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Favoring Framework Formation through Structure-Directing Effects in Uranyl Ion Complexes with 1,2,3,4-(Cyclo)butanetetracarboxylate Ligands

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ABSTRACT: Six uranyl ion complexes with 1,2,3,4-cyclobutanetetracarboxylic acid (H₄CBTC) and one with 1,2,3,4-butanetetracarboxylic acid (H₄BTC) have been obtained under solvo-hydrothermal conditions in the presence of diverse, organic or metallic counterions. The different conformations found for the cyclic ligand (*cis,trans,cis* or *trans,trans,trans* in most cases, with one instance of *cis,trans,trans*), the diverse coordination modes adopted, and the presence of additional metal cations in some cases result in variations in dimensionality and topology of the complexes formed. Two complexes involve protonated azamacrocycles as counterions, [*R,S*-Me₆cyclamH₂][UO₂(CBTC)] (**1**) and [cyclamH₄][UO₂(CBTC)]₂ (**2**), where cyclam = 1,4,8,11-tetraazacyclotetradecane and *R,S*-Me₆cyclam = 7(*R*),14(*S*)-5,5,7,12,12,14-hexamethylcyclam, which crystallize as a one-dimensional (1D) ribbon-like coordination polymer and a two-dimensional (2D) network with sql topology, respectively, the counterions providing additional hydrogen bonding connectivity. The heterometallic complex [(UO₂)₂(HCBTC)₂Cu(*R,S*-Me₆cyclam)(H₂O)₂] (**3**) crystallizes as a 2D network with the V₂O₅ topology, in which the Cu^{II} cations link uranyl-based 1D subunits, while [UO₂(CBTC)Cu(bipy)(H₂O)] (**4**) displays also a 2D arrangement in which the Cu^{II} cations do not directly contribute to dimensionality increase. The high coordination number of Pb^{II} in the heterometallic complexes [UO₂Pb(CBTC)(H₂O)]·0.5H₂O (**5**) and [UO₂Pb(BTC)(H₂O)]·0.5H₂O (**6**) allows the formation of intricate three-dimensional (3D) frameworks, with the presence of channels in **6**; in both cases, columns of face- or edge-sharing lead(II) coordination polyhedra are found, with edge- or apex-sharing uranium coordination polyhedra attached to them. The homometallic complex [H₂NMe₂]₄[(UO₂)₄(CBTC)₃] (**7**) crystallizes as a cubic 3D framework with ctn topology different from the other cubic framework with tfg topology previously reported; the presence of channels in **7** results in the lowest packing index of the series. The uranyl emission spectra of compounds **1** and **2** display maxima positions of the vibronic fine structure peaks in agreement with those usually found for carboxylate complexes with uranyl O₅ equatorial environments.

INTRODUCTION

As is well-known, the quasi-planar arrangement of ligands around the linear uranyl cation results in inorganic lattices or coordination polymers based on this ion being most often one- or two-dimensional (1D or 2D) and either close to planarity or gently corrugated.¹ Although many three-dimensional (3D) frameworks as well as discrete, closed polynuclear species have been reported,^{2–6} finding the right ligands and conditions to promote 3D polymerization is still a trial-and-error process. Polytopic ligands (such as polycarboxylates) displaying non-planar connectivity to several metal cations are obvious candidates, but even in such cases some degree of flexibility is retained and the proper structure-directing species may have to be found.⁶ Additional metal cations interacting either with carboxylates or with uranyl cations through oxo-bonding are an efficient means, and possibly one of the most reliable, of increasing polymerization dimensionality, often through linking 2D uranyl-based subunits.^{4,7} Counterions, either metallic or organic,⁸ and even coordinated solvents⁹ exert less predictable but nevertheless exploitable structure-directing effects.

With the aim to further explore the effects of counterions on the dimensionality and topology of uranyl-containing polymeric species formed with ligands of high connectivity potential, we turned to two tetracarboxylic acids, 1,2,3,4-butanetetracarboxylic acid (H₄BTC) and 1,2,3,4-cyclobutanetetracarboxylic acid (H₄CBTC). In their partially or fully deprotonated forms, these are ligands potentially able to give 3D frameworks, provided the right conditions are found. Uranyl ion complexes with the former, in its fully deprotonated form, are difficult to crystallize, and, prior to the present work, only a complex displaying a 2D square lattice arrangement has been crystallographically characterized.¹⁰ Five uranyl ion complexes are known with the latter, more geometrically constrained acid, either fully or partially deprotonated and assuming either the *cis,trans,cis* (*ctc*) or *trans,trans,trans* (*ttt*) conformation, which crystallize as 2D or 3D assemblies.^{10–12} Using different counterions, we have now

obtained a second complex with BTC^{4-} , and six with HCBTC^{3-} or CBTC^{4-} , which crystallize as 1D, 2D or 3D species. The counterions used are the protonated azamacrocycles cyclamH_4^{4+} (cyclam = 1,4,8,11-tetra-azacyclotetradecane) and $R,S\text{-Me}_6\text{cyclamH}_2^{2+}$ ($R,S\text{-Me}_6\text{cyclam}$ = 7(*R*),14(*S*)-5,5,7,12,12,14-hexamethylcyclam, meso isomer), and the complex $[\text{Cu}(R,S\text{-Me}_6\text{cyclam})]^{2+}$, one of the 3d block metal ion complexes with tetraazamacrocycles previously exploited as counterions with other polycarboxylates,^{13,14} the $\text{Cu}(\text{bipy})^{2+}$ moiety (bipy = 2,2'-bipyridine), Pb^{2+} , which its large coordination number makes useful for increasing the dimensionality of uranyl complexes,^{8,15-18} and finally the dimethylammonium cation, commonly present adventitiously due to hydrolysis of DMF solvent. All these complexes have been characterized by their crystal structure and, when possible, their emission spectrum in the solid state.

EXPERIMENTAL SECTION

Syntheses. *Caution!* Uranium is a radioactive and chemically toxic element, and uranium-containing samples must be handled with suitable care and protection.

$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (depleted uranium, R. P. Normapur, 99%) and $\text{Pb}(\text{NO}_3)_2$ were purchased from Prolabo, 1,2,3,4-butanetetracarboxylic acid (H_4BTC), 1,2,3,4-cyclobutanetetracarboxylic acid (H_4CBTC), and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ were from Aldrich, and 2,2'-bipyridine was from Fluka. $R,S\text{-Me}_6\text{cyclam} \cdot 4\text{HNO}_3$ was obtained by treating $R,S\text{-Me}_6\text{cyclam}$ with excess 2M HNO_3 , slow evaporation of the solution at room temperature giving large colorless tablets of the salt. $[\text{Ni}(\text{cyclam})(\text{NO}_3)_2]$ and $\text{N}(R,S,R,S)\text{-}[\text{Cu}(R,S\text{-Me}_6\text{cyclam})(\text{NO}_3)_2]$ were synthesized as previously reported.^{13,14} The sample of H_4CBTC used was previously shown to contain only the *cis,trans,cis* (*ctc*) isomer.¹⁰ Elemental analyses were performed by MEDAC Ltd. at Chobham, UK. For all syntheses, the mixtures in demineralized

water were placed in 10 mL tightly closed glass vessels and heated at 140 °C under autogenous pressure.

[R,S-Me₆cyclamH₂][UO₂(CBTC)] (1). H₄CBTC (23 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (35 mg, 0.07 mmol), and *R,S*-Me₆cyclam·4HNO₃ (54 mg, 0.10 mmol) were dissolved in water (1.0 mL) and DMF (0.2 mL). Yellow crystals of complex **1** were obtained in low yield within three days, mixed with a powder which was not further characterized. A quantity of crystals sufficient for luminescence measurements was separated by hand.

[cyclamH₄][UO₂(CBTC)]₂ (2). H₄CBTC (23 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (35 mg, 0.07 mmol), and [Ni(cyclam)(NO₃)₂] (20 mg, 0.05 mmol) were dissolved in water (0.7 mL). Yellow crystals of complex **2** were obtained overnight (18 mg, 43% yield based on U). Anal. Calcd for C₂₆H₃₆N₄O₂₀U₂: C, 26.01; H, 3.02; N, 4.67. Found: C, 25.63; H, 2.94; N, 4.49%.

*[(UO₂)₂(HCBTC)₂Cu(*R,S*-Me₆cyclam)(H₂O)₂] (3)*. H₄CBTC (23 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (35 mg, 0.07 mmol), and N(*R,S,R,S*)-[Cu(*R,S*-Me₆cyclam)(NO₃)₂] (24 mg, 0.05 mmol) were dissolved in water (0.6 mL) and acetonitrile (0.2 mL). Purple crystals of complex **3** were obtained in low yield within two days.

[UO₂(CBTC)Cu(bipy)(H₂O)] (4). H₄CBTC (23 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (50 mg, 0.10 mmol), Cu(NO₃)₂·2.5H₂O (23 mg, 0.10 mmol), and 2,2'-bipyridine (16 mg, 0.10 mmol) were dissolved in water (1.2 mL). Green crystals of complex **4** were obtained in low yield within two weeks.

[UO₂Pb(CBTC)(H₂O)]·0.5H₂O (5). H₄CBTC (23 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (50 mg, 0.10 mmol), and Pb(NO₃)₂ (33 mg, 0.10 mmol) were dissolved in water (0.7 mL) and acetonitrile (0.2 mL). Yellow crystals of complex **5** were obtained in low yield within two months.

[UO₂Pb(BTC)(H₂O)]·0.5H₂O (6). H₄BTC (23 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (50 mg, 0.10 mmol), Pb(NO₃)₂ (33 mg, 0.10 mmol), and 2,2'-bipyridine (16 mg, 0.10 mmol) were

dissolved in water (0.7 mL) and acetonitrile (0.2 mL). Yellow crystals of complex **6** were obtained in low yield within two weeks.

$[H_2NMe_2]_4[(UO_2)_4(CBTC)_3]$ (**7**). H_4CBTC (23 mg, 0.10 mmol), $UO_2(NO_3)_2 \cdot 6H_2O$ (50 mg, 0.10 mmol), and PPh_3MeBr (36 mg, 0.10 mmol) were dissolved in water (0.6 mL) and DMF (0.2 mL). Yellow crystals of complex **7** were obtained in low yield within two weeks.

Crystallography. The data were collected at 100(2) or 150(2) K on a Nonius Kappa-CCD area detector diffractometer¹⁹ using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The crystals were introduced into glass capillaries with a protective coating of Paratone-N oil (Hampton Research). The unit cell parameters were determined from ten frames, then refined on all data. The data (combinations of ϕ - and ω -scans with a minimum redundancy of at least 4 for 90% of the reflections) were processed with HKL2000.²⁰ Absorption effects were corrected empirically with the program SCALEPACK.²⁰ The structures were solved by intrinsic phasing with SHELXT,²¹ expanded by subsequent difference Fourier synthesis and refined by full-matrix least-squares on F^2 with SHELXL-2014.²² All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen and nitrogen atoms were retrieved from difference Fourier maps when possible, and the carbon-bound hydrogen atoms were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH_3 , with optimized geometry). Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with ORTEP-3,²³ and the polyhedral representations with VESTA.²⁴ The topological analyses and nodal representations were made with TOPOS.²⁵ Special details are as follows.

Compound **3**. One of the methyl substituents of the centrosymmetric Me₆cyclam moiety is disordered over the two possible carbon atoms of the ring, and the two positions were refined with occupancy parameters constrained to sum to unity.

Compound **4**. Two-component twinning was detected with TwinRotMat (PLATON²⁶) and taken into account in the refinement.

Compound **5**. The lattice water molecule is disordered over two sites which were refined with occupancy parameters constrained to sum to unity. Its hydrogen atoms were neither found, nor introduced.

Compound **6**. Atom Pb1 is disordered over two sites close to one another, one of them being largely dominant (occupancy parameter 0.94); the position of the minor component may not be perfectly determined, and it may be associated with unresolved disorder of the ligand. The water solvent molecule was given an occupancy parameter of 0.5 so as to retain an acceptable displacement parameter.

Compound **7**. The two dimethylammonium counterions are heavily disordered and badly resolved, and both have been refined with occupancy parameters of 1/6, both for charge equilibrium and to retain acceptable displacement parameters.

Luminescence Measurements. Emission spectra were recorded on solid samples using a Horiba-Jobin-Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon arc lamp, double-grating excitation and emission monochromators (2.1 nm mm⁻¹ of dispersion; 1200 grooves mm⁻¹), and a TBX-04 single photon-counting detector. The powdered compound was pressed between two silica plates which were mounted such that the faces were oriented vertically and at 45° to the incident excitation radiation. An excitation wavelength of 420 nm, a commonly used point although only part of a broad manifold, was used in all cases and the emission was monitored between 450 and 650 nm.

Table 1. Crystal Data and Structure Refinement Details

	1	2	3	4	5	6	7
chemical formula	C ₂₄ H ₄₂ N ₄ O ₁₀ U	C ₂₆ H ₃₆ N ₄ O ₂₀ U ₂	C ₃₂ H ₅₀ CuN ₄ O ₂₂ U ₂	C ₁₈ H ₁₄ CuN ₂ O ₁₁ U	C ₈ H ₇ O _{11.5} PbU	C ₈ H ₉ O _{11.5} PbU	C ₃₂ H ₄₄ N ₄ O ₃₂ U ₄
<i>M</i> (g mol ⁻¹)	784.64	1200.65	1382.36	735.88	732.36	734.37	1948.83
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	cubic
space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>m</i>	<i>C</i> 2/ <i>c</i>	<i>I</i> -43 <i>d</i>
<i>a</i> (Å)	8.6568(4)	9.3916(7)	10.8390(4)	11.0333(7)	7.2046(3)	26.0713(17)	18.7901(4)
<i>b</i> (Å)	11.1063(7)	9.5919(5)	18.6329(10)	13.9154(11)	16.6491(12)	7.3555(3)	18.7901(4)
<i>c</i> (Å)	15.6213(15)	9.8049(7)	11.3003(6)	25.537(2)	10.7003(8)	16.2349(10)	18.7901(4)
<i>α</i> (deg)	88.047(3)	111.545(5)	90	90	90	90	90
<i>β</i> (deg)	86.968(5)	104.426(4)	115.281(3)	102.334(5)	104.749(4)	104.421(3)	90
<i>γ</i> (deg)	69.987(3)	95.625(5)	90	90	90	90	90
<i>V</i> (Å ³)	1409.04(18)	777.84(10)	2063.65(18)	3830.3(5)	1241.21(14)	3015.2(3)	6634.2(4)
<i>Z</i>	2	1	2	8	4	8	4
<i>T</i> (K)	100	150	100	150	100	150	100
reflns colld	75459	42589	69898	46276	50086	97621	63021
indep reflns	5346	2958	3911	7211	3302	2857	1427
obsd reflns [<i>I</i> > 2σ(<i>I</i>)]	4804	2633	3417	5997	2692	2625	1250
<i>R</i> _{int}	0.059	0.059	0.031	0.045	0.044	0.022	0.019
params refined	358	235	291	596	221	209	102
<i>R</i> ₁	0.029	0.026	0.025	0.052	0.029	0.026	0.028
<i>wR</i> ₂	0.078	0.061	0.063	0.126	0.061	0.069	0.074
<i>S</i>	1.054	1.032	1.048	1.028	1.014	1.086	1.059
Δρ _{min} (e Å ⁻³)	-1.53	-1.54	-1.49	-2.58	-1.87	-1.70	-0.79
Δρ _{max} (e Å ⁻³)	1.94	1.58	1.25	2.52	1.84	1.86	0.46
Flack parameter							-0.01(3)

RESULTS AND DISCUSSION

Synthesis. Single crystals of complexes **1–7** were obtained under either purely hydrothermal (**2** and **4**) or solvo-hydrothermal conditions (DMF for **1** and **7**, CH₃CN for **3**, **5** and **6**) at a temperature of 140 °C. In all cases, the crystals were grown at high temperature and not upon subsequent cooling of the solutions. The uranyl/ligand stoichiometry is 1:1 for complexes **1–6**, and 4:3 for **7**. In complexes **1** and **3–6**, the counterions present are those which were intended. In the case of complex **2**, it appears that the expected [Ni(cyclam)]²⁺ cation was decomposed, and the fully protonated cyclamH₄⁴⁺ species is found instead as counterion. Since [Ni(cyclam)]²⁺ is highly resistant to acid-catalysed dissociation,²⁷ as shown by several cases in which it was incorporated in compounds obtained under conditions similar to the present ones,¹³ it appears that the CBTC⁴⁻ anion must have some role in displacing the macrocycle here. This provides yet another example of reactions occurring under solvo-hydrothermal conditions which are unexpected on the basis of observations under ambient conditions. In complex **7**, the

PPh_3Me^+ cation present in the solution is absent from the final solid complex, the counterion present being the ubiquitous H_2NMe_2^+ cation formed in situ from DMF hydrolysis. In the many known structures in which this cation is present, its hydrogen bonding capacity appears to be an important factor stabilizing the lattice. The $\text{CBTC}^{4-}/\text{HCBTC}^{3-}$ ligand retains its original *cis,trans,cis* (*ctc*) or *R,S,S,R* conformation in complexes **1–4**, but it appears to have undergone isomerization in complex **7**, to give the *trans,trans,trans* (*ttt*) or *R,R,R,R/S,S,S,S* conformation, as previously observed in other complexes synthesized under hydrothermal conditions,^{10–12,28} possibly as a result of carbanion formation through acid/base equilibria followed by pyramidal inversion.¹⁰ More unusually, complex **5** contains an equimolar mixture of *ctc* and *cis,trans,trans* (*ctt*) forms, the latter previously unobserved among the 65 crystal structures containing the CBTC skeleton reported in the Cambridge Structural Database (CSD, Version 5.40).²⁹ Thus, although the precise rates of isomerization are unknown, it would appear that a mixture of isomers may have been present in all the reaction mixtures. The nature of complex **3** indicates that the carboxylate ligands may also be present in various degrees of protonation. The single crystalline complex of BTC^{4-} presently isolated contains, as in other known instances of its uranyl ion complexes,¹⁰ the ligand as its *R,S* isomer.

Crystal Structures. The complex $[\text{R,S-Me}_6\text{cyclamH}_2][\text{UO}_2(\text{CBTC})]$ (**1**) contains a unique uranyl cation which is bound through 7-membered chelate ring formation involving adjacent carboxylate groups of two separate ligands (atoms O3 and O5 from one ligand, and O7^j and O9^j from the other), and is also bound to one more carboxylate donor from a third ligand (O4ⁱ), as shown in Figure 1. The uranium atom environment is thus pentagonal bipyramidal, with unexceptional bond lengths [U–O(oxo) 1.784(3) and 1.790(3) Å, U–O(carboxylato) 2.334(3)–2.434(3) Å]. The CBTC^{4-} ligand is in the *ctc* conformation and the

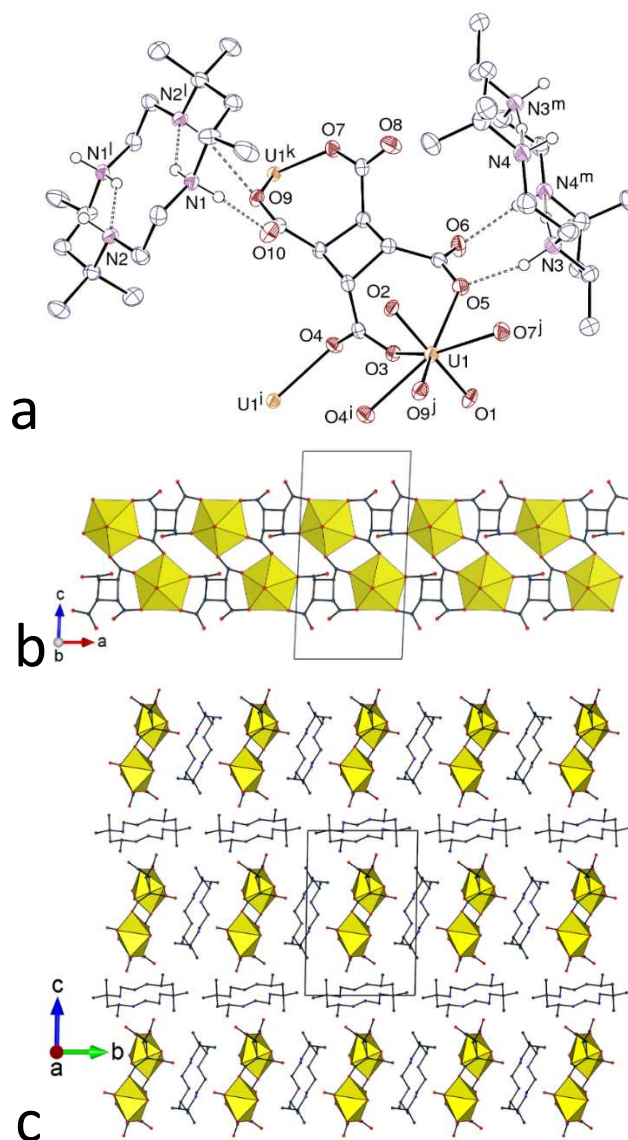


Figure 1. (a) View of compound **1**. Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Symmetry codes: $i = 1 - x, 1 - y, 1 - z$; $j = x - 1, y, z$; $k = x + 1, y, z$; $l = 2 - x, 2 - y, 1 - z$; $m = 1 - x, 1 - y, 2 - z$. (b) View of the 1D coordination polymer. (c) Packing with chains viewed end-on. Uranium coordination polyhedra are colored yellow and hydrogen atoms are omitted in the last two views.

cyclobutane ring is only slightly puckered, with a root mean square (rms) deviation of 0.085 Å. This form of the ligand provides two oppositely directed pairs of carboxylate units (each involved in metal chelation) where the spatial disposition of the two carboxylates of each pair is very similar to that in phthalate or *cis*-1,2-cyclohexanedicarboxylate^{7,13} dianions. Each

CBTC⁴⁻ ligand is bound to three uranium atoms, so that both metal and ligand are 3-connected nodes. This results in the formation of a ribbon-like, double-stranded 1D coordination polymer running along [100]. The two strands in the chain consist of alternating uranyl and CBTC⁴⁻ entities, one otherwise uncoordinated carboxylate oxygen atom of every second 7-membered ring serving to link the two strands together. These polymer chains are surrounded on four sides by the doubly protonated tetraazamacrocycles, [R,S-Me₆cyclamH₂]²⁺, in such manner that layers of alternate cations and anions parallel to (001) are separated by thinner layers of cations, the overall packing being quite compact, as shown by the Kitaigorodski packing index (KPI, estimated with PLATON²⁶) of 0.71. The cocoon of protonated macrocycle units about each chain provides multiple NH...O interactions to each side of the macrocycle, involving both oxo and carboxylate oxygen atoms as acceptors [N...O 2.746(5)–3.259(5) Å, N–H...O 127–174°], thus giving a 3D structure to the lattice. There are also two intramolecular NH...N hydrogen bonds in each centrosymmetric tetraazamacrocycle [N...N 2.817(5) and 2.811(6) Å, N–H...N 141 and 146°], and the four nitrogen atoms are consequently pointing toward the macrocycle internal space, the conformation of the macrocycle being essentially the same as that found in its Ni^{II} and Cu^{II} complexes.

Replacement of [R,S-Me₆cyclamH₂]²⁺ by [cyclamH₄]⁴⁺, while retaining the same uranyl/CBTC⁴⁻ stoichiometry as in **1**, gives the complex [cyclamH₄][UO₂(CBTC)]₂ (**2**). The unique uranyl cation is here also chelated by two carboxylate groups from the same ligand forming a 7-membered chelate ring, and it is also bound to three carboxylate oxygen atoms from three more ligands, which gives a pentagonal bipyramidal uranium coordination environment geometry [U–O(oxo) 1.771(4) and 1.804(4) Å, U–O(carboxylato) 2.323(3)–2.394(3) Å] (Figure 2). The CBTC⁴⁻ ligand is in the *ctc* conformation, with the cyclobutane ring slightly puckered (rms deviation 0.069 Å), and the two carboxylate groups not involved in chelation are coordinated in either the monodentate or the bridging bidentate (μ_2 - $\kappa^1 O:\kappa^1 O'$)

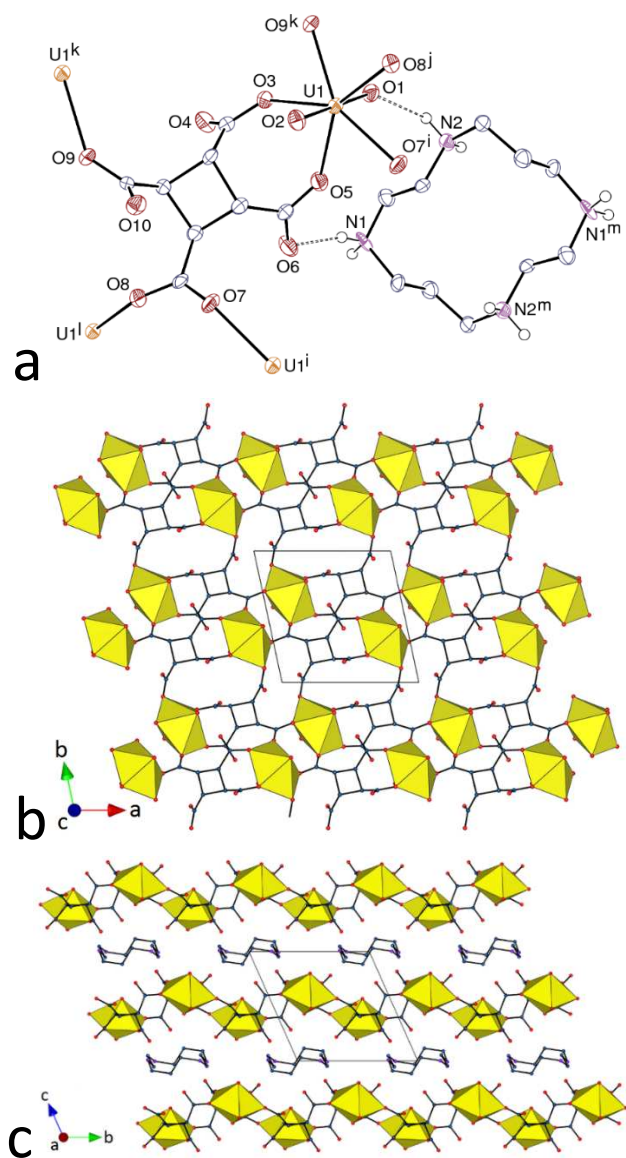


Figure 2. (a) View of compound **2**. Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Symmetry codes: $i = 1 - x, 1 - y, 1 - z$; $j = x + 1, y, z$; $k = 1 - x, -y, 1 - z$; $l = x - 1, y, z$; $m = 2 - x, 2 - y, 2 - z$. (b) View of the 2D network. (c) Packing with layers viewed edge-on. Uranium coordination polyhedra are colored yellow and hydrogen atoms are omitted in the last two views.

modes. Both metal and ligand are 4-connected nodes and the polymeric assembly formed is 2D and parallel to (001). Its point (Schläfli) symbol is $\{4^4.6^2\}$ and its topological type is the common sql (tetragonal net). In contrast to the tetraazamacrocycle in complex **1**, the centrosymmetric cyclamH₄⁴⁺ adopts a conformation with the four nitrogen atoms pointing

outward (as usual for this tetracation, as shown by the structures reported in the CSD), so that no intramolecular NH...N hydrogen bond is present. NH...O hydrogen bonds, some of them bifurcated, involve oxo and carboxylato groups (the latter mainly uncoordinated) as acceptors [N...O 2.655(6)–3.073(5) Å, N–H...O 119–161°]. The counterions are arranged in sheets located in between the anionic layers, which they unite into a hydrogen bonded 3D framework (KPI 0.77).

Using the copper(II) complex of *R,S*-Me₆cyclam instead of the diprotonated macrocycle as in **1** yields the complex [(UO₂)₂(HCBTC)₂Cu(*R,S*-Me₆cyclam)(H₂O)₂] (**3**). The asymmetric unit contains one uranyl cation, one mono-protonated HCBTC³⁻ ligand, and one centrosymmetric Cu(*R,S*-Me₆cyclam)²⁺ moiety (Figure 3). The uranyl cation is chelated by one carboxylate group and bound to two carboxylate donors from two more ligands and one water molecule [U–O(oxo) 1.767(3) and 1.769(3) Å, U–O(carboxylato) 2.315(3)–2.484(3) Å, U–O(water) 2.422(3) Å], the uranium atom being thus in a pentagonal bipyramidal environment. The copper(II) cation is bound to the four nitrogen donors of the macrocycle and to two axial carboxylate groups, its coordination environment being thus distorted octahedral [Cu–N 2.027(4) and 2.036(3) Å, Cu–O 2.413(3) Å]. Such axial coordination, which may be assisted or even dominated by hydrogen bonding of the adjacent NH units, is not always observed when Ni^{II} or Cu^{II} complexes with tetraazamacrocycles are used as counterions in uranyl carboxylate species,^{13,14} but, when present, it provides an efficient means of increasing the dimensionality of the coordination polymer. The HCBTC³⁻ ligand is in the *ctc* conformation, with very slight puckering of the cyclobutane ring (rms deviation 0.044 Å). There is no formation here of a 7-membered chelate ring, the carboxylic group in *cis* position with respect to the chelating carboxylate retains its proton and is uncoordinated, and the other two carboxylate groups are either syn monodentate or syn-anti bridging bidentate. The tetraazamacrocycle is in the usual trans-III conformation with the *R,S,R,S* configuration of the nitrogen atoms.³⁰ One of the two

crystallographically independent NH groups is hydrogen bonded to the carboxylate oxygen atom O6, adjacent to the copper-bound O5, thus forming a pattern with the graph set^{31,32} descriptor $R_1^1(6)$ [$N1\cdots O6$ 2.974(4) Å, $N1-H\cdots O6$ 161°], an arrangement found in other

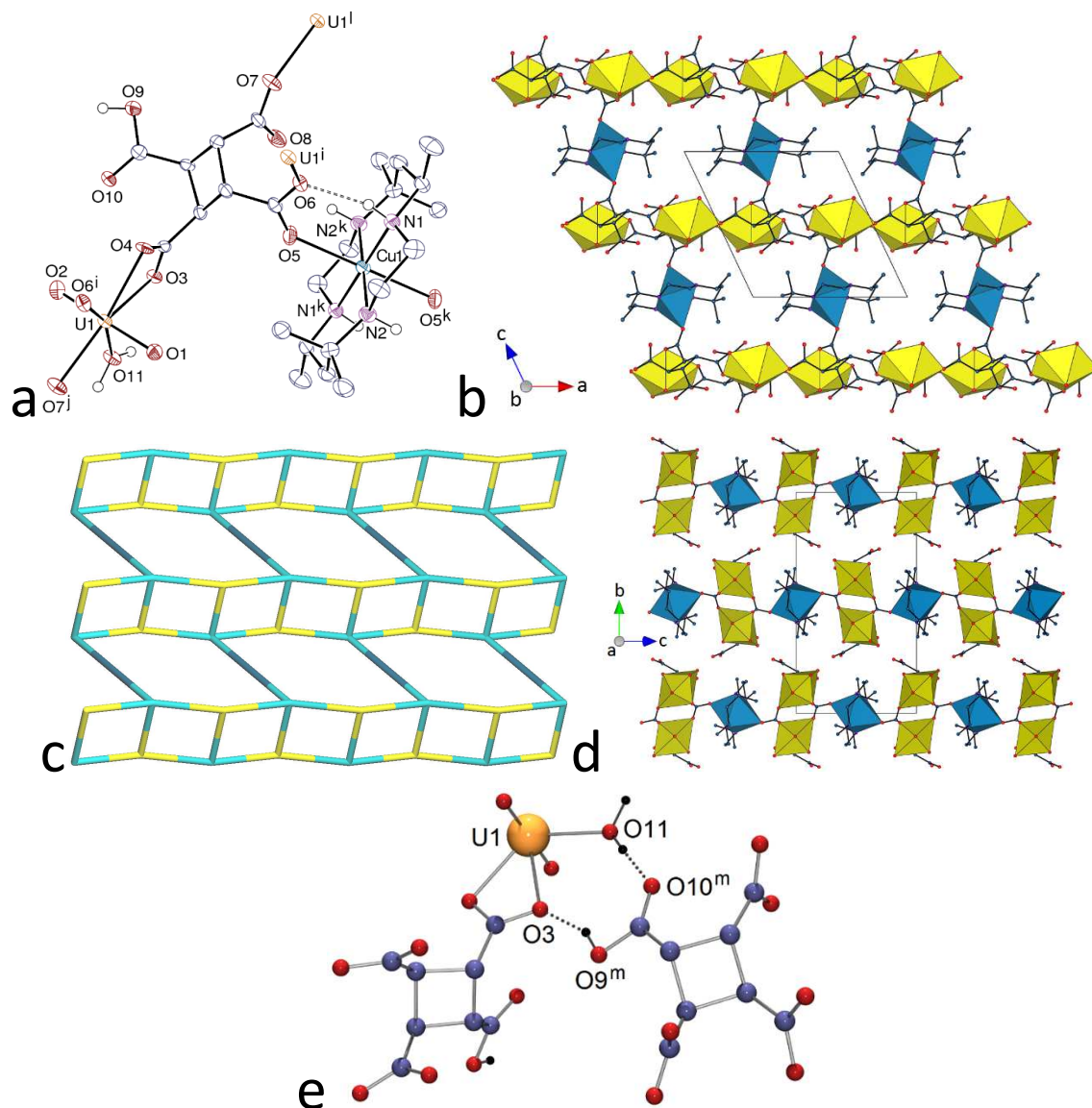


Figure 3. (a) View of compound **3**. Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Symmetry codes: $i = 1 - x, 1 - y, 1 - z$; $j = x - 1, y, z$; $k = 1 - x, 1 - y, -z$; $l = x + 1, y, z$. (b) View of the 2D network. (c) Nodal representation of the 2D network (uranium nodes, yellow; copper links, dark blue; carboxylate nodes, light blue). (d) Packing with layers viewed edge-on. Uranium coordination polyhedra are colored yellow and those of copper(II) blue, and hydrogen atoms are omitted in (b) and (d). (e) Interlayer cyclic hydrogen bonding with hydrogen bonds shown as dotted lines. Symmetry code: $m = x - 1/2, 3/2 - y, z - 1/2$.

complexes,¹³ and which may stabilize the metal ion axial coordination. The second NH group is only loosely hydrogen bonded to atom O5. Uranium atoms are 3-connected nodes, HCBTC³⁻ ligands 4-connected nodes and copper(II) cations simple links in the 2D network formed, which is parallel to (010) and has the point symbol $\{4^2.6^3.8\}\{4^2.6\}$ and the topological type V_2O_5 , an arrangement previously found in a homometallic uranyl complex with mono-protonated tetrahydrofuran tetracarboxylate.¹⁷ Ribbon-like uranyl–HCBTC³⁻ subunits running along [100] are connected to one another by the Cu^{II} links, the resulting sheets being packed in bump-to-hollow fashion (KPI 0.71). The uncoordinated carboxylic groups point outward and sideways on the two sides of the sheets, and they are involved in hydrogen bonding with carboxylate groups of adjacent sheets [O \cdots O 2.607(4) Å, O–H \cdots O 155°], while the water ligands form one intra- and one interlayer hydrogen bonds [O \cdots O 2.626(4) and 2.709(4) Å, O–H \cdots O 162 and 178°]. A cyclic hydrogen bond pattern is thus formed, which has the graph set descriptor $R_2^2(8)$, and which unites the layers into a 3D assembly (Figure 3e).

The coordination complexes formed by d block metal cations with 2,2'-bipyridine or 1,10-phenanthroline molecules, with metal/ligand stoichiometries of 1:1, 1:2, or 1:3, are particularly appealing as counterions for uranyl-based anionic species. They are generally present as separate cations,^{8,33,34} as in the previously reported [Ni(bipy)₃][UO₂(HCBTC)]₂·5H₂O,¹² but 1:1 and 1:2 cations are occasionally part of the polymer species itself,^{35–42} of which the complex [UO₂(CBTC)Cu(bipy)(H₂O)] (**4**) is an example. The asymmetric unit in **4** contains two uranyl cations, two fully deprotonated CBTC⁴⁻ ligands and two Cu(bipy)(H₂O)²⁺ moieties (Figure 4). Both uranium atoms are in identical environments, being chelated by one carboxylate group and bound to three more carboxylate oxygen atoms from three different ligands [U–O(oxo) 1.766(10)–1.793(9) Å, U–O(carboxylato) 2.201(12)–2.457(10) Å]. Both copper(II) cations are chelated by one bipy molecule and bound to two carboxylate donors from two different ligands and one water

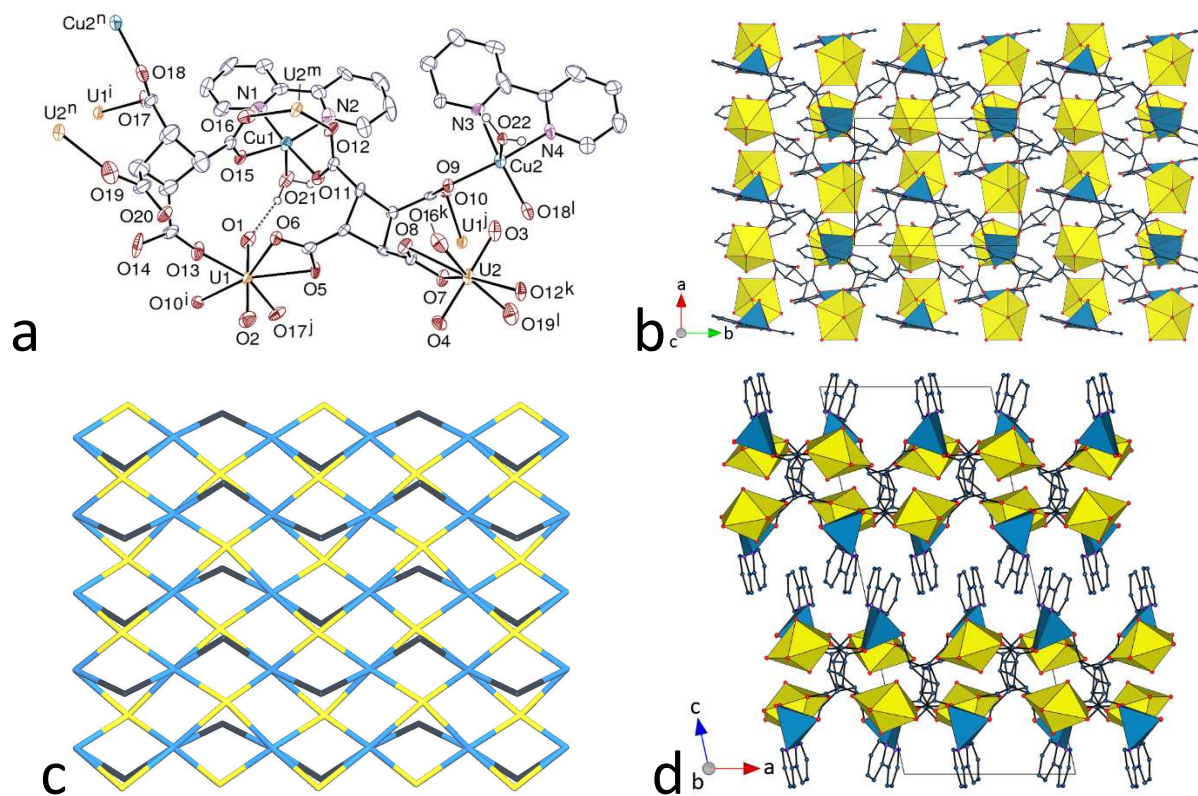


Figure 4. (a) View of compound **4**. Displacement ellipsoids are drawn at the 40% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Symmetry codes: $i = 2 - x, y + 1/2, 3/2 - z$; $j = 2 - x, y - 1/2, 3/2 - z$; $k = 1 - x, y - 1/2, 3/2 - z$; $l = x, y - 1, z$; $m = 1 - x, y + 1/2, 3/2 - z$; $n = x, y + 1, z$. (b) View of the 2D network. (c) Nodal representation of the 2D network (uranium nodes, yellow; copper links, dark blue; carboxylate nodes, light blue). (d) Packing with layers viewed edge-on. Uranium coordination polyhedra are colored yellow and those of copper(II) blue, and hydrogen atoms are omitted in (b) and (d).

molecule [Cu–N 1.990(12)–2.020(11) Å, Cu–O(carboxylato) 1.956(11)–1.984(9) Å, Cu–O(water) 2.191(10) and 2.180(10) Å], being thus in square pyramidal coordination environments with the water molecule at the apex. The two CBTC⁴⁻ ligands are in the *ctc* conformation, with the cyclobutane rings more puckered than in the previous complexes (rms deviations 0.104 and 0.159 Å), but their coordination modes are somewhat different. One of them (atoms O5 to O12) has two chelating groups adjacent to one another and in *trans* positions, the two other groups being syn-anti bridging bidentate, while the other (O13 to O20) has two *cis* groups monodentate, and two *cis* groups syn-anti bridging bidentate. Overall, each ligand is

thus bound to six metal cations, while uranium atoms connect four ligands, and the copper(II) centres are simple links. The assembly formed is 2D and parallel to (001), the uranium nodes having the point symbol $\{3^2.4^2.5^2\}$ and the ligands $\{3^4.4^4.5^4.6^3\}$ (the difference in connectivity having no impact on the topology). It is notable that the Cu^{II} cations do not contribute as nodes to the formation of the 2D assembly, but act as structure-directing species nonetheless. The layers formed have a thickness of $\sim 14 \text{ \AA}$, and the bipy molecules are protruding on both sides, so that the packing displays interdigitation (KPI 0.75). As a result, four parallel-displaced π -stacking interactions may be present [centroid...centroid distances $3.864(9)$ – $4.158(9) \text{ \AA}$, dihedral angles 0 – $20.5(8)^\circ$].

The complex $[\text{UO}_2\text{Pb}(\text{CBTC})(\text{H}_2\text{O})]\cdot 0.5\text{H}_2\text{O}$ (**5**) crystallizes in the space group $P2_1/m$, with one uranyl cation, two lead(II) cations located on a mirror plane (Wyckoff position $2e$), and two ligands with either inversion or mirror symmetry in the asymmetric unit (Figure 5). The uranyl cation forms two 7-membered chelate rings with two ligands, and is bound to one more oxygen donor from a third ligand, as in complex **1** [$\text{U}-\text{O}(\text{oxo})$ $1.755(4)$ and $1.768(4) \text{ \AA}$, $\text{U}-\text{O}(\text{carboxylato})$ $2.355(4)$ – $2.423(4) \text{ \AA}$]. The two lead(II) cations are in slightly different environments. Pb1 is bound to two chelating carboxylate groups and three more carboxylate oxygen donors pertaining overall to five ligands, with Pb1–O bond lengths in the range of $2.414(6)$ – $2.994(4) \text{ \AA}$, and it makes also three longer contacts (not represented in Figure 5a for clarity, but taken into account in the other views), one with atom O11 at $3.045(6) \text{ \AA}$ and two with one chelating group (O7 and its symmetry equivalent) from one more ligand at $3.090(5) \text{ \AA}$. The upper limit chosen for Pb–O bonds is somewhat arbitrary,⁴³ and, depending on whether the last contacts are considered as coordination bonds or not, Pb1 is 7- or 10-coordinate, with rather irregular coordination environment geometries, hemidirected in the first case and holodirected in the second case (Figure 5f), the latter being usual for large coordination numbers.⁴⁴ Pb2 is part of two 7-membered chelate rings, and bound to two more carboxylate

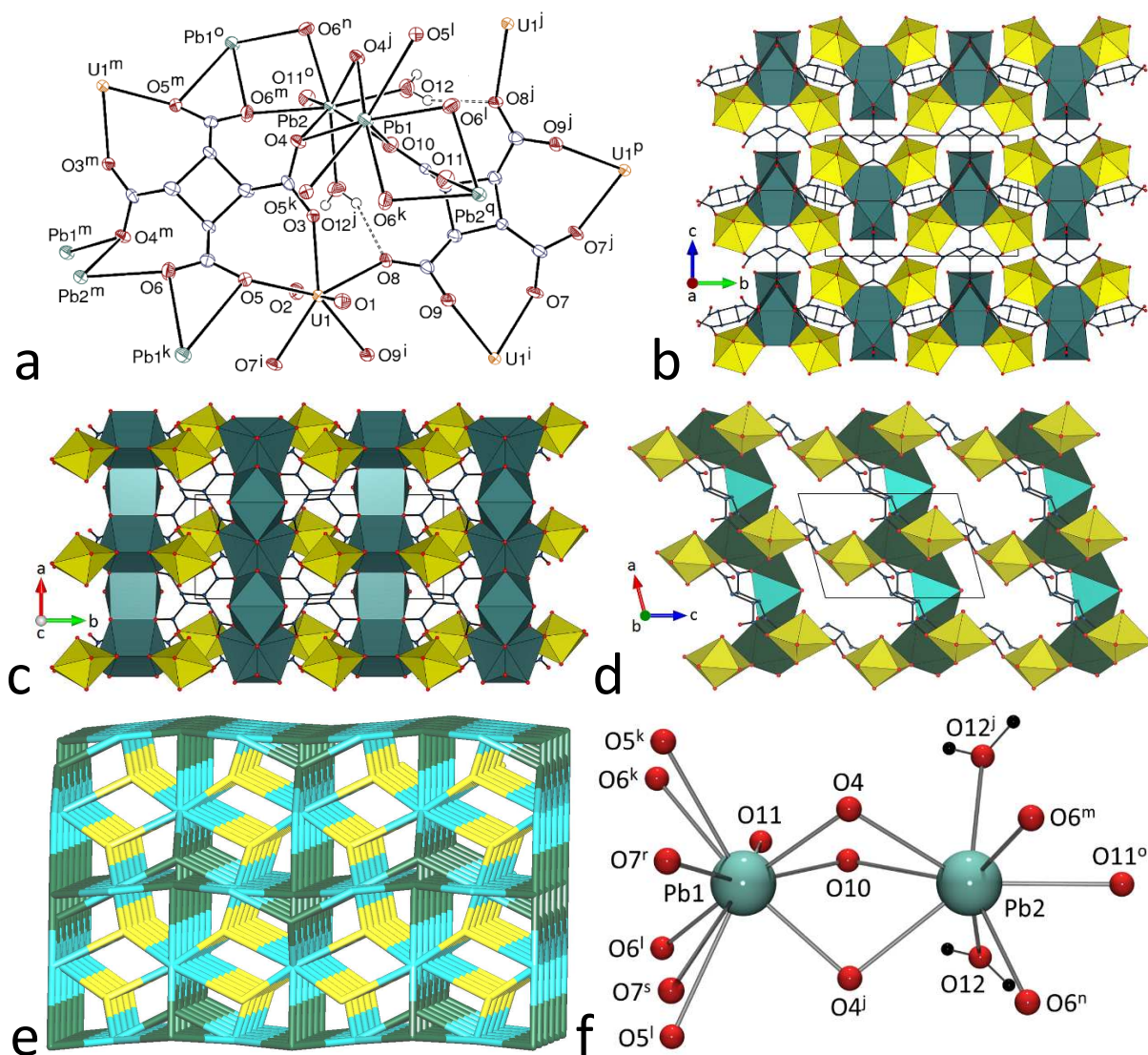


Figure 5. (a) View of compound **5**. Displacement ellipsoids are drawn at the 50% probability level. Solvent molecules and carbon-bound hydrogen atoms are omitted, and hydrogen bonds are shown as dashed lines. Symmetry codes: $i = 1 - x, 1 - y, 2 - z$; $j = x, 3/2 - y, z$; $k = 1 - x, 1 - y, 1 - z$; $l = 1 - x, y + 1/2, 1 - z$; $m = 2 - x, 1 - y, 1 - z$; $n = 2 - x, y + 1/2, 1 - z$; $o = x + 1, y, z$; $p = 1 - x, y + 1/2, 2 - z$; $q = x - 1, y, z$. (b) and (c) Two views of the 3D framework. (d) View of one of the layers parallel to (010). Uranium coordination polyhedra are colored yellow and those of lead(II) green, and solvent molecules and hydrogen atoms are omitted in the last three views. (e) Nodal representation of the framework (orientation slightly rotated with respect to that in (b); uranium, yellow; lead, dark green; carboxylate ligands, light blue). (f) Coordination environment of the lead(II) cations. Symmetry codes: as for (a), and $r = x, y, z - 1$; $s = x, 3/2 - y, z - 1$.

donors from two more ligands, and to two water molecules, with Pb2–O bond lengths in the range of 2.582(4)–2.688(4) Å. Its 8-coordinate environment can be viewed as an example of bicapped trigonal prism,⁴⁵ with the two trigonal faces corresponding to atoms O4, O6 (which are involved in the formation of the 7-membered ring) and O12 or their symmetry equivalents, and the two atoms O10 and O11^o, located on the mirror plane, being in capping position. The two CBTC⁴⁻ ligands assume different conformations, one being *ctc* and the other providing a unique example of the *cis,trans,trans* (*ctt*) form; the cyclobutane rings are either planar or puckered (rms deviation 0.147 Å), respectively. The uranium atom is bound to three CBTC⁴⁻ ligands, Pb1 to either five or six ligands (see above), and Pb2 to four. The coordination polyhedron of Pb1 shares two edges with the polyhedra of two uranium atoms, while the polyhedra of lead(II) cations share faces so as to form columns parallel to [100], these columns being decorated by the edge-sharing uranium polyhedra. The *ctc* ligand connects eight metal atoms (two U and six Pb) and the *ctt* ligand connects either seven or eight atoms (four U and three or four Pb), depending on the limit fixed for Pb–O bonds. As a result of this intricate connectivity, a 3D framework is formed, in which the columnar arrangement of lead(II) cations is best seen through isolating one layer parallel to (010), as shown in Figure 5d. This framework is very compact, with a KPI of 0.76 (with disordered water molecules excluded), and no significant channel is apparent.

The only complex in this series which involves the acyclic BTC⁴⁻ ligand, here as its *R,S* isomer, is [UO₂Pb(BTC)(H₂O)]·0.5H₂O (**6**), which incorporates Pb^{II} cations, as complex **5**. The asymmetric unit contains one uranyl cation chelated by one carboxylate group and bound to three carboxylate groups from three more ligands, the coordination environment of the uranium atom being thus pentagonal bipyramidal [U–O(oxo) 1.759(5) and 1.760(5) Å, U–O(carboxylato) 2.284(5)–2.457(5) Å] (Figure 6). The Pb^{II} cation is disordered (see Experimental Section), and the major component only will be taken into account in the

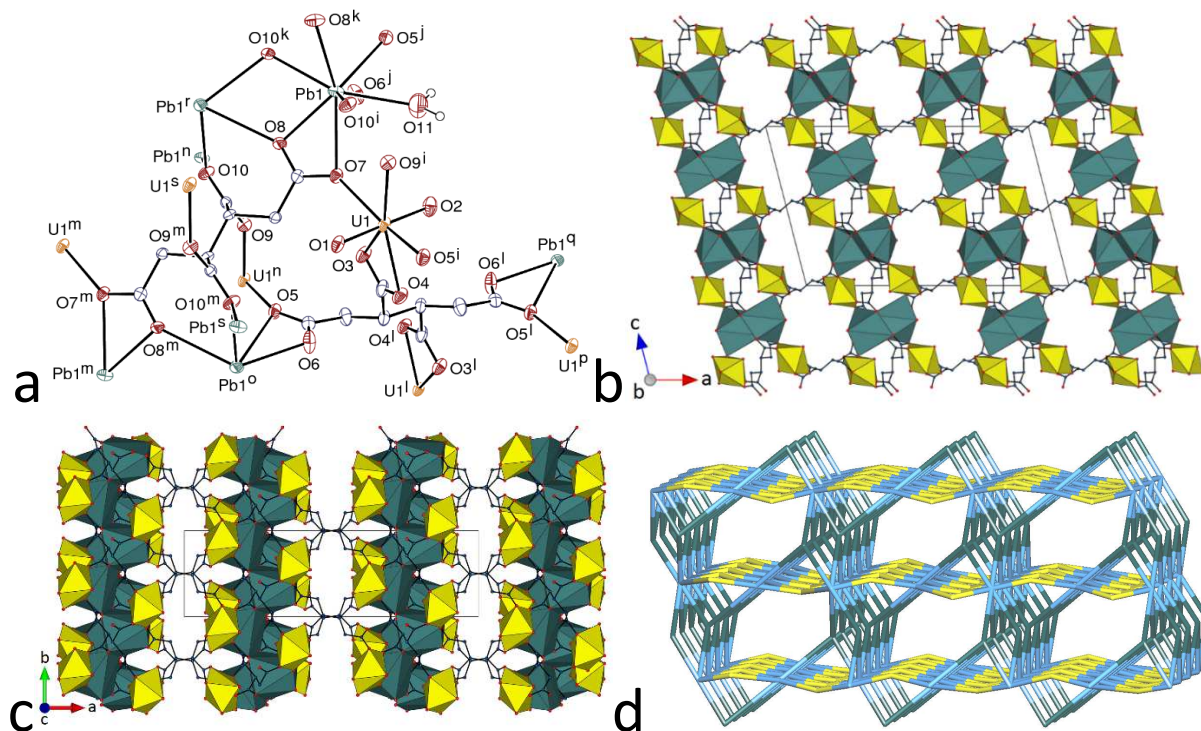


Figure 6. (a) View of compound **6**. Displacement ellipsoids are drawn at the 40% probability level. The solvent molecule and carbon-bound hydrogen atoms are omitted. Symmetry codes: $i = x, y - 1, z$; $j = x, 2 - y, z - 1/2$; $k = 3/2 - x, y - 1/2, 3/2 - z$; $l = 1 - x, 2 - y, 2 - z$; $m = 3/2 - x, 5/2 - y, 2 - z$; $n = x, y + 1, z$; $o = x, 2 - y, z + 1/2$; $p = 1 - x, 1 - y, 2 - z$; $q = 1 - x, y, 3/2 - z$; $r = 3/2 - x, y + 1/2, 3/2 - z$; $s = 3/2 - x, 3/2 - y, 2 - z$. (b) and (c) Two views of the 3D framework with uranium coordination polyhedra colored yellow and those of lead(II) green, and hydrogen atoms omitted. (d) Nodal representation of the framework (orientation slightly rotated with respect to that in (b); uranium, yellow; lead, dark green; carboxylate ligands, light blue). Only the major component of the disordered lead(II) cation is shown in all views.

discussion. Pb^{II} is bound to seven carboxylate oxygen atoms, with two chelating carboxylate groups and 7-membered ring chelation by two other groups [Pb–O 2.507(5)–2.948(5) Å], and to one water molecule [2.649(8) Å], its coordination environment being quite irregular but distinctly holodirected, an unsurprising geometry for a rather large coordination number.⁴⁴ Two centrosymmetric BTC^{4-} ligands are present, and both assume a conformation similar to that in the only other uranyl complex known with this ligand, $[(\text{UO}_2)_2(\text{BTC})(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$,¹⁰ with a C_6 skeleton regularly extended and defining a nearly planar divergent dicarboxylate subunit,

the other two carboxylate groups pointing on either side of the plane. Both uranyl and lead(II) cations are bound to four ligands, and the BTC^{4-} ligands to either six or ten metal cations, with the carboxylate groups bound in the $\kappa^2\text{O},\text{O}'$, $\mu_2\text{-}\kappa^1\text{O}:\kappa^2\text{O},\text{O}'$, $\mu_3\text{-}\kappa^1\text{O}:\kappa^1\text{O}:\kappa^1\text{O}'$, and $\mu_3\text{-}\kappa^1\text{O}:\kappa^2\text{O},\text{O}':\kappa^1\text{O}'$ coordination modes. Columns of edge-sharing lead(II) coordination polyhedra run along [010], each of these columns being surrounded by four rows of uranyl polyhedra sharing apexes with those of lead(II). Here also, the connectivity is quite intricate and a 3D framework is formed, in which channels running along [010] and with a section of $7 \text{ \AA} \times 5 \text{ \AA}$ can be seen. As a consequence, the KPI (0.65, with solvent and disorder excluded) is lower than in complex **5**. It is notable that 2D and 3D assemblies based on CBTC and BTC ligands and lead(II) cations alone, synthesized under hydrothermal conditions, have also been reported.⁴⁶

The last complex in this series, $[\text{H}_2\text{NMe}_2]_4[(\text{UO}_2)_4(\text{CBTC})_3]$ (**7**), includes dimethylammonium counterions formed in situ from DMF hydrolysis, and not PPh_3Me^+ cations as was intended. This complex crystallizes in the non-centrosymmetric cubic space group $I\bar{4}3d$, with the unique uranyl cation having 3-fold rotation symmetry (Wyckoff position 16c), and the CBTC^{4-} ligand, in the *ttt* conformation, has 4-fold rotoinversion symmetry (Figure 7). The uranyl cation is chelated by three carboxylate groups [U-O(oxo) 1.757(13) and 1.759(13) \AA , U-O(carboxylato) 2.457(7) and 2.477(6) \AA]. The cyclobutane ring is puckered, with a rms deviation of 0.123 \AA . The uranium atom is a 3-connected node, and the ligand is a 4-connected node in the 3D framework formed, which is much simpler than those in complexes **5** and **6** since it has the point symbol $\{8^3\}_4\{8^6\}_3$ and the topological type ctn in RCSR notation, with tetrahedral coordination of the four-connected node.⁴⁷ Channels with a diameter of $\sim 4 \text{ \AA}$ run parallel to the three cell axes. With the disordered counterions excluded, the KPI amounts to 0.38 only, indicating the presence of large voids occupied by the counterions. Another uranyl complex with *ttt*- CBTC^{4-} crystallizing as a different framework with cubic symmetry was

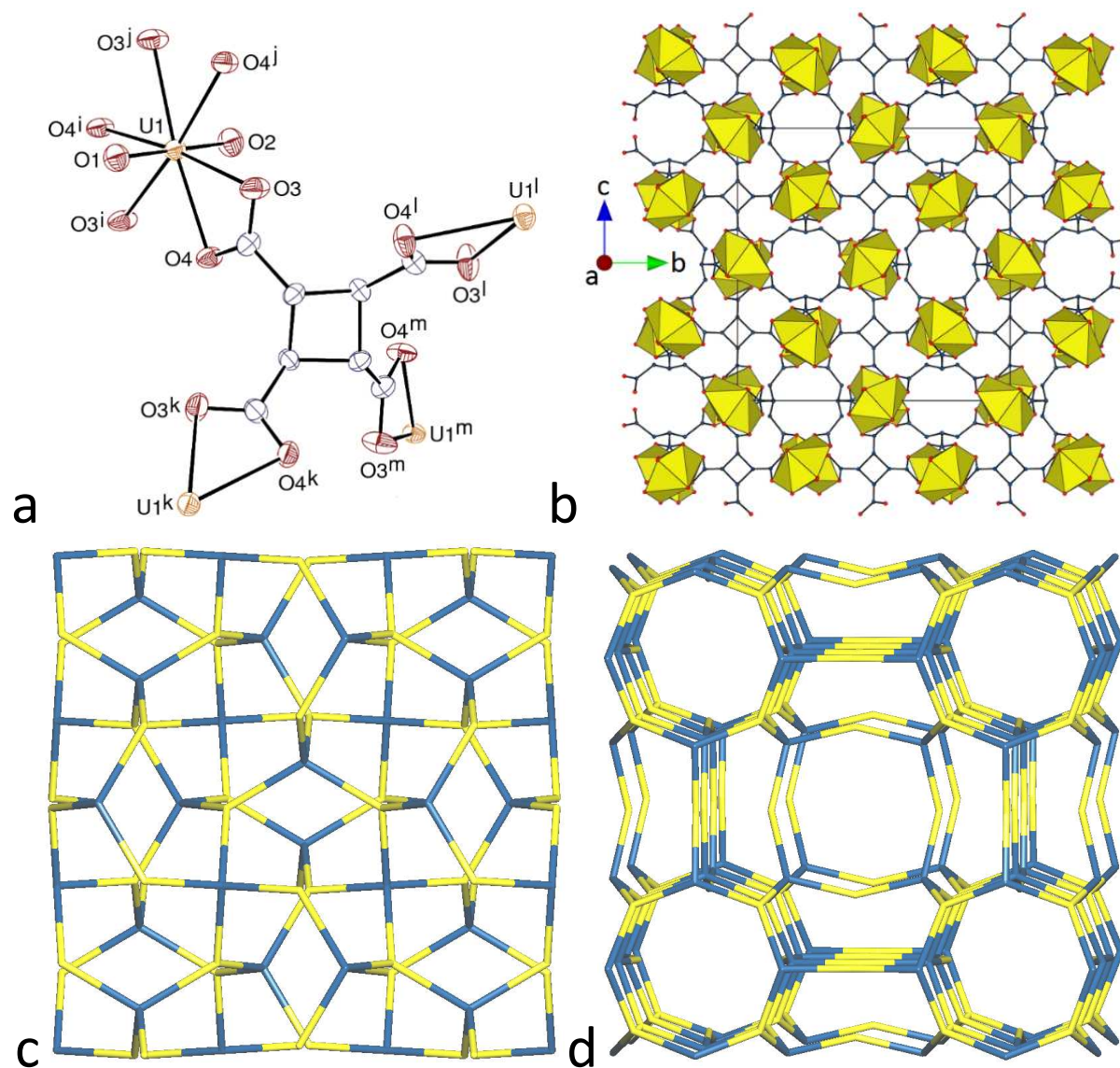


Figure 7. (a) View of compound **7**. Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes: $i = 3/2 - y, 1 - z, x - 1/2$; $j = z + 1/2, 3/2 - x, 1 - y$; $k = y + 1/4, 7/4 - x, 1/4 - z$; $l = 7/4 - y, x - 1/4, 1/4 - z$; $m = 2 - x, 3/2 - y, z$. (b) View of the 3D framework with uranium coordination polyhedra colored yellow. (c) Nodal representation of the framework in **7** (uranium, yellow; carboxylate ligands, blue). (d) Nodal representation of the framework in the previously reported cubic complex.¹⁰ The counterions and hydrogen atoms are omitted in all views.

reported previously, $[\text{H}_3\text{O}]_2[(\text{UO}_2)_5(\text{CBTC})_3(\text{H}_2\text{O})_6]$, with however some uncertainty as to the nature of the counterion.¹⁰ This complex has larger channels than **7** and an even smaller KPI of about 0.30. Its framework can be seen as containing 4:4 (metal/ligand) metallacycles and 8:12

cubic cages, with uranyl and tetracarboxylate 3- and 4-connected nodes, respectively, as in **7**, and additional uranyl links. Its point symbol is $\{4.6^4.8\}_3\{6^3\}_2$ and its topological type is tfg^{48} (Figure 7d). The different stoichiometries of the two complexes, and the presence of water ligands in the latter result in topological variations, while retaining the 4-connected node nature of CBTC^{4-} and the lattice cubic symmetry.

Luminescence properties. The uranyl emission spectra⁴⁹ of compounds **1**, **2** and **3**, which are the only ones for which a sufficient amount of pure compound could be obtained, were recorded at room temperature under excitation at a wavelength of 420 nm, a value suitable for excitation of the uranyl chromophore,⁵⁰ and they are shown in Figure 8, together with the

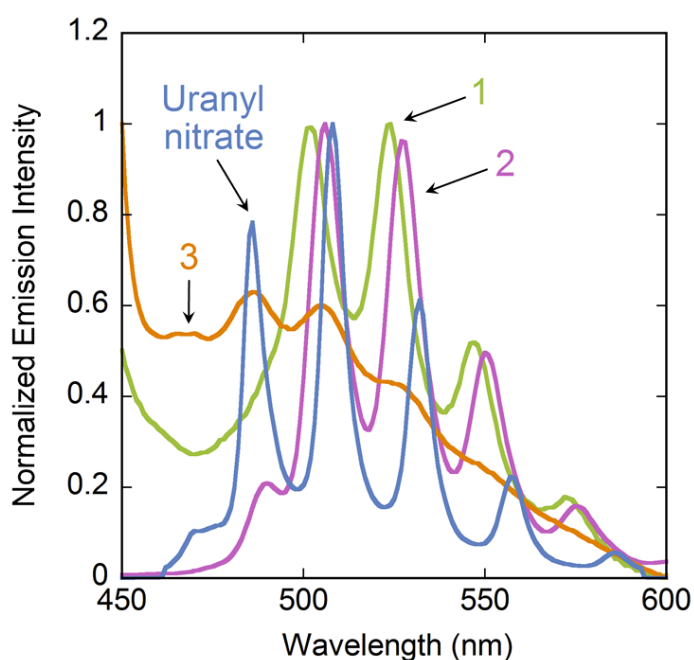


Figure 8. Emission spectra of compounds **1–3**, and uranyl nitrate hexahydrate in the solid state, under excitation at a wavelength of 420 nm.

spectrum of uranyl nitrate hexahydrate as a reference. The spectrum of **2** is well resolved and displays the usual series of maxima associated with the vibronic progression corresponding to the $S_{11} \rightarrow S_{00}$ and $S_{10} \rightarrow S_{0\nu}$ ($\nu = 0-4$) electronic transitions,⁵¹ with the four main maxima at

506, 527, 550, and 575 nm. The spectrum of **1** is less intense (based on comparison of the un-normalized intensities for similar molar amounts of the two compounds) but still well resolved, and the positions of the four maxima are slightly blue-shifted, at 502, 524, 547, and 572 nm. In both complexes, uranyl cations are in pentacoordinated equatorial environments and the maxima positions are in agreement with those generally found for uranyl carboxylate complexes with O₅ equatorial environments.⁸ These values are red-shifted with respect to those measured for uranyl nitrate hexahydrate (486, 508, 532, and 557 nm) and even more with respect to those usual in carboxylate complexes with O₆ equatorial environments. The copper(II)-containing complex **3** is nearly non-luminescent, with only three large features blue-shifted with respect to the maxima of **1** and **2**. Quenching of uranyl luminescence due to the presence of d block metal cations has frequently been observed and is attributed to their providing nonradiative relaxation pathways.^{52–55}

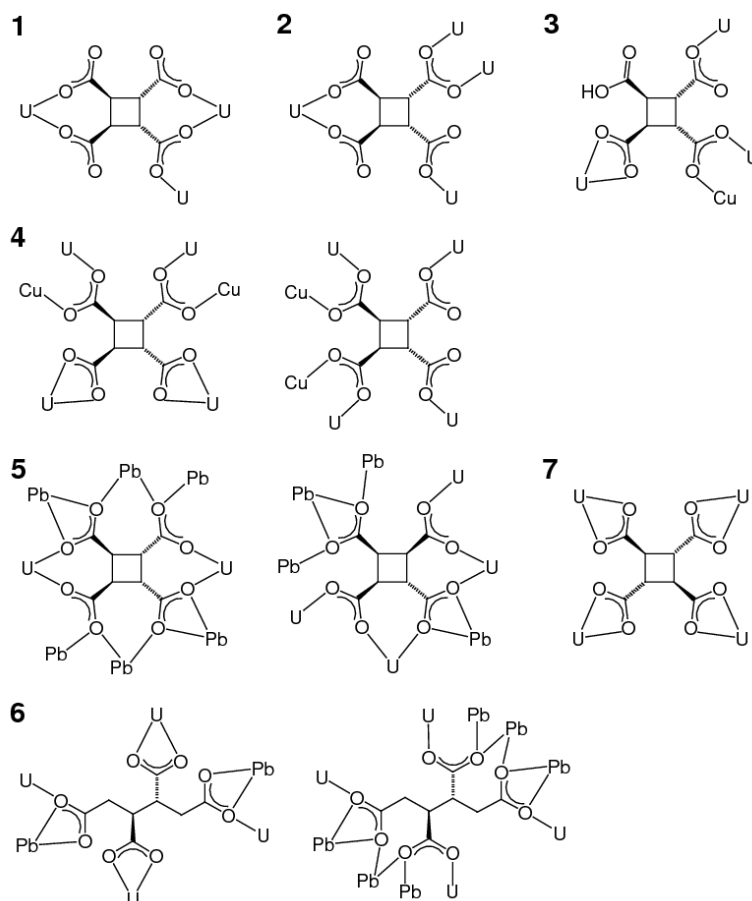
CONCLUSIONS

We have reported here the synthesis and crystal structure of six uranyl complexes with the CBTC⁴⁻ or HCBTC³⁻ ligands, and one with the acyclic analogue BTC⁴⁻ ligand. Variation of the counterions has enabled different connectivities, dimensionalities, and topologies to be produced, as summarized in Table 2, which defines also the complexes described in previous work. These ligands derived from tetracarboxylic acids are able to connect a large number of metal cations, as shown in Scheme 1, where a summary of the coordination modes found is given. These coordination modes span the whole possible range, including 4- and 7-membered-ring chelation, associated with various bridging interactions. In most complexes, all the carboxylate oxygen atoms are bound to at least one metal atom. The minimum number of connected metal cations is three in complex **1**, and the maximum ten for one of the ligands in **6**, which appears close to saturation of its connecting capacity. Such high denticity, and the non-planar geometry of these ligands makes them suitable for the synthesis of intricate 3D

Table 2. Uranyl Ion Complexes with 1,2,3,4-(Cyclo)butane(tri/tetra)carboxylate Ligands

Ligand	Additional Cation	Dimensionality	Ligand Conformation	Reference
CBTC ⁴⁻		3D	<i>ctc</i>	10
CBTC ⁴⁻	H ₃ O ⁺	3D	<i>ttt</i>	10
HCBTC ³⁻	Hbipy ⁺	2D	<i>ttt</i>	11
HCBTC ³⁻	Ni(bipy) ₃ ²⁺	2D	<i>ttt</i>	12
CBTC ⁴⁻	<i>R,S</i> -Me ₆ cyclamH ₂ ²⁺	1D	<i>ctc</i>	this work (1)
CBTC ⁴⁻	cyclamH ₄ ⁴⁺	2D	<i>ctc</i>	this work (2)
HCBTC ³⁻	Cu(<i>R,S</i> -Me ₆ cyclam) ²⁺	2D	<i>ctc</i>	this work (3)
CBTC ⁴⁻	Cu(bipy) ²⁺	2D	<i>ctc</i>	this work (4)
CBTC ⁴⁻	Pb ²⁺	3D	<i>ctc</i> / <i>ctt</i>	this work (5)
CBTC ⁴⁻	H ₂ NMe ₂ ⁺	3D	<i>ttt</i>	this work (7)
BTC ⁴⁻		2D		10
BTC ⁴⁻	Pb ²⁺	3D		this work (6)

frameworks. The outcome of the reactions is however extremely dependent on the additional metal cations and/or counterions, as shown by the present results, since 1D and 2D coordination polymers were obtained with CBTC⁴⁻ with protonated azamacrocycles as counterions (the latter of course unsuitable to increase the dimensionality other than through hydrogen bonding), 2D assemblies were found with CBTC⁴⁻ or HCBTC³⁻ and copper(II) counterions (either bound to an azamacrocycle or to a bipy molecule), heterometallic 3D frameworks with CBTC⁴⁻ or BTC⁴⁻ in the presence of Pb²⁺, a cation able to adopt high coordination numbers and hence to have a high assembling power. Finally, a homometallic 3D framework of cubic symmetry and *ctn* topology, displaying significant free space in its lattice, resulted from the presence of dimethylammonium counterions. It is notable that none of the present complexes crystallizes



Scheme 1. Coordination modes of the tetracarboxylate ligands in complexes **1–7**. The two independent ligands are shown for complexes **4**, **5** and **6**.

as a 2D network with honeycomb topology, as previously found in the case of HCBTC^{3-} with Hbipy^+ or $[\text{Ni}(\text{bipy})_3]^{2+}$ counterions;^{11,12} this 3-fold deprotonated ligand is well suited to act as a 3-connected node but formation of a simple network is prevented by the presence of coordinated copper(II) cations in complex **3**. Part of the richness of this system comes from the different (and seemingly quite unpredictable under the conditions used) possible configurations of the $\text{CBTC}^{4-}/\text{HCBTC}^{3-}$ ligand, *ctc*, *ttt* and the more unusual *ctt*, sometimes coexisting in the same compound. It appears that the noncentrosymmetric, saddle-shaped *ttt* form is that found in the more symmetric 3D assemblies. Through a proper choice of directing species, be they separate counterions or metallic cations part of the coordination polymer, it thus appears possible to favour the formation of 3D frameworks with these very versatile ligands, and even

of potentially porous frameworks. An aspect of the versatility of the CBTC⁴⁻ ligand which places it in a class of polycarboxylate ligands with rather few members is the capacity to form 7-membered chelate rings and thus to provide alternative anionic uranyl complex arrays, different from the more usual ones containing 4-membered chelate rings, and possibly better suited to the binding preferences of any metallic counteranion, such as lead(II), as illustrated here.

ASSOCIATED CONTENT

Accession Codes

CCDC 1911946–1911952 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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