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Chain, Network and Framework Formation in Uranyl Ion Complexes with 1,1'-Biphenyl-3,3',4,4'-tetracarboxylate

Dr. Pierre Thuéry*[a] and Dr. Jack Harrowfield*[b]

[a] Université Paris-Saclay, CEA, CNRS, NIMBE, 91191 Gif-sur-Yvette, France

E-mail: pierre.thuery@cea.fr

http://iramis.cea.fr/nimbe/

[b] ISIS, Université de Strasbourg, 8 allée Gaspard Monge, 67083 Strasbourg, France

E-mail: harrowfield@unistra.fr

https://isis.unistra.fr/fr/

Abstract

1,1'-Biphenyl-3,3',4,4'-tetracarboxylic acid dianhydride has been reacted with uranyl nitrate under solvo-hydrothermal conditions and in the presence of different counterions to give three complexes of varying periodicity. $[Co(en)_3][UO_2(bptc)(HCOO)]\cdot 2.5H_2O$ (**1**) crystallizes as a monoperiodic coordination polymer in which the $bptc^{4-}$ ligand is exclusively bound through formation of two 7-membered chelate rings. The $[Co(en)_3]^{3+}$ counterion is essentially a hydrogen bond donor, forming 15 hydrogen bonds with carboxylate and water oxygen atoms. In $[H_2NMe_2]_2[UO_2(bptc)]\cdot 0.5H_2O$ (**2**), half the ligand forms a 7-membered chelate ring, and the other half bridges two uranium atoms, resulting in the formation of a diperiodic network with **hcb** topology, the $H_2NMe_2^+$ counterions being located between the undulating sheets. $[PPh_4]_4[(UO_2)_4(bptc)_3]\cdot 6H_2O$ (**3**) contains a mixture of ligands forming either four 4-membered or two 7-membered chelate rings, the latter with further bridging, which gives a triperiodic framework displaying large channels, each of which contains two rows of PPh_4^+ counterions. These results are compared to those of previous studies with this ligand, and of similar studies of phthalate complexes of uranyl ion, in particular in relation to 7-membered chelate ring formation.

Introduction

When using polycarboxylates for synthesizing uranyl-containing networks or polymers,[1–5] one means of obtaining large rings, cavities or channels relies on ligands with rigid and elongated carbon skeletons, among which the biphenyl motif is most obvious. The simplest biphenyl-based, divergent ligand is 1,1′-biphenyl-4,4′-dicarboxylate, which has given several original diperiodic networks,[6–9] some of which display polycatenation,[8] or guest-dependent single-crystal-to-single-crystal phase transitions.[9] A larger, curved dicarboxylate ligand including three aromatic rings, 1,1′,3′,1″-terphenyl-4,4″-dicarboxylate, has been shown to give ribbon-like chains,[10] and a linear dicarboxylate ligand including four aromatic rings (two phenyl and two pyridinium) has also been investigated,[11] as well as a species involving three biphenylcarboxylate units.[12]

The biphenyldicarboxylate motif itself can be modulated through modification of the positions of the carboxylate groups, and/or through addition of other groups, coordinating or not. In the first category, 1,1′-biphenyl-2,4′-dicarboxylate, which is a distinctly curved and not a divergently linear ligand, yields diperiodic networks effective in photocatalytic degradation of rhodamine B,[13] and 1,1′-biphenyl-2,2′-dicarboxylate gives mainly monoperiodic polymers with different chelating modes of the two carboxylate groups.[14] In the second category, the ligand with one additional methyl group on each ring has been used to synthesize a mixed uranyl–thorium(IV) framework,[15] while 1,1'-biphenyl-3,3′-disulfonyl-4,4′-dicarboxylate gives mixed uranyl–potassium frameworks.[16] Several biphenyl-based ligands with four carboxylate groups, and thus a potentially increased assembling power, are known. 1,1'-Biphenyl-4-fluoro-3,3′,5,5′-tetracarboxylate only forms a diperiodic network with uranyl ions,[17] whereas 1,1'-biphenyl-2,2′,6,6′-tetracarboxylate gives mono-,

di- and triperiodic assemblies depending on the choice of additional metal cations present.[18]

We have previously used the anions derived from the less symmetrical 1,1'-biphenyl-3,3',4,4'-tetracarboxylic acid (H_4bptc) to synthesize two homometallic uranyl ion complexes, the monoperiodic $[UO_2(H_2bptc)(H_2O)_2]\cdot 2H_2O$,[19] and $[(UO_2)_2(bptc)(NMP)_{1.5}(H_2O)_{1.5}]\cdot 1.5H_2O$ (NMP = *N*-methyl-2-pyrrolidone), which crystallizes as a triperiodic framework,[20] and also two heterometallic complexes involving either Ag^{I} or Pb^{II} as additional cations, $[UO_2Ag(bptc)(4,4'\text{-bipyH})]$ and $[UO_2Pb(bptc)(2,2'\text{-bipy})_2]$ (bipy = bipyridine), which are both diperiodic networks with the additional cations having a simple decorating role.[20] Notwithstanding the ability of $bptc^{4-}$ to form a framework with uranyl as sole cation, which is unusual in this family of biphenyl-based ligands, few complexes have been synthesized and crystallographically characterized, possibly as a result of the difficulty in growing single crystals of sufficient quality. This ligand is nonetheless of some particular interest as a phthalate homologue and thus as a species favouring 7-membered chelate ring formation on uranyl ion, a relatively uncommon feature in uranyl carboxylate coordination chemistry. We have now obtained three novel anionic uranyl complexes with $bptc^{4-}$ which illustrate all the range of periodicity attainable upon variation of the counterions, these being $[Co(en)_3]^{3+}$ (en = ethylenediamine) and $H_2NMe_2^+$, which are both hydrogen bond donors, and PPh_4^+, which influences the structure through its bulkiness and ability to be involved in aromatic···aromatic interactions.

Results and Discussion

The complex $[Co(en)_3][UO_2(bptc)(HCOO)]\cdot 2.5H_2O$ (**1**) involves a counterion known to be an efficient hydrogen bond donor[21] and which has proven to be an efficient structure-directing

species in uranyl complexes.[22–25] As noted above, the bptc^{4-} ligand is effectively a bis(phthalate) species and thus would be expected to form a 7-membered chelate ring at each phthalate-like site. This, in fact, is what is observed but, unlike most other known phthalate complexes, there are no other interactions of the oxygen donors with the metal cation. The unique uranyl cation is chelated by two ligands and bound to one more oxygen donor from the formate moiety, the latter formed in situ from *N,N*-dimethylformamide (DMF) hydrolysis, as commonly observed. The uranium atom environment is thus pentagonal-bipyramidal [U–O(oxo), 1.7750(17) and 1.7838(17) Å; U–O(carboxylato), 2.3486(17)–2.4392(16) Å] (Figure 1). The non-involvement of four oxygen atoms in bptc^{4-}

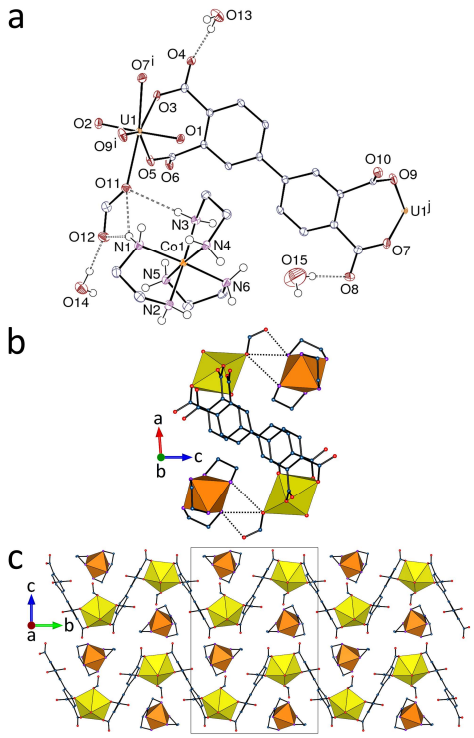


Figure 1. (a) View of complex **1**. Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Symmetry codes: i = –*x*, *y* – 1/2, 1/2 – *z*; j = –*x*, *y* + 1/2, 1/2 – *z*. (b) Location of the counterions with respect to one chain viewed end-on. Hydrogen bonds with formate are shown as dashed lines. Uranium coordination polyhedra are colored yellow and those of cobalt orange. (c) View of the packing with solvent molecules and hydrogen atoms omitted.

and one in formate in coordination severely limits the periodicity of the coordination polymer, which is a zigzag chain parallel to [010] having a marked S-shape when viewed end-on. This undulating form defines gaps which, somewhat like the cavities found in a Kemp's tricarboxylate complex where the same countercation is present,[25] are approached from both sides by cations forming NH···O bonds. The cation is present in its *lel₂ob* conformation,[26] again as found in the Kemp's tricarboxylate complex, and all 12 amino group protons are involved in 15 NH···O bonding interactions, some of them bifurcated, with two pairs of protons being bridged by water molecules and the others interacting with both $bptc^{4-}$ and formate oxygen atoms, either coordinated or not [N···O distances, 2.846(3)–3.369(3) Å; N–H···O angles, 112–169°]. In particular, two protons of type C_3 (i.e. such that the C–H bond is nearly parallel to the pseudo-C_3 axis of the anion) form three hydrogen bonds with the formate ligand, possibly explaining the rather unusual monodentate nature of the latter (less than one third of all uranyl formate species reported in the Cambridge Structural Database (CSD, version 5.42[27]) are neither chelating, nor bridging). The water molecules form hydrogen bonds between one another and with carboxylate groups, thus giving an intricate hydrogen bonding pattern. The packing does not contain significant free spaces and it has a Kitaigorodski packing index (KPI, calculated with PLATON[28]) of ~0.74.

While complex **1** incorporated formate anions, complex **2**, $[H_2NMe_2]_2[UO_2(bptc)]\cdot 0.5H_2O$, contains the other component resulting from DMF hydrolysis, the dimethylammonium cation. The $bptc^{4-}$ ligand behaves here in an unsymmetrical way, with formation of a 7-membered chelate ring similar to that found in **1** by one dicarboxylate unit, while the other two carboxylate groups are bound to two different uranium atoms either in the κ^2*O,O'*-chelated or in the monodentate mode (Figure 2). The uranium atom is

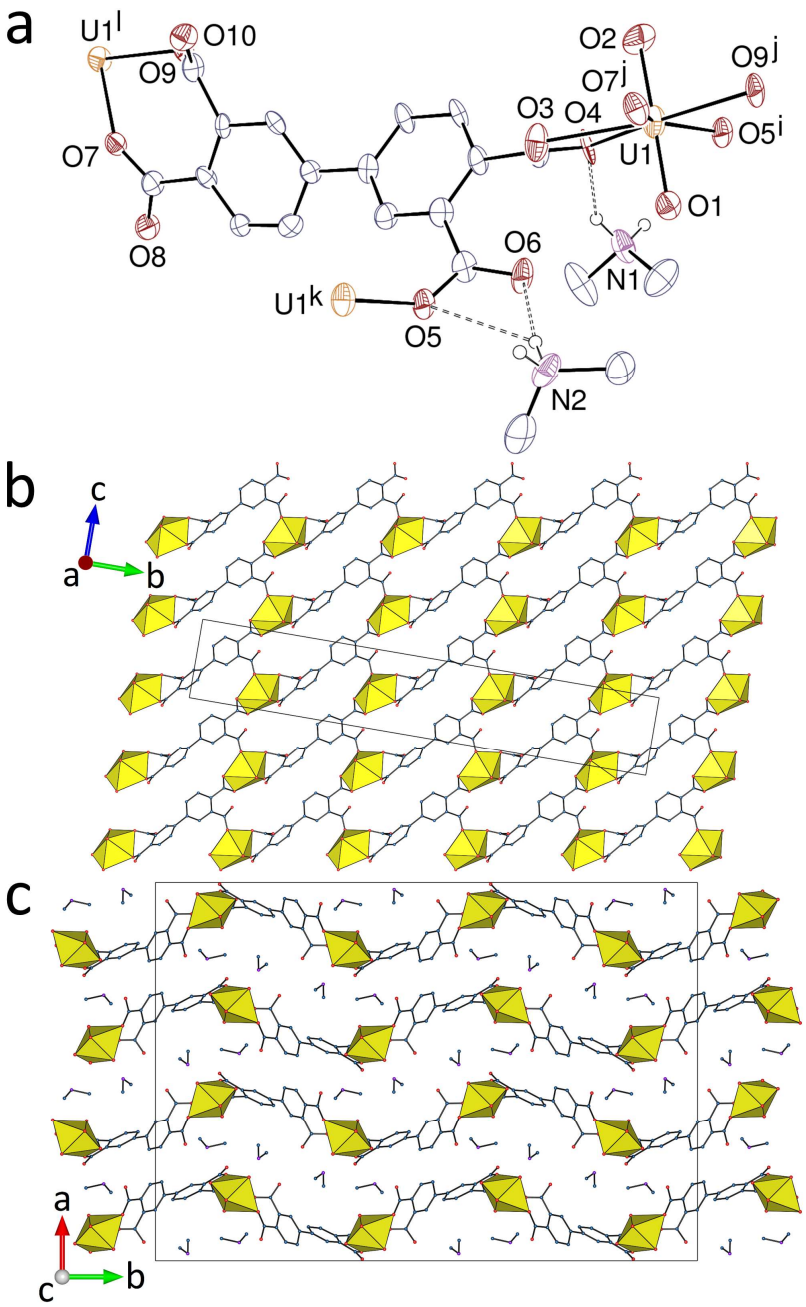


Figure 2. (a) View of complex **2**. Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Symmetry codes: i = *x*, *y*, *z* – 1; j = 3/4 – *x*, *y* + 1/4, *z* – 5/4; k = *x*, *y*, *z* + 1; l = 3/4 – *x*, *y* – 1/4, *z* + 5/4. (b) View of the diperiodic network. (c) Packing with layers viewed edge-on.

thus in a pentagonal-bipyramidal environment [U–O(oxo), 1.768(5) and 1.776(5) Å; U–O(carboxylato), 2.466(4) and 2.506(4) Å for the κ^2*O,O′*-chelating group, and 2.303(4)–

2.321(5) Å for the others]. Both uranium and bptc^{4-} are three-coordinated (3-c) nodes, and the diperiodic, uninodal polymer formed has the vertex symbol {6^3} and the very common honeycomb (**hcb**) topological type (another common form of such networks found in uranyl complexes has uranium as a 3-c node and the ligand as a simple link, a situation giving larger rings). The network lies as undulating sheets parallel to (100), each sheet containing both enantiomers of the chiral ligand conformation. The packing of the sheets does not generate large channels as could have resulted from hollow-to-hollow type stacking, but only sinuous, thin spaces containing the counterions. The latter are hydrogen bonded to carboxylate oxygen atoms, both coordinated or not [N···O distances, 2.720(7)–3.232(7) Å; N–H···O angles, 132–173°]. No parallel-displaced π-stacking interaction is present, and there is no significant free space (KPI, 0.68).

In contrast to **1** and **2**, $[PPh_4]_4[(UO_2)_4(bptc)_3]\cdot 6H_2O$ (**3**) does not include any product of DMF hydrolysis, and the large tetraphenylphosphonium cation plays an obvious structure-directing role. The two independent uranium atoms are in different environments, that of U1 being pentagonal-bipyramidal, and comprising one κ^2*O,O'*-chelating carboxylate group, two groups from another ligand forming a 7-membered chelate ring, and one more donor from a third ligand in the equatorial plane, while that of U2 is hexagonal-bipyramidal, with three κ^2*O,O'*-chelating groups, both metal ions being thus 3-c nodes [U–O(oxo), 1.758(4)–1.771(4) Å; U–O(carboxylato), 2.443(4)–2.481(4) Å for the κ^2*O,O'*-chelating groups, and 2.318(4)–2.364(4) Å for the others] (Figure 3). As in complex **1**, both bptc^{4-} ligands behave as symmetrical linkers, but they have different connectivities. One of them, which has inversion symmetry, forms two 7-membered chelate rings, as in **1**, but here extra bridging by two

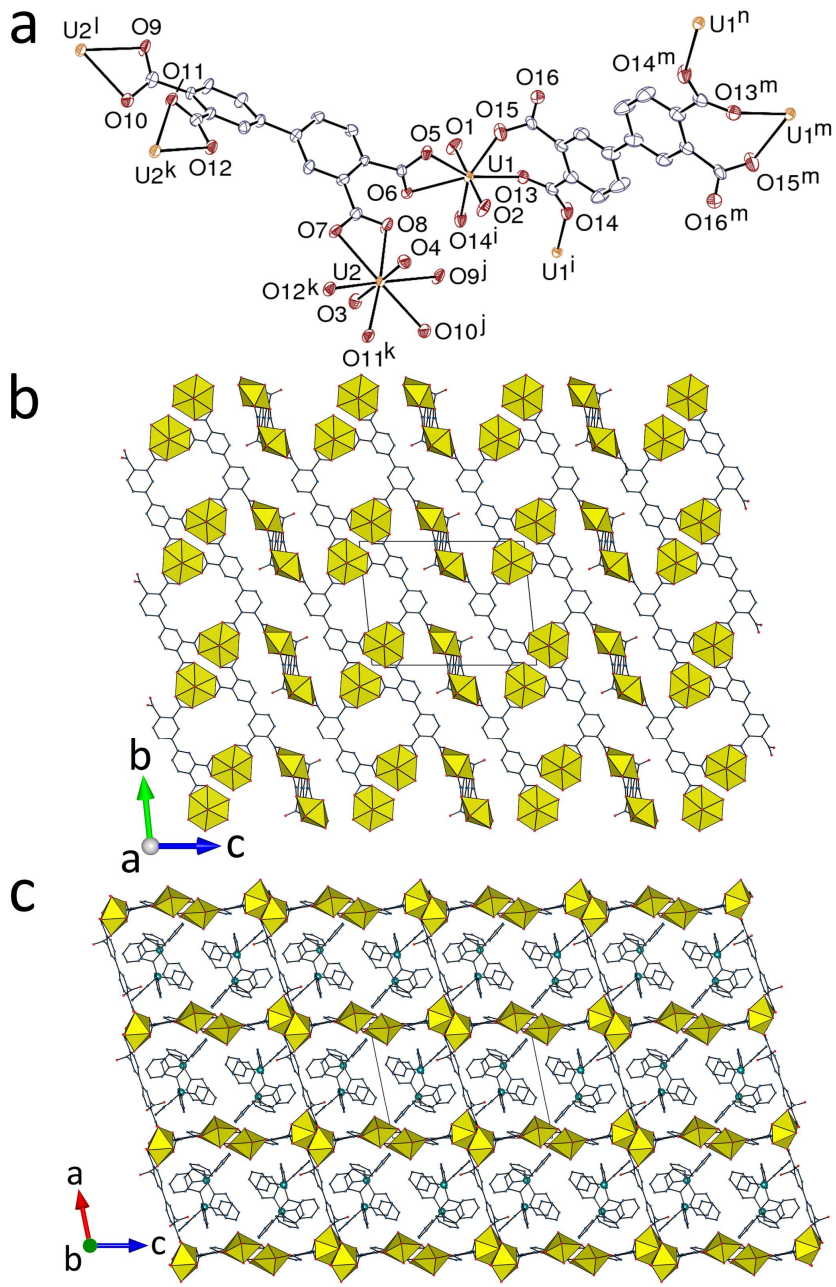


Figure 3. (a) View of complex **3** with displacement ellipsoids drawn at the 50% probability level. Counterions, solvent molecules and hydrogen atoms are omitted. Symmetry codes: i = –*x*, 2 – *y*, 1 – *z*; j = *x*, *y* + 1, *z*; k = –*x*, 1 – *y*, 2 – *z*; l = *x*, *y* – 1, *z*; m = –*x* – 1, 2 – *y*, 1 – *z*; n = *x* – 1, *y*, *z*. (b) View of the triperiodic framework. (c) View of the framework showing the channels occupied by the counterions.

carboxylate groups, in the *syn/anti* μ_2-κ^1O:κ^1O' mode, makes it a 4-c node, as is also the other ligand, with four κ^2O,O'-chelating carboxylate groups. The 4-nodal coordination polymer formed is triperiodic and it has the point symbol $\{4.12^2\}_2\{4^2.12^4\}\{4^2.6.12^3\}_2\{4^2.6\}_2$.

Two views of the nodal representation of the framework, drawn with ToposPro,[29] are shown in Figure 4. The framework contains near-orthogonal strands, or monoperiodic

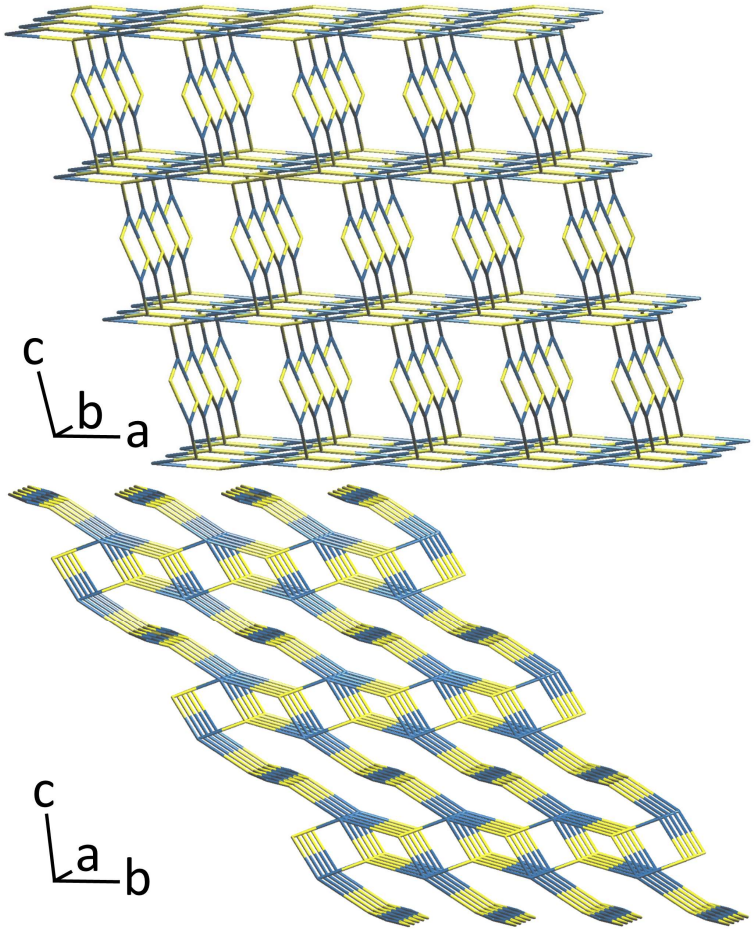


Figure 4. Two views of the nodal representation of the framework in complex **3** (uranium, yellow; bptc^{4-}, blue). The two types of monoperiodic subunits run in alternate horizontal planes.

subunits, in which the ligand–uranium interactions are quite different. In strands running parallel to [100], dinuclear units containing U1 are linked by ligands forming 7-membered chelate rings and bridging so that the dinuclear units are 8-membered dimetallacycles. In contrast, the strands running along [010] and containing U2 consist of alternating 14- and 22-membered metallacyclic units which are clearly visible in Figure 3b (much larger rings can be identified in the complete framework). These two strands are connected to one another by the κ^2*O,O′*-chelating carboxylate group containing O5 and O6 and bound to U1, each

strand being connected to its neighbours on both sides along the [001] axis, thus generating the triperiodic assembly. If only the arrangement and linking of strands is considered, it can be viewed as akin to the **cds** rod packing.[30] Large channels based on a section of ~13 × 18 Å^2 (the available space being reduced by protruding oxygen atoms) run along [010], each of them containing two rows of PPh_4^+ counterions (Figure 5). In each of these rows, the

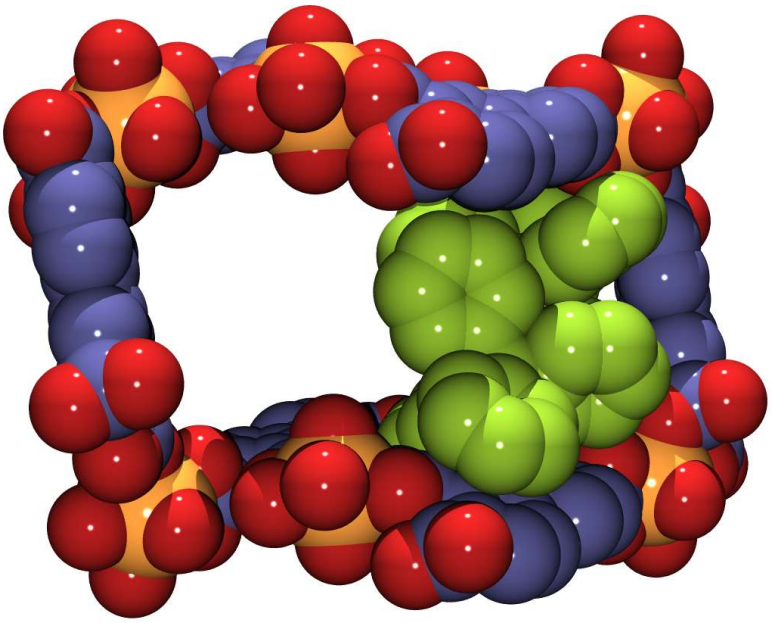
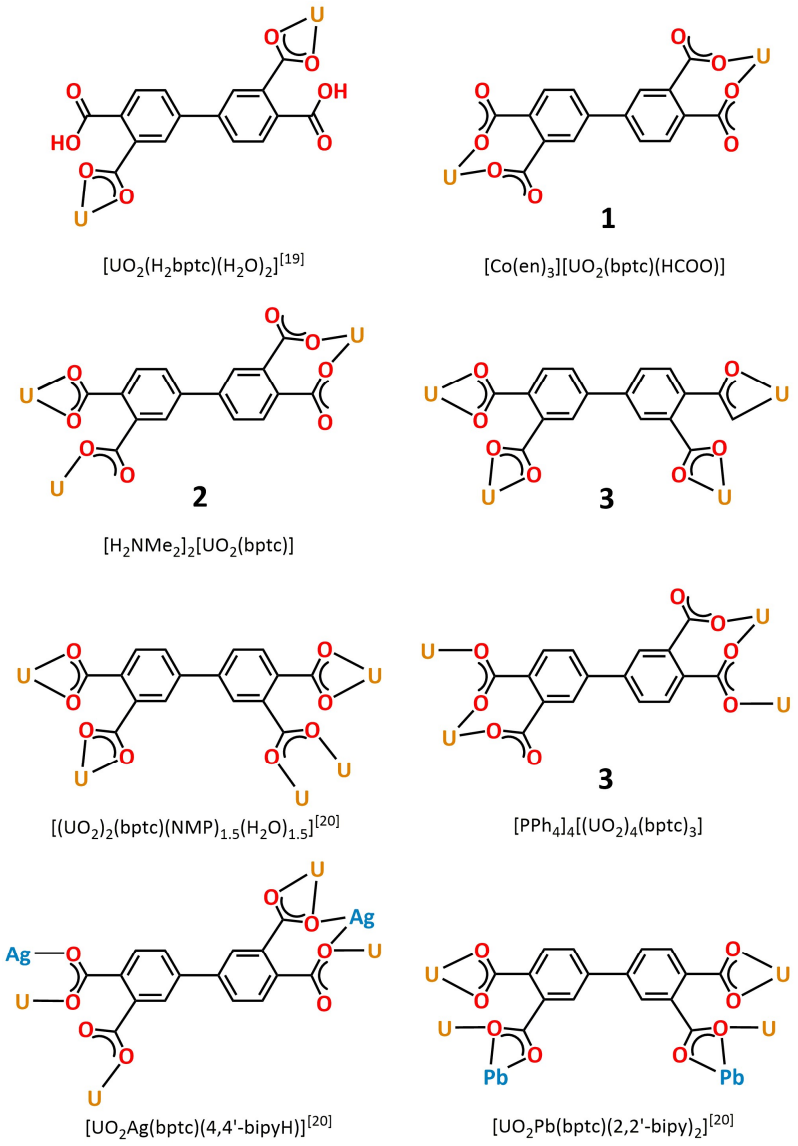


Figure 5. Space filling view of the section of one channel in complex **3**, with one of the two rows of counterions omitted (uranium, yellow; oxygen, red; phosphorus, green; carbon, blue in the polymer, green in the counterions).

counterions are associated through "phenyl embrace" interactions,[31] with an alternation of short and long P1···P2 distances, 6.656(2) and 8.380(2) Å corresponding to interactions involving three or two aromatic rings from each cation, respectively. Short contacts analysis with PLATON[28] indicates the possible presence of two parallel-displaced π-stacking interactions between $bptc^{4-}$ and PPh_4^+ [centroid···centroid distances, 3.901(5) and 4.083(4) Å; dihedral angles, 10.9(4) and 17.2(4)°; slippage, 1.38 and 1.48 Å]. Examination of the Hirshfeld surface (HS)[32] calculated with CrystalExplorer (ver. 3.1)[33] indicates that, as usual,

the PPh_4^+ cations are involved in several CH···O hydrogen bonds,[34] while water solvent molecules occupy the remaining spaces (KPI, 0.68).

Whereas 4-membered chelate ring formation through κ^2*O,O′*-chelation is expected to be a favoured mode for carboxylate binding to a large metal cation[35] like uranyl ion, in di- and higher polycarboxylates, formation of larger chelate rings through binding to one oxygen donor in each of two carboxylate groups is possible. 5-Membered chelate rings are found with oxalate,[36] as well as with various 2-hydroxycarboxylates,[37] and 6-membered rings are found with malonate.[38] There are 90 cases of 7-membered rings reported in the CSD, which involve, for example, citrate,[37] phthalate,[39] 4,4′-(1,1,1,3,3,3-hexafluoroisopropylidene)diphthalate[40] and 1,2-cyclohexanedicarboxylates.[41] Larger, 8-membered rings are known with citrate[42] and Kemp's tricarboxylate,[25,43] and 9-membered rings are found with 2,2'-bipyridine-3,3'-dicarboxylate,[44] 1,1′-biphenyl-2,2′-dicarboxylate,[14] and 1,1′-biphenyl-2,2′,6,6′-tetracarboxylate.[18] 7-Membered ring formation is present in all complexes **1**–**3**, and it is the only coordination mode found in **1**, in which two such rings are found in the equatorial plane of the uranyl ion, but this is at variance with previously reported uranyl ion complexes with this ligand, in which the only 7-membered ring involves Ag^I and not U^{VI}. The coordination modes observed in all known uranyl ion complexes with this ligand are shown in Scheme 1. The situation in which one 4-membered and one 7-membered rings are found around the same uranyl ion is found in **2** and **3**, but there is no example here of two 4-membered rings associated with a 7-membered one, although one such case is known in which the two 4-membered rings are formed by nitrate anions[45] (no example is known for larger rings, while such coexistence is possible, although not frequent,



Scheme 1. Coordination modes of $bptc^{4-}$ or H_2bptc^{2-} in uranyl ion complexes (solvent molecules are omitted from formulas).

with a 6-membered ring[38a,46]). In complex **3**, one ligand is exclusively involved in 4-membered ring formation, while the other is involved in 7-membered ring formation (with extra bridging) indicating that the difference between these two modes must be small.

Apart from the coordination mode of the ligand, rotation of the two aromatic rings around the central bond, related to the proximal or distal geometry of the two carboxylate groups in the 3-position, and of the carboxylate groups with respect to the aromatic rings

introduces another source of structure variations. Table 1 gives the values of the dihedral angles α_1 and α_2 formed by the carboxylate groups in the 4-position with respect to the attached aromatic ring, α_3 and α_4 formed by the carboxylate groups in the 3-position with respect to the attached aromatic ring, β_1 and β_2 between the two adjacent carboxylate groups on each ring, and γ between the two aromatic rings; the relative location of the two carboxylate groups in the 3-position, proximal or distal, is also indicated. As could be

Table 1. Dihedral angles (°) in $bptc^{4-}$/H_2bptc^{2-} ligands in uranyl ion complexes.

Complex	α_1	α_2	α_3	α_4	β_1	β_2	γ	Geometry
1	31.9(2)	33.9(2)	71.50(9)	65.24(10)	86.1(3)	83.5(3)	12.12(11)	distal
2	67.4(3)	11.9(10)	29.4(6)	53.1(5)	63.1(5)	52.7(7)	39.6(2)	distal
3	78.6(3) 15.4(6)	45.4(4)	0.9(4) 80.8(3)	21.1(8)	77.8(5) 88.6(6)	48.3(5)	28.0(2) 0	proximal distal
$[UO_2(H_2bptc)(H_2O)_2]$[19]	12.8(9)		74.1(2)		76.5(5)		0	distal
$[(UO_2)_2(bptc)(NMP)_{1.5}(H_2O)_{1.5}]$[20]	9.6(5)	20.9(5)	71.3(5)	67.5(6)	69.9(10)	72.0(10)	19.4(4)	proximal
$[UO_2Ag(bptc)(4,4'\text{-bipyH})]$[20]	75.98(12)	18.22(11)	21.0(2)	72.68(13)	79.1(2)	70.1(3)	9.67(5)	distal
$[UO_2Pb(bptc)(2,2'\text{-bipy})_2]$[20]	9.4(8)		72.6(3)		75.4(5)		65.41(15)	proximal

expected, the smaller rotations between the two aromatic rings are found in species with the distal geometry, and the two rings are coplanar in centrosymmetric, distal ligands, whereas the largest rotation is found in the proximal heterometallic complex with Pb^{II} additional cations. The rotation angles of the carboxylate groups with respect to the aromatic rings vary widely, with no clearcut relation to the coordination mode, and the two adjacent carboxylate groups on each ring make dihedral angles greater than 48°, and most often in the ~70–89° range. A similar situation has been found in a series of uranyl phthalate complexes,[47] and it suggests that easy rotation of the coordinating groups endows these

ligands with sufficient flexibility to be very sensitive to the effect of structure-directing species, while the proximity of the carboxylate groups bound to the same aromatic ring ensures that these ligands are never perfectly planar.

Taking a broader viewpoint, an eclectic selection from the recent literature[13,48–53] illustrates that the solid state coordination chemistry of uranyl carboxylates continues to be an active area of research concerned with a variety of possible applications. In our own work in this area, largely focussed on anionic coordination polymers, it has been apparent that hydrogen bonding interactions can have a major influence on the form of the complexes and even upon the coordination sphere of the uranyl ion. Our use of solvo-hydrothermal methods for the syntheses has also made it apparent that the solvents employed can not only influence the solubility of a product but that, through their own reactions under the conditions imposed, they can as well influence the composition of the product in various ways. The present work has provided further illustration of the operation of both these factors. Thus, complex **1** provides a unique example of a phthalate-like ligand being bound to uranyl ion exclusively through the formation of 7-membered chelate rings, apparently as a result of proton competition (hydrogen bonding) for the donor sites which in other complexes bind to uranyl ion and expand the periodicity of coordinative interactions. Hydrogen bonding by the multivalent $[Co(en)_3]^{3+}$ cation may also explain in part why the solvent-derived formate ligand is bound in a κ^1*O* and not a κ^2*O,O'* fashion, although the pentagonal-bipyramidal coordination of U^{VI} in the complex can also be considered a consequence of steric crowding of the equatorial coordination plane due to the presence of two 7-membered chelate rings, such a restriction being long known with 6-membered chelates such as 1,3-diketonates. Where even just a single 7-membered ring is present, as in complex **2** and one component of complex **3**, pentagonal-bipyramidal coordination of U^{VI}

applies, as is the case in various complexes of phthalate itself. Hexagonal-bipyramidal coordination can be attained, however, when three $bptc^{4-}$ ligands act as κ^2*O,O'*-chelates to one uranyl centre, as seen in one component of complex **3** and as is again known for phthalate itself. The somewhat unpredictable influence of the cosolvent in solvo-hydrothermal synthesis is well illustrated in the structures of complexes **1** and **2**, where the two products of DMF hydrolysis, formate and dimethylammonium, respectively, are separately present. As an NH donor, dimethylammonium ion is sterically a rather different species to $[Co(en)_3]^{3+}$ and the 2:1 cation/U stoichiometry in **2** does not provide even an equal number of interaction sites. These differences are reflected in the structures, though it may be noted that the Hirshfeld surfaces for both cations provide evidence of secondary CH···O interactions that are more prominent for dimethylammonium and thus may also play a role in determining the structures. Substitution in complex **3** of a CH donor, tetraphenylphosphonium cation, for the NH donors of **1** and **2** results not only in the crystallisation of a species lacking any solvent-derived components but also in a triperiodic polymer in which all known modes of phthalate ligand coordination to uranyl ion are present. Aromatic···aromatic interactions, both between cations and between cations and $bptc^{4-}$ units, have an influence on the polymer structure but it is again evident from consideration of all three present structures that equatorial coordination of carboxylate to uranyl ion must be an interaction of energy comparable to that of an NH···O bond. While this means that an effective mechanism of structure control exists, it is not yet obvious how this may be rationally exploited to generate triperiodic frameworks.

Conclusions

We have reported the synthesis and crystal structure of three uranyl ion complexes with 1,1'-biphenyl-3,3',4,4'-tetracarboxylate, a ligand which can be viewed as a phthalate dimer. These three complexes, which include $[Co(en)_3]^{3+}$, $H_2NMe_2^+$ or PPh_4^+ as counterions, are mono-, di- and triperiodic coordination polymers, respectively. These structures provide further evidence that the appropriate juxtaposition of two carboxylate groups on a scaffold of limited flexibility can favour the formation of 7-membered chelate rings, which are present in all cases, either exclusively in the monoperiodic polymer, or mixed with other coordination modes in the other two cases. The relatively large bite angle of such a ring appears to limit the number of additional donor atoms in the equatorial region of uranyl ion complexes to three and to thus enforce pentagonal bipyramidal coordination geometry, although two of the three additional donor atoms may derive from another 7-membered chelate ring. The presence of hydrogen bond donor species is clearly an important influence on the structure in the present series, with κ^2*O,O'* carboxylate chelation being favoured the weaker is this influence.

Experimental Section

General: $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (RP Normapur, 99%) was purchased from Prolabo, 1,1'-biphenyl-3,3',4,4'-tetracarboxylic acid dianhydride was from Aldrich, and $[Co(en)_3]Cl_3\cdot 3H_2O$ was from Alfa-Aesar. The elemental analysis of **1** was performed by MEDAC Ltd. Except for **1**, the low yields of the syntheses prevented further characterization. For all syntheses, the mixtures in demineralized water were placed in 10 mL tightly closed glass vessels and heated at 140 °C in a sand bath, under autogenous pressure. The crystals formed directly from the pressurized and heated reaction mixtures and not as a result of subsequent cooling.

Caution! Uranium is a radioactive and chemically toxic element, and uranium-containing samples must be handled with suitable care and protection. Small quantities of reagents and solvents were employed to minimize any potential hazards arising both from the presence of uranium and the use of pressurized vessels for the syntheses.

$[Co(en)_3][UO_2(bptc)(HCOO)]\cdot 2.5H_2O$ (1): 1,1'-Biphenyl-3,3',4,4'-tetracarboxylic acid dianhydride (30 mg, 0.10 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (50 mg, 0.10 mmol), and $[Co(en)_3]Cl_3\cdot 3H_2O$ (24 mg, 0.06 mmol) were dissolved in a mixture of water (0.9 mL) and DMF (0.3 mL), giving bright orange crystals of complex **1** within one month (45 mg, 81% yield based on Co). $C_{23}H_{36}CoN_6O_{14.5}U$ (925.54): calcd. C 29.85, H 3.92, N 9.08; found C 29.29, H 3.73, N 8.96.

$[H_2NMe_2]_2[UO_2(bptc)]\cdot 0.5H_2O$ (2): 1,1'-Biphenyl-3,3',4,4'-tetracarboxylic acid dianhydride (30 mg, 0.10 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (50 mg, 0.10 mmol), and $(Me_6trien)(HCF_3SO_3)_4$ (30 mg, 0.04 mmol) were dissolved in a mixture of water (0.9 mL) and DMF (0.3 mL), giving a few light yellow crystals of complex **2** within one month.

$[PPh_4]_4[(UO_2)_4(bptc)_3]\cdot 6H_2O$ (3): 1,1'-Biphenyl-3,3',4,4'-tetracarboxylic acid dianhydride (30 mg, 0.10 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (50 mg, 0.10 mmol), and PPh_4Br (42 mg, 0.10 mmol) were dissolved in a mixture of water (0.9 mL) and DMF (0.3 mL), giving a few light yellow crystals of complex **3** within ten days.

Crystallography: The data were collected at 100(2) K either on a Bruker D8 Quest diffractometer equipped with an Incoatec Microfocus Source (IμS 3.0 Mo) and a PHOTON III area detector, and operated through the APEX3 software[54] (complexes **1** and **2**), or on a Nonius Kappa-CCD area detector diffractometer[55] using graphite-monochromated Mo Kα radiation (complex **3**). The data were processed with SAINT[56] or HKL2000,[57] and absorption effects were corrected for empirically with SADABS[58] or SCALEPACK.[57] The structures were solved by intrinsic phasing with SHELXT[59] and refined by full-matrix least-squares on F^2 with SHELXL,[60] using the ShelXle interface.[61] All non-hydrogen atoms were refined with anisotropic displacement parameters. In complex **1**, the hydrogen atoms bound to water oxygen atoms were found on a residual electron density map and were refined with restraints, but those in **2** were neither found, nor introduced, and those in **3** only partially found. The hydrogen atoms bound to nitrogen atoms in **1** and **2** were introduced at calculated positions. In **2** and **3**, some water molecules have been given occupancy factor of 0.5 in order to retain an acceptable displacement parameter. The carbon-bound hydrogen atoms were introduced at calculated positions and 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). The Flack parameter for complex **2** was 0.031(9). Crystal data and structure refinement parameters are given in Table 2. The molecular plots were drawn with ORTEP-3[62] and the polyhedral representations with VESTA.[63]

CCDC 2084850 (for **1**), 2084851 (for **2**), and 2084852 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystal data and structure refinement details.

	1	**2**	**3**
Empirical formula	$C_{23}H_{36}CoN_6O_{14.5}U$	$C_{20}H_{23}N_2O_{10.5}U$	$C_{144}H_{110}O_{38}P_4U_4$
M (g mol^{-1})	925.54	697.43	3524.31
Crystal system	monoclinic	orthorhombic	triclinic
Space group	$P2_1/c$	$Fdd2$	$P\bar{1}$
a (Å)	8.3035(3)	30.2257(8)	13.5485(8)
b (Å)	15.7282(6)	43.1520(11)	13.7423(4)
c (Å)	23.0166(9)	7.4235(2)	18.2212(10)
α (°)	90	90	93.975(3)
β (°)	94.2492(17)	90	100.588(2)
γ (°)	90	90	99.613(3)
V (Å^3)	2997.7(2)	9682.5(4)	3270.4(3)
Z	4	16	1
Reflections collected	170406	162891	145767
Independent reflections	7730	7401	12421
Observed reflections [$I > 2\sigma(I)$]	7122	7324	9526
R_{int}	0.057	0.063	0.055
Parameters refined	433	317	850
R_1	0.019	0.026	0.038
wR_2	0.041	0.060	0.092
S	1.085	1.313	1.056
$\Delta\rho_{min}$ (e Å^{-3})	−0.70	−1.83	−1.38
$\Delta\rho_{max}$ (e Å^{-3})	1.26	1.54	2.09

Keywords: Carboxylic acids / Metal–organic frameworks / Structure elucidation / Tetracarboxylate ligands / Uranyl cation

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