow crystalline powder in 48% yield. Anal. calcd. for $C_6H_{13}NaO_{12}U$: C, 13.39; H, 2.44; Na, 4.27. Found: C, 13.46; H, 2.42; Na, 4.22%.

‡ Crystal data for **1**: $[(UO_2)_3(Hcit)_2(H_2O)_3] \cdot 2H_2O$, $C_{12}H_{20}O_{25}U_3$, M = 1278.37, orthorhombic, space group $P2_12_12_1$, a = 8.2331(4), b = 10.8651(7), c = 28.5582(18) Å, V = 2554.6(3) $Å^3$, Z = 4, T = 100(2) K. Refinement of 362 parameters on 4812 independent reflections out of 46951 measured reflections (R_{int} = 0.086) led to R_1 = 0.029, wR_2 = 0.076 and S = 1.061. Crystal data for **2**: $[(UO_2)Na(tca)(H_2O)_4]$, $C_6H_{13}NaO_{12}U$, M = 538.18, orthorhombic, space group $P2_12_12_1$, a = 7.8259(6), b = 10.0351(5), c = 16.9494(14) Å, V = 1331.10(16) $Å^3$, Z = 4, T = 100(2) K. Refinement of 182 parameters on 2522 independent reflections out of 26091 measured reflections (R_{int} = 0.072) led to R_1 = 0.036, wR_2 = 0.094 and S = 1.170. Data were collected on a Nonius Kappa-CCD area-detector diffractometer and processed with HKL2000.[14] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXTL.[15] CCDC 292337 and 292338. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516191f

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