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Stepwise Introduction of Flexibility into Aromatic Dicarboxylates Forming Uranyl Ion Coordination Polymers: a Comparison of 2-Carboxyphenylacetate and 1,2-Phenylenediacetate

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/

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Abstract

2-Carboxyphenylacetate (cpa^{2-}) and 1,2-phenylenediacetate ($1,2\text{-}pda^{2-}$) have been reacted with uranyl cations under solvo-hydrothermal conditions to generate six homo- or heterometallic complexes. Both $[UO_2(cpa)]$ (**1**) and $[UO_2(cpa)(phen)]$ (**2**), where phen is 1,10-phenanthroline, crystallize as monoperiodic coordination polymers. $[Ni(bipy)_3][(UO_2)_2(cpa)_3]\cdot 2.5H_2O$ (**3**), is a diperiodic network with the **hcb** topology, in which the hexagonal cells distort to accommodate the counterions. $[UO_2(cpa)_2Ni(R,S\text{-}Me_6cyclam)]$ (**4**) crystallizes as a heterometallic diperiodic network, in which uranyl dicarboxylate chains are assembled by bridging Ni^{II} cations. While $[dmaepH_2][(UO_2)_2(1,2\text{-}pda)_3]\cdot 3H_2O$ (**5**), where dmaep is 1,4-bis(2'-dimethylaminoethyl)piperazine, is a diperiodic **hcb** network, $[QH]_2[(UO_2)_2(1,2\text{-}pda)_3]\cdot 3CH_3CN$ (**6**), where Q is quinuclidine, is the first example of a triperiodic framework in the uranyl–phenylenediacetate family, its topological type being **bto**. The complex involving the related ligand 1,4-phenylenediacetate ($1,4\text{-}pda^{2-}$), $[QH]_2[(UO_2)_2(1,4\text{-}pda)_3]\cdot 2CH_3CN$ (**7**), is a daisy-chain-like monoperiodic polymer. These and previously reported results are discussed in terms of ligand flexibility and ability to form large chelate rings.

Introduction

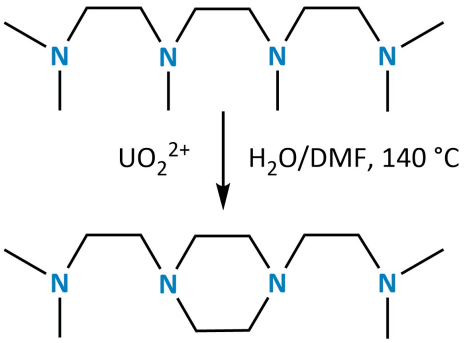
Polycarboxylates are ligands among the most used for the synthesis of uranyl ion-containing coordination polymers and frameworks,[1–5] and, considering the huge range of geometries and denticities covered by these anions, this allows for detailed studies of the effect of fine modifications of the ligands upon the structure of the complexes formed. In particular, comparison of the structures of uranyl ion complexes of homologous pairs of ligands such as adamantane-dicarboxylate and -diacetate,[6–9] or phthalate[10] and 1,2-phenylenediacetate[11–13] has enabled some assessment of the influence of rotation about additional C–C single bonds to be made. In these particular cases, however, the influence is that of the addition of two such bonds and comparisons involving the singly modified ligands 3-carboxylato-adamantane-1-acetate or 2-carboxyphenylacetate are lacking. For the former, its chirality introduces a further complication so that the latter, even though it may adopt chiral conformations, is the simpler system for initial investigation. The present report concerns the crystal structures of four uranyl ion complexes of 2-carboxyphenylacetate (cpa^{2-}) and two new complexes of 1,2-phenylenediacetate (1,2-pda^{2-}) to be placed within the context of their known relatives, as well as a new complex of 1,4-phenylenediacetate (1,4-pda^{2-}) for purpose of comparison with 1,2-pda^{2-}. These complexes have been synthesized under solvo-hydrothermal conditions, in the presence of different possible additional ligands or counterions. The counterions used have been either the bulky, metal-containing $[Ni(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) and [Ni(*R,S*-Me_6cyclam)]$^{2+}$ (*R,S*-Me_6cyclam (meso isomer) = 7(*R*),14(*S*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), or protonated quinuclidine (HQ^+). An attempt to use protonated Me_6trien (1,1,4,7,10,10-hexamethyltriethylenetetramine) as a counterion resulted in an in situ transformation of the latter into 1,4-bis(2′-dimethylaminoethyl)piperazine (dmaep). A search of the Cambridge

Structural Database (CSD, version 5.41[14]) shows that, although 2-carboxyphenylacetate is a common ligand for d-block metal cations and has also been used with lanthanide cations, no structure with an actinide cation has been reported previous to the present examples.

Results and Discussion

Syntheses

Crystals of all complexes were grown under solvo-hydrothermal conditions at a temperature of 140 °C, the crystals being formed directly from the pressurized and heated reaction mixtures and not as a result of subsequent cooling. The organic cosolvents used were either acetonitrile (**1**, **6** and **7**), *N,N*-dimethylformamide (DMF) (**3**–**5**), or tetrahydrofuran (THF) (**2**), but only in **6** and **7** are solvent (acetonitrile) molecules retained in the final compound. The most unexpected observation here is that of the reaction affecting protonated Me_6trien in the synthesis of complex **5**. As indicated in Scheme 1, under the conditions used, this molecule underwent a transalkylation reaction giving a central piperazine ring, similarly to



Scheme 1. Transalkylation of Me_6trien during the synthesis of complex **5**. Protonation of the amine groups is not indicated.

the known reaction of *N,N,N',N'*-tetramethylethylenediamine,[15] the lateral amine groups being untouched. It may be possible that uranyl cations act as catalysts for this reaction, this

being one more example of the occurrence of unexpected organic reactions when using metal cations under solvo-hydrothermal conditions requiring prolonged heating. It is known that, when photo-excited, uranyl is able to abstract a hydrogen atom to form an organic radical,[16] and this may be the mechanism at play here. Except for compound **1**, for which the metal/dicarboxylate ligand stoichiometry is 1:1 in both the solution and the isolated complex, the 7:10 stoichiometry has been chosen for all syntheses in order to favor the formation of an anionic uranium polycarboxylate species and consequent inclusion of counterions, which indeed occurs in all cases but **2**, for which the Pb^{II} cations present are not included in the complex, the 1,10-phenanthroline (phen) coligand being bound to uranyl. The stoichiometry in the solid state is generally 2:3 as expected, except for complexes **2** and **4** in which it is 1:1 and 1:2, respectively.

Crystal Structures

The complex $[UO_2(cpa)]$ (**1**), shown in Figure 1, is the simplest species obtainable with this ligand. The carboxylate substituent of the cpa^{2-} anion bridges two cations in the *syn/anti* μ_2-κ^1O:κ^1O' mode, while the acetate group is both chelating and bridging in the μ_2-κ^2O,O':κ^1O mode. One metal cation being common to both groups, an eight-membered chelate ring is formed, analogous to the seven-membered rings frequent in uranyl phthalate complexes.[10] The uranyl cation is bound to three cpa^{2-} ligands, two of them chelating, the uranium coordination environment being thus pentagonal-bipyramidal [U–O(oxo), 1.7611(15) and 1.7663(15) Å; U–O(carboxylato), 2.4854(15) and 2.4956(15) Å for the κ^2O,O'-chelating group,

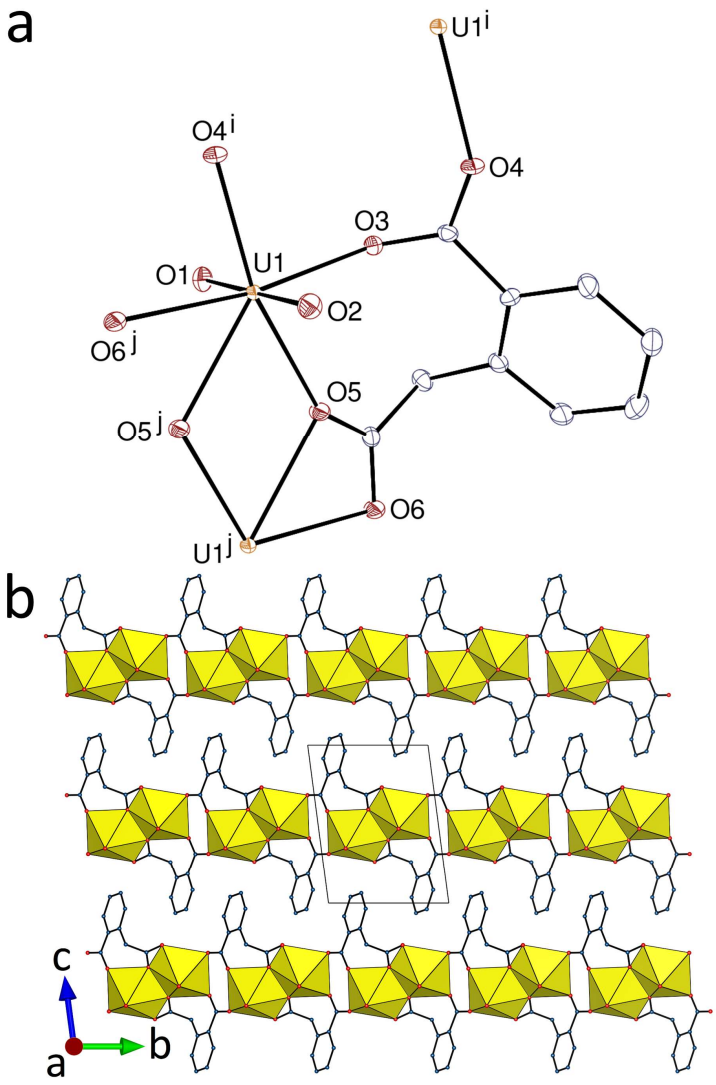


Figure 1. (a) View of complex **1**. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: i = 2 – *x*, 2 – *y*, 1 – *z*; j = 1 – *x*, 1 – *y*, 1 – *z*. (b) View of the packing with uranium coordination polyhedra colored yellow. Hydrogen atoms are omitted in both views.

and 2.2965(15)–2.4048(15) Å for the others]. The coordination polymer formed is monoperiodic and parallel to [110], and it contains centrosymmetric, dimeric units of edge-sharing uranium coordination polyhedra. While unsolvated forms of the neutral complexes containing phthalate (pht^{2-}) or 1,2-pda^{2-} have not been structurally characterized, at least in the complex $[UO_2(1,2\text{-pda})]\cdot CH_3CN$,[13] unlike $[UO_2(pht)(H_2O)]\cdot H_2O$,[17] the solvent molecule is not coordinated. The 1,2-pda^{2-} complex is a diperiodic polymer in which the ligand acts as a

bis(κ^2*O,O′*) bridging unit only and although the pht^{2-} complex is a monoperiodic (but double stranded) polymer, the carboxylate groups are involved in seven-membered chelate ring formation along with μ_2-κ^1*O*:κ^1*O*′ bridging. In neither case is there formation of a four-membered κ^2*O,O*′ chelate ring, even though such rings are seen in other uranyl ion complexes of both ligands.[10–13,18] The chains in **1** are arranged in layers parallel to (001), which are interdigitated and tightly packed, with a Kitaigorodski packing index (KPI, calculated with PLATON[19]) of 0.74. Analysis of short contacts with PLATON indicates that interlayer parallel-displaced π-stacking interactions may be present [centroid···centroid distance, 3.8326(14) Å; dihedral angle, 0°; slippage, 1.31 Å]. Examination of the Hirshfeld surface (HS)[20] calculated with CrystalExplorer (ver. 3.1)[21] indicates that these interactions are complemented by CH···O hydrogen bonds,[22,23] as is usual in such carboxylate complexes.

In contrast to **1**, [UO_2(cpa)(phen)] (**2**) shows a strong resemblance to its 1,2-pda^{2-} analogues with both phen and bipy as coligands[12] in that cpa^{2-} is bound in a bis(κ^2*O,O′*) bridging manner in a monoperiodic polymer (Figure 2). The uranium atom is chelated by two cpa^{2-} ligands and one phen molecule and its environment is hexagonal-bipyramidal [U–O(oxo), 1.766(5) and 1.769(5) Å; U–O(carboxylato), 2.434(5)–2.509(5) Å; U–N, 2.684(6) and 2.687(6) Å]. As usual, the phen molecule is tilted with respect to the uranyl equatorial plane.[24] This bis(κ^2*O,O′*) mode of ligand binding is almost unknown (see ahead) in phthalate (pht^{2-}) complexes, seemingly because formation of a seven-membered chelate ring is more favoured generally, although the exact compositional analogue of **1** is yet to be structurally

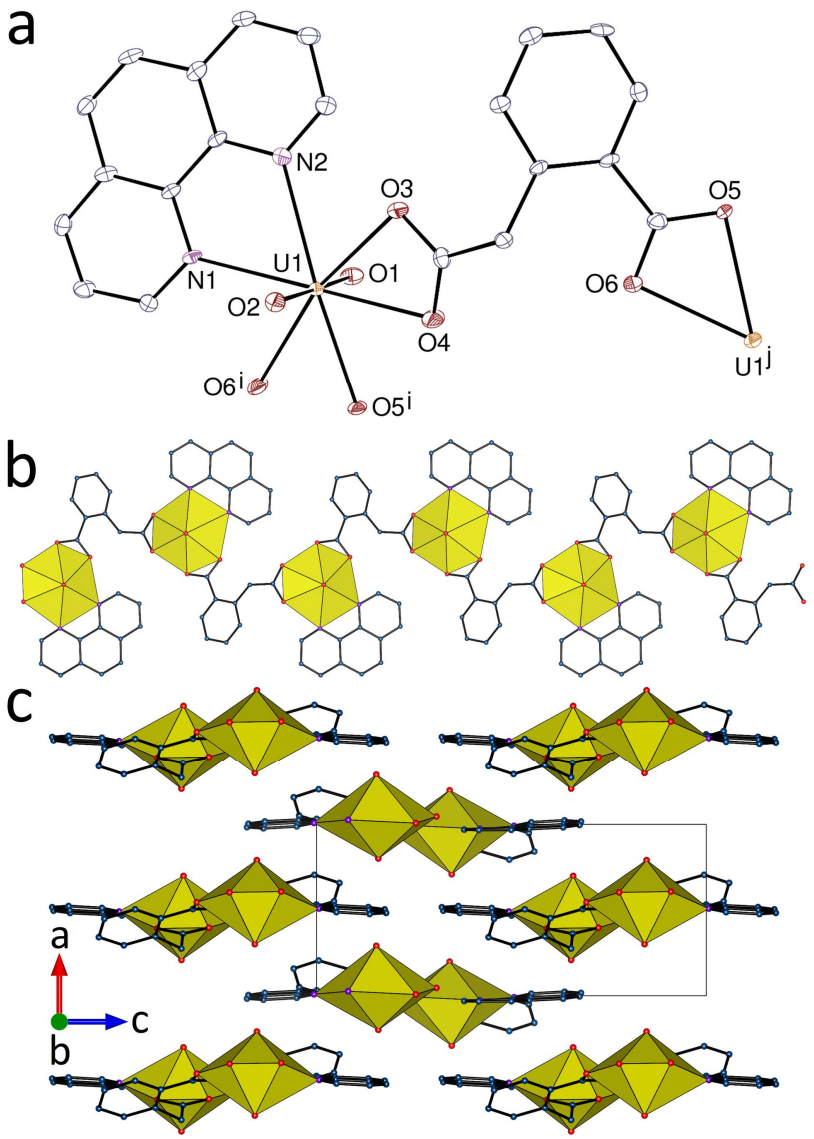


Figure 2. (a) View of complex **2**. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: i = 1 – *x*, *y* – 1/2, 3/2 – *z*; j = 1 – *x*, *y* + 1/2, 3/2 – *z*. (b) View of the monoperiodic coordination polymer. (c) View of the packing. Hydrogen atoms are omitted in all views.

characterized, and in the nanotubular complex $[UO_2(pht)(H_2O)]\cdot 0.32H_2O$,[18] pht^{2-} binds in a bis(μ_2-κ^1O:κ^1O') manner. In the complex of the aliphatic analogue of phthalate, maleate (mal^{2-}), $(NH_4)_2[UO_2(mal)_2]$,[25] the bis(κ^2O,O') bridging mode is found, so it is perhaps premature to conclude that it must necessarily be rare in uranyl phthalate species. The monoperiodic assembly in **2** assumes the shape of a flat ribbon directed along [010], these

chains being further arranged in layers parallel to (100). The calculation of short contacts indicates that several parallel-displaced π-stacking interactions involving phen aromatic rings are possibly present [centroid···centroid distances, 3.652(4)–3.854(4) Å; dihedral angles, 3.0(4)–5.4(4)°; slippages, 1.05–1.41 Å], resulting in a compact packing (KPI, 0.73).

Complex **3**, $[Ni(bipy)_3][(UO_2)_2(cpa)_3]\cdot 2.5H_2O$, provides a second example of cpa^{2-} binding in a bis(κ^2O,O') bridging mode (Figure 3). Both independent uranyl cations are tris-chelated, with the uranium atom in a hexagonal-bipyramidal environment [U–O(oxo), 1.7643(19)–1.7748(19) Å; U–O(carboxylato), 2.443(2)–2.5154(18) Å]. The uranium atoms are thus three-coordinated (3-c) nodes and the cpa^{2-} ligands are simple links in the diperiodic coordination polymer formed, which is parallel to (010) and has the $\{6^3\}$ vertex symbol and

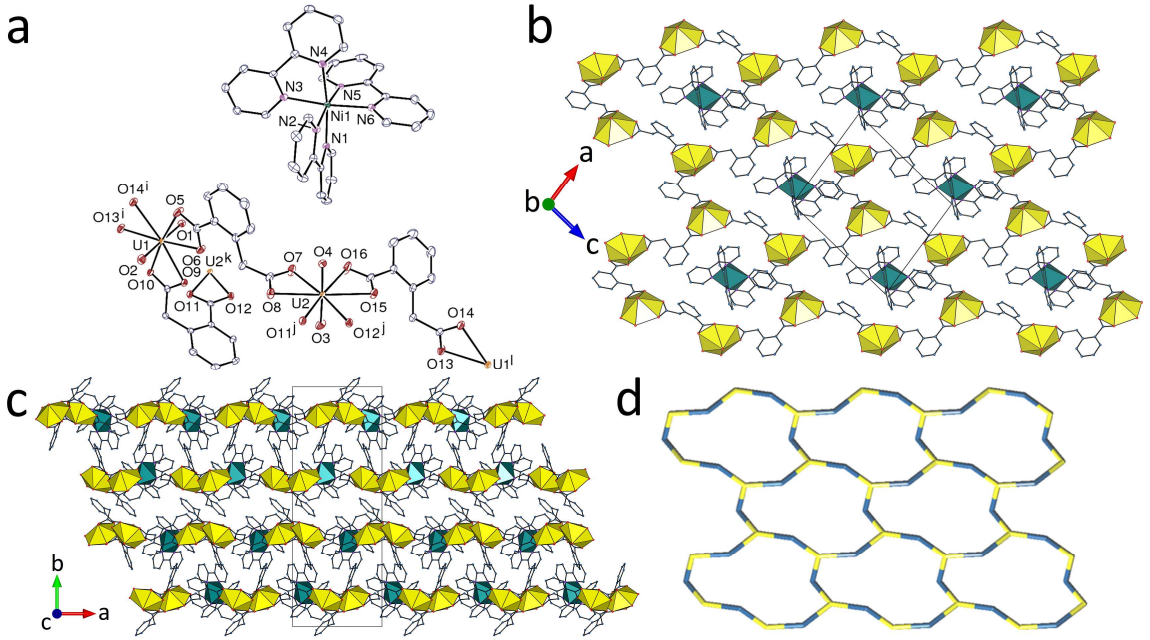


Figure 3. (a) View of complex **3** with displacement ellipsoids drawn at the 50% probability level. Solvent molecules and hydrogen atoms are omitted. Symmetry codes: i = *x* + 1, *y*, *z* + 1; j = *x* – 1, *y*, *z*; k = *x* + 1, *y*, *z*; l = *x* – 1, *y*, *z* – 1. (b) View of the diperiodic coordination polymer and the counterions with uranium coordination polyhedra yellow and those of nickel green. (c) Packing with layers viewed edge-on. (d) Nodal representation of the network (yellow, uranium nodes; blue, dicarboxylate links; same orientation as in (b)).

the **hcb** topological type. The cells in the network are much distorted with respect to the ideal hexagon, presumably due to inclusion of part of the counterion, which results in a compact packing (KPI, 0.69). The two possible parallel-displaced π-stacking interactions are between cpa^{2-} and bipy, the counterion interacting only with the polymer sheet in which it is included [centroid···centroid distances, 3.9775(15) and 3.9936(16) Å; dihedral angles, 6.56(12) and 15.65(13)°; slippages, 1.68 and 1.53 Å]. Only one CH···π interaction possibly links one cpa^{2-} ligand to a counterion associated to a neighbouring sheet [H···centroid distance, 2.84 Å; C–H···centroid angle, 153°]. The HS shows however that the main interactions are OH···O and CH···O hydrogen bonds. There are certain similarities between the structure of **3** and that of the monoperiodic, helical complex $[Ni(bipy)_3][UO_2(pht)(NO_3)]_2$,[10] isolated as a chiral crystal in which the uranium centres, as here, have hexagonal-bipyramidal coordination and the polymer involves bis(κ^2*O,O'*) bridging, providing the only known example of exclusive adoption of this coordination mode for phthalate on uranyl ion. In essence, for complex **3** one cpa^{2-} unit can be regarded as replacing the nitrate ion of the phthalate structure. While no exact analogue of **3** is known for 1,2-pda^{2-}, bis(κ^2*O,O'*) coordination can be said to be typical of this ligand[11–13] and is frequently associated with uranium in a hexagonal-bipyramidal environment, indicating that this may be a factor opposing large chelate ring formation.

The unique uranyl cation in $[UO_2(cpa)_2Ni(R,S\text{-}Me_6cyclam)]$ (**4**) is κ^2*O,O'*-chelated by one ligand and it is bound to three more oxygen donors from three additional cpa^{2-} ligands, the uranium atom environment being pentagonal-bipyramidal [U–O(oxo), 1.770(3) and 1.780(3) Å; U–O(carboxylato), 2.456(3) and 2.515(3) Å for the chelating group, and 2.277(3)–2.395(3) Å for the others] (Figure 4). Axial coordination of carboxylate oxygen atoms to both

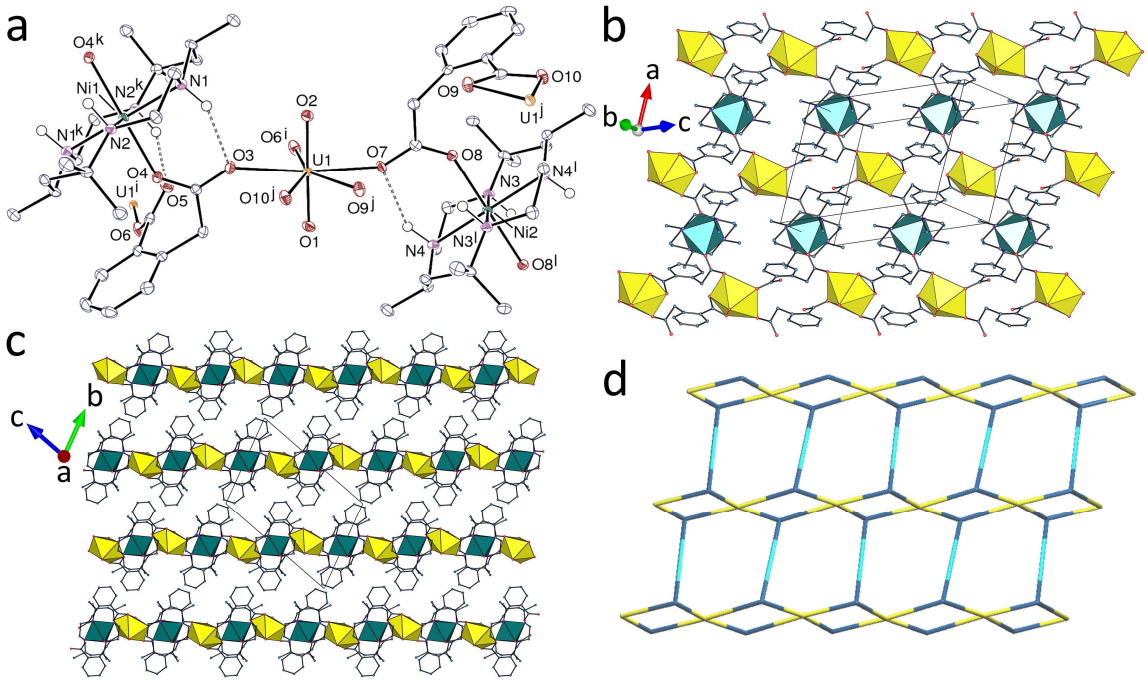


Figure 4. (a) View of complex **4** with displacement ellipsoids drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Symmetry codes: i = 1 – *x*, 1 – *y*, – *z*; j = 1 – *x*, –*y*, 1 – *z*; k = 2 – *x*, 1 – *y*, –*z*; l = –*x*, –*y*, 1 – *z*. (b) View of the diperiodic coordination polymer with uranium coordination polyhedra yellow and those of nickel green. (c) Packing with layers viewed edge-on. (d) Nodal representation of the network (yellow, uranium nodes; dark blue, dicarboxylate nodes; light blue, nickel links; orientation slightly rotated with respect to that in (b)).

trans positions on the two centrosymmetric Ni^{II} macrocycle complexes modifies the behaviour of cpa^{2-} in such a way that it adopts two different uranyl-bridging modes. Each of the two independent ligands has one carboxylate group bridging uranium and nickel in the *syn/anti* μ_2-κ^1O:κ^1O' mode, but the second carboxylate group is monodentate in one ligand and chelating in the other. Ignoring the further interactions with Ni^{II}, these bridging modes alternate in pairs to give a monoperiodic polymer. These polymer units are linked into diperiodic sheets parallel to (011) by the coordination to the two inequivalent Ni^{II} sites, both located on inversion centres. Uranium atoms are 4-c nodes, cpa^{2-} are 3-c nodes and nickel atoms are simple links, and the network has the vertex symbol $\{4.6^2\}_2\{4^2.6^2.8^2\}$ and the

topological type 3,4L13, previously found in some transition metal ion complexes,[26,27] and also in some uranyl compounds,[9,28,29] with one particular example involving 1,4-pda^{2-}.[13] No significant π-stacking interaction is apparent in this case, the only weak interactions worthy of note being the hydrogen bonds between the amine groups of *R,S*-Me$_6$cyclam and carboxylate groups [N···O distances, 3.007(5)–3.196(5) Å; N–H···O angles, 141(4)–148(4)°], as well as the usual CH···O hydrogen bonds. The network is quite planar, with the aromatic groups pointing outward on either side, and the KPI is 0.72.

The complex [dmaepH$_2$][(UO$_2$)$_2$(1,2-pda)$_3$]·3H$_2$O (**5**), where dmaep is the piperazine derivative generated in situ from Me$_6$trien (see above), is shown in Figure 5. The unique

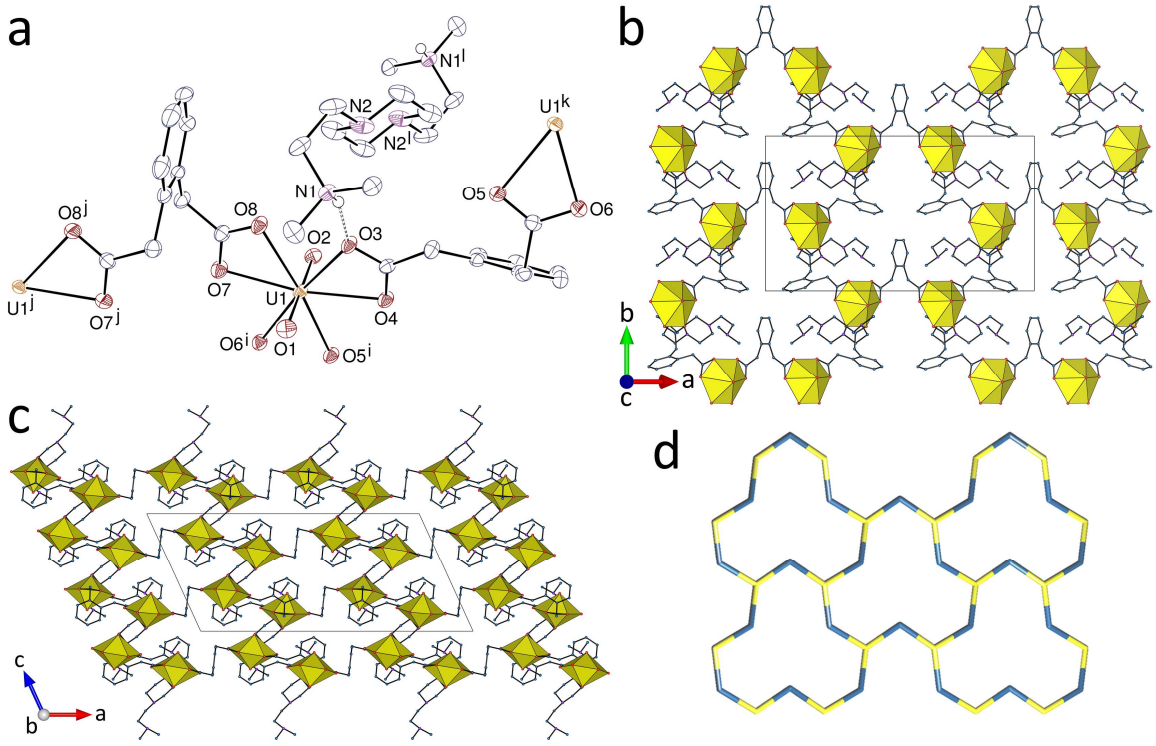


Figure 5. (a) View of complex **5** with displacement ellipsoids drawn at the 50% probability level. Solvent molecules and carbon-bound hydrogen atoms are omitted, and the hydrogen bond is shown as a dashed line. Symmetry codes: i = 3/2 – *x*, *y* + 1/2, 3/2 – *z*; j = 2 – *x*, *y*, 3/2 – *z*; k = 3/2 – *x*, *y* – 1/2, 3/2 – *z*; l = 3/2 – *x*, 1/2 – *y*, 1 – *z*. (b) View of the diperiodic coordination polymer with the counterions. (c) Packing with layers viewed edge-on. (d) Nodal representation of the network (yellow, uranium nodes; dark blue, dicarboxylate links; same orientation as in (b)).

uranyl cation is κ^2*O,O'*-chelated by three carboxylate groups [U–O(oxo), 1.7745(15) and 1.7752(16) Å; U–O(carboxylato), 2.4284(15)–2.5196(15) Å], and the two 1,2-pda^{2-} ligands (one of them on a twofold rotation axis) are bis-chelated. The diperiodic polymer formed, parallel to (001), has the **hcb** topology with distorted, pseudo-trigonal cells and a step-like profile, and is essentially identical to that found in $[C(NH_2)_3]_2[(UO_2)_2(1,2\text{-pda})_3]\cdot 0.5H_2O\cdot CH_3CN$.[13] The centrosymmetric, diprotonated dmaepH_2^{2+} cation, where the piperazine ring has a chair conformation and the two dimethylaminoethyl groups are attached equatorially, with protons located on the terminal dimethylamino groups, is involved in fewer hydrogen bonding interactions than guanidinium, being bound to two carboxylate groups pertaining to different layers [N···O distance, 2.739(2) Å; N–H···O angle, 157(3)°], and thus assembling the layers into a triperiodic assembly (KPI, 0.70). No significant parallel π-stacking interaction is apparent in this case, with no centroid···centroid distance shorter than 5.9 Å, but CH···π interactions involving the $-CH_2-CH_2-$ groups of the cations may be significant [H···centroid distances, 2.72 and 2.89 Å; C–H···centroid angles, 132 and 129°], and they appear on the HS, as well as CH···O hydrogen bonds involving the terminal methyl groups of the cation and carboxylate groups.

The consequences of limiting strong hydrogen bonding of a countercation to a single site are rather strikingly revealed in the structure of $[QH]_2[(UO_2)_2(1,2\text{-pda})_3]\cdot 3CH_3CN$ (**6**) where the coordination polymer is triperiodic, the first found to be formed with the 1,2-pda^{2-} ligand (Figure 6). The two independent uranyl cations are tris-chelated by carboxylates from three separate ligands, two of one chirality and one of the other [U–O(oxo), 1.773(3)–

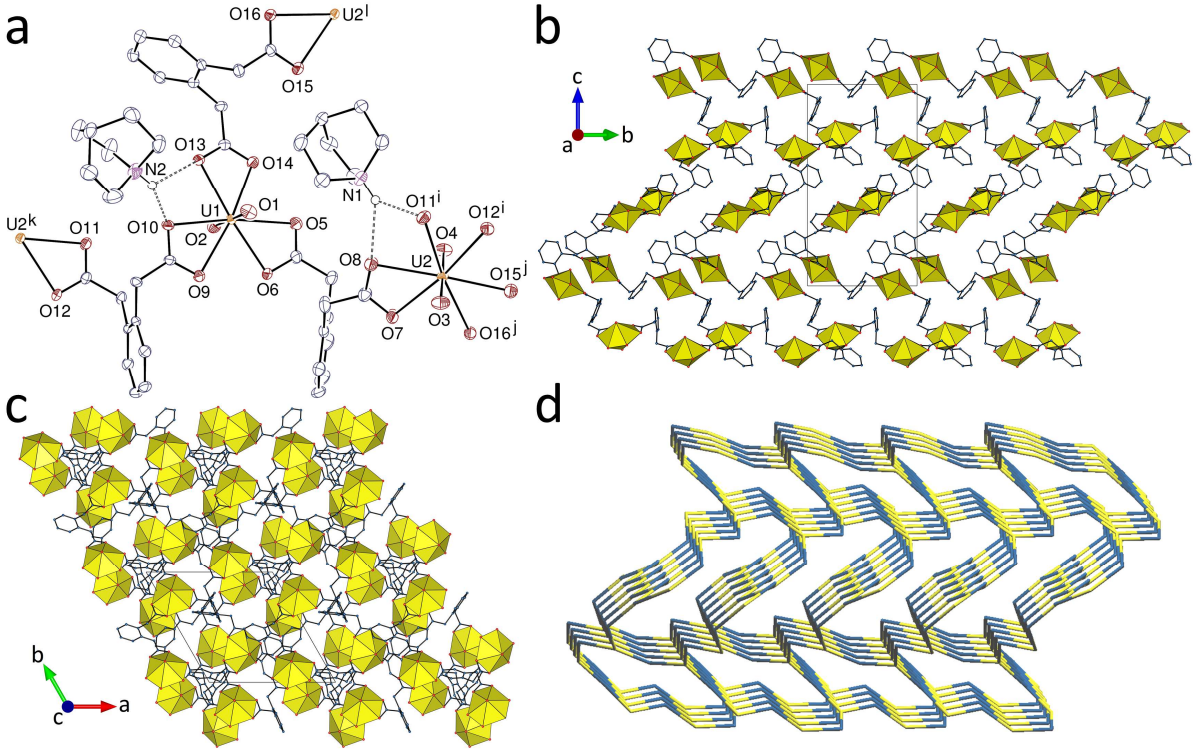


Figure 6. (a) View of complex **6** with displacement ellipsoids drawn at the 50% probability level. Solvent molecules and carbon-bound hydrogen atoms are omitted, and the hydrogen bonds are shown as dashed lines. Symmetry codes: i = 1 – *y*, *x* – *y*, *z* + 1/3; j = 1 – *y*, *x* – *y* + 1, *z* + 1/3; k = *y* – *x* + 1, 1 – *x*, *z* – 1/3; l = *y* – *x*, 1 – *x*, *z* – 1/3. (b) and (c) Two views of the triperiodic framework with hydrogen atoms, counterions and solvent molecules omitted. (d) Nodal representation of the framework (yellow, uranium nodes; dark blue, dicarboxylate links; orientation slightly rotated with respect to that in (b)).

1.776(3) Å; U–O(carboxylato), 2.414(3)–2.510(3) Å], the ligand role and pseudo-C_2 conformation being as in **5**. The uninodal, 3-c framework formed has the point symbol $\{10^3\}$ and the topological type **bto**, a uninodal subnet of **qtz**. The NH···O interactions are bifurcated and involve two carboxylate oxygen atoms coordinated to the same uranium atom, so as to form rings with the graph set descriptor[30,31] $R_1^2(4)$ [N···O distances, 2.730(5)–3.270(5) Å; N–H···O angles, 127(5)–156(6)°]. In this case, there is no contribution of π-stacking or CH···π interactions, but CH···O interactions are present. The triperiodic nature of the polymer is now associated with cavities in the form of flat channels running parallel to

the (001) plane, which enclose the hydrophobic tail of the quinuclidine units and the acetonitrile molecules, the packing having no significant free space (KPI, 0.70).

The complex $[QH]_2[(UO_2)_2(1,4\text{-pda})_3]\cdot 2CH_3CN$ (**7**), shown in Figure 7, illustrates the effect of the same quinuclidinium cation on the structure involving the related, but divergent ligand 1,4-pda^{2-}. Here also, the unique uranyl cation is chelated by three carboxylate groups [U–O(oxo), 1.7802(16) and 1.7806(16) Å; U–O(carboxylato), 2.4391(16)–2.5156(16) Å], but the coordination polymer formed is monoperiodic and it has the daisy-

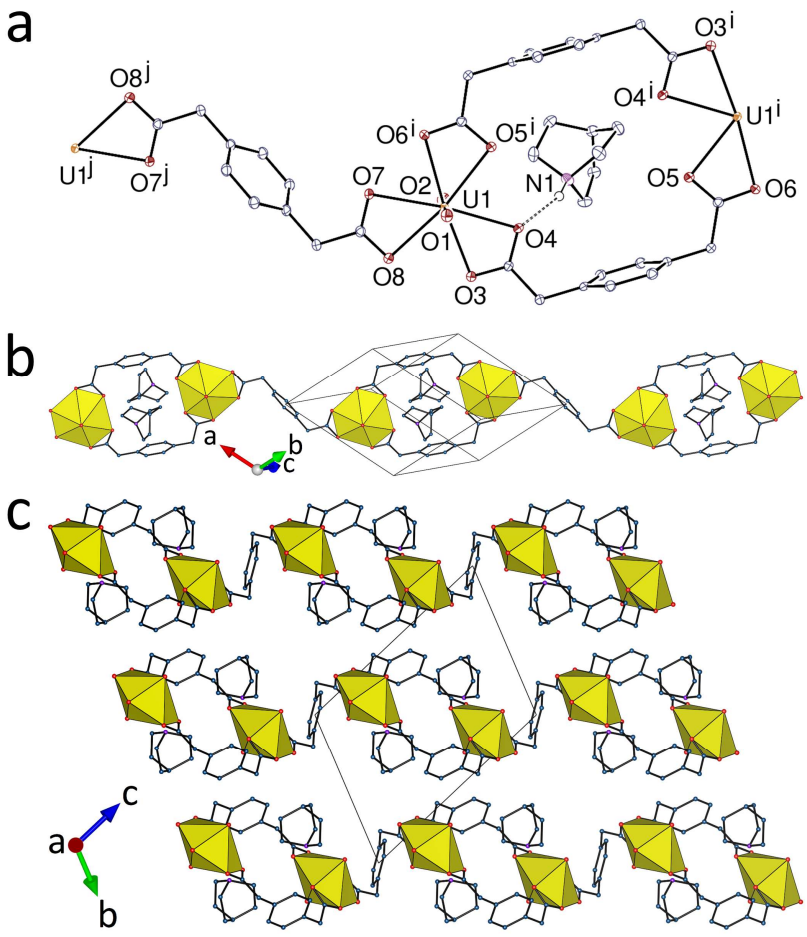


Figure 7. (a) View of complex **7** with displacement ellipsoids drawn at the 50% probability level. Solvent molecules and carbon-bound hydrogen atoms are omitted, and the hydrogen bond is shown as a dashed line. Symmetry codes: i = 1 – *x*, 1 – *y*, 1 – *z*; j = –*x*, 2 – *y*, 2 – *z*. (b) View of the monoperiodic coordination polymer with the counterions. (c) Packing with chains viewed obliquely.

chain-like shape familiar from earlier studies of 1,4-pda^{2-} complexes where 22-membered diuranacyclic units with the ligands in a cis configuration are linked by single ligands in a trans configuration, resulting in the formation of a quasi-linear chain (zigzag chains are formed when all ligands are cis, such as in $[H_2NMe_2]_2[(UO_2)_2(1,4\text{-pda})_3]$),[13] and further confirming the nature of the ligand as a bis(κ^2*O,O'*)-bridging unit. A very similar structure is found in $[PPh_3Me][H_2NMe_2][(UO_2)_2(1,4\text{-pda})_3]\cdot H_2O$, in which the dimethylammonium cation is held by two hydrogen bonds within the dinuclear ring.[13] Here, two QH^+ counterions are associated with each diuranacyclic unit, and they form single hydrogen bonds with carboxylate oxygen atoms [N···O distance, 3.034(3) Å; N–H···O angle, 161(3)°]. The orientation of the phenyl rings of the diuranacycles is such as to provide walls to a small cavity, into which the NH part of the protonated quinuclidine cations partly intrude, the packing being quite compact (KPI, 0.73). Adjacent chains are associated by parallel-displaced π-stacking interactions between the cis 1,4-pda^{2-} ligands of the dinuclear units [centroid···centroid distance, 3.5909(12) Å; dihedral angle, 0°; slippage, 1.30 Å]. Further weak bonding is provided by the aromatic ring of the trans ligand being involved in two CH···π interactions with QH^+ cations [H···centroid distance, 2.70 Å; C–H···centroid angle, 175°].

Where ligand flexibility, as in the presently described species, is the result of rotation about relatively unencumbered single bonds, the barriers to conformational rearrangements appear to be of comparable energy to solid state interactions such as hydrogen bonding and aromatic···aromatic attractions, as well as inter-ligand repulsions within the uranyl ion equatorial coordination sites. Where no strong hydrogen bond donors are present and carboxylate oxygen atoms are the only centres available for coordination to uranium, as in complex **1**, all four donor atoms of cpa^{2-} are used, with the ligand constrained to a

conformation where an eight-membered chelate ring with a separation between proximal coordinated oxygen atoms of 2.872(2) Å can form. If another chelate ligand such as 1,10-phenanthroline, well-known to cause congestion of the uranyl ion equatorial donor atom array,[24] is present, as in complex **2**, formation of the large chelate ring by cpa^{2-} does not occur and the ligand acts as a bis(κ^2*O,O'*) bridging species where the minimum O···O separation (between the two carboxylate entities of a single ligand) is 3.831(7) Å. Where the complex stoichiometry is such that six carboxylate oxygen donors are available for every uranyl ion, as in complex **3**, the ligand provides this environment by acting again as a bis(κ^2*O,O'*) bridging species, with minimum O···O separations in the three inequivalent ligand units of 3.432(3), 4.735(3) and 4.862(3) Å. In complex **4**, where the U:ligand ratio is 1:2 with thus more than enough carboxylate donors for six to be bound to each uranium centre but where there is competition for them through weak axial binding to Ni^{II}, the ligand acts as a κ^2*O,O'*:κ^1*O''* or κ^1*O*:κ^1*O''* bridging species towards U^{VI}, with minimum O···O separations in the two inequivalent ligand units of 3.260(4) and 4.421(4) Å. The substantial variation in the minimum O···O separations in these four cases is an index of the ligand flexibility, which is clearly considerable and provides a means of adapting to various other influences upon the uranium-ligand interaction.

In known complexes of 1,2-pda^{2-},[11–13] none of which involves a nine-membered chelate ring, minimum O···O separations again vary over a large range of ~1.5 Å, very similar to that for cpa^{2-} if the one case there of chelation is ignored. In contrast, for known complexes of phthalate (pht^{2-}), minimum O···O separations, most of which apply to seven-membered chelate rings, have a much smaller range of < 0.5 Å. For the three ligands pht^{2-}, cpa^{2-} and 1,2-pda^{2-}, it appears that the introduction of but one extra single bond as in pht^{2-} *vs* cpa^{2-} provides sufficient flexibility to reduce markedly the probability of large chelate ring

formation, even though such chelation does remain possible. In the formation of carbocycles, kinetic factors are responsible for favouring the formation of five- and six-membered rings but with a labile metal ion such as uranyl the thermodynamic difference between chelating and bridging modes must be determinant. Here, however, there is a complication in that with dicarboxylates a large chelate ring involves only one oxygen atom of each carboxylate while bridging can involve four in a bis(κ^2*O,O'*) form. In fact, in all known uranyl ion complexes of pht^{2-} in the solid state, at least 3 and commonly all 4 oxygen atoms are involved in coordination to uranium as a result of interactions in addition to (and in some cases, in place of) seven-membered chelate ring formation, so that no direct comparison of the one instance of bis(κ^2*O,O'*) bridging with any species in which there is exclusively seven-membered ring chelation is possible. Similarly, where cpa^{2-} forms an eight-membered chelate ring (complex **1**), additional interactions result in all 4 oxygen donors being coordinated to uranium, so again no simple comparisons with species such as complexes **2** and **3** where bis(κ^2*O,O'*) bridging alone occurs can be made.

The obvious reasons for this frustrating situation are that the stoichiometry and composition of the known complexes vary greatly. Where at least the stoichiometry is such as to give a carboxylate:uranium ratio of 3:1, the ligands cpa^{2-} and 1,2-pda^{2-} (as well as 1,3- and 1,4-pda^{2-}, the latter exemplified in complex **7**) act as bis(κ^2*O,O'*) bridging units and give the uranyl ion hexagonal-bipyramidal coordination geometry, possibly implying that this is a favoured situation. Unfortunately, no structurally characterized uranyl phthalate complex has this stoichiometry, even when resulting from a reaction mixture with the appropriate composition. Thus, it appears that solid state interactions in addition to those of coordinate bond formation which simply determine the solubility of a given species are the determinants of a given coordination mode observed within a crystal. Note that in phthalate

complexes where only 3 of the 4 oxygen donor atoms are coordinated to uranium, the fourth donor is involved in O···HO, O···HN, O···HC or O···(heterometal) interactions, indicating that these may be competitive in energy with weak coordination to U^{VI}.

From a topological viewpoint, it is notable that cpa^{2-}, as 1,4-pda^{2-},[12] has a propensity to give monoperiodic coordination polymers with the uranyl ion, and diperiodic networks have only been obtained in the presence of a metal-containing, bulky counterion, either separated (**3**) or included in the polymeric assembly (**4**). Ligand flexibility may be important in the case of complex **3** in enabling significant distortions of the **hcb** topology of the diperiodic uranyl–cpa^{2-} polymer to occur in such a way as to optimize interactions with the countercation. Surprisingly, the use of an organic countercation of moderate size and limited in its hydrogen bonding capabilities, quinuclidinium, allowed isolation of the first triperiodic framework in the uranyl phenylenediacetate family (**6**).

Conclusions

One of the difficulties involved in assessing the influence of increased flexibility of a ligand molecule when this flexibility enhancement results from insertion of additional single bonds, is that chelation may simply become not just improbable but actually impossible. This, however, is not the case with the presently considered ligands. Thus, pht^{2-} and cpa^{2-} are known to form complexes involving seven-and eight-membered chelate rings, respectively, and while 1,2-pda^{2-} is not yet known to form complexes involving nine-membered chelate rings, it is pertinent to note that for the conformationally restricted 1,1'-biphenyl-2,2',6,6'-tetracarboxylate, nine-membered ring chelation is common[32,33] and it is also seen in complexes of 2,2'-bipyridine-3,3'-dicarboxylate.[34–36] If an increase in rotational flexibility results in a higher population of conformations incompatible with chelation, the probability

of finding species involving chelation must be reduced and this would certainly explain the current observations on uranyl ion complexes of pht^{2-}, cpa^{2-} and 1,2-pda^{2-}. There is, however, an extra matter to consider relating to the coordination sphere of uranyl ion. As is evident from a variety of facts such as pentagonal-bipyramidal coordination in adducts of $UO_2(acac)_2$,[37] major distortions of the coordination geometry by ligands such as 1,10-phenanthroline,[38] and the limitation of hexagonal-bipyramidal coordination to species involving at least partly small-bite ligands such as nitrate and carboxylate,[10] coordination in the equatorial plane of uranyl ion is sensitive to inter-ligand repulsions. This is further seen in that species where two nine-membered chelate rings are present[32–36] have uranium in octahedral (square-bipyramidal) coordination, any addition to the four donor atoms in the equatorial plane apparently being excluded. As U–(equatorial donor atom) bond lengths shorten with decrease in coordination number, implying that the individual bonds are stronger, this means that all systems must reflect different balance points between the number and strength of coordinative interactions. In cases, such as the present, where chelate ring sizes differ, this need not have anything to do with ligand flexibility other than as a means of adjusting the distance spanned by the ligand. Were it to be assumed that the most favourable interaction of carboxylate ligands with uranium(VI) would be that of hexagonal-bipyramidal, tris(κ^2*O,O'*) coordination, then the increasing frequency of this mode in passing from pht^{2-} through cpa^{2-} to 1,2-pda^{2-} can be seen as an effect of stepwise increase in flexibility.

Experimental Section

General: $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (RP Normapur, 99%) was purchased from Prolabo. 2-carboxyphenylacetate was from EGA, and 1,2- and 1,4-phenylenediacetates were from

Aldrich. [Ni(*R,S*-Me_6cyclam)$(NO_3)_2$] was synthesized as previously described.[39] When possible, elemental analyses were performed by Service Chromato-Masse Microanalyse (UMR 8076) of Université Paris-Saclay. For complexes **2** and **5**–**7**, the low yield 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.

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.

[UO_2(cpa)] (1): cpaH_2 (18 mg, 0.10 mmol) and [$UO_2(NO_3)_2(H_2O)_2$]·4H_2O (50 mg, 0.10 mmol) were dissolved in a mixture of water (0.7 mL) and acetonitrile (0.2 mL), giving yellow crystals of complex **1** overnight (8 mg, 18% yield). $C_9H_6O_6U$ (448.17): calcd. C 24.12, H 1.35; found C 24.06, H 1.44.

[UO_2(cpa)(phen)] (2): cpaH_2 (18 mg, 0.10 mmol), [$UO_2(NO_3)_2(H_2O)_2$]·4H_2O (35 mg, 0.07 mmol), $Pb(NO_3)_2$ (33 mg, 0.10 mmol), and 1,10-phenanthroline (18 mg, 0.10 mmol) were dissolved in a mixture of water (0.8 mL) and THF (0.2 mL), giving a few yellow crystals of complex **2** overnight.

[Ni(bipy)$_3$][(UO_2)$_2$(cpa)$_3$]·2.5H_2O (3): cpaH_2 (18 mg, 0.10 mmol), [$UO_2(NO_3)_2(H_2O)_2$]·4H_2O (35 mg, 0.07 mmol), $Ni(NO_3)_2$·6H_2O (15 mg, 0.05 mmol), and 2,2’-bipyridine (24 mg, 0.15 mmol)

were dissolved in a mixture of water (0.6 mL) and DMF (0.2 mL), giving orange crystals of complex **3** within one week (27 mg, 49% yield based on the acid). $C_{57}H_{47}N_6NiO_{18.5}U_2$ (1646.77): calcd. C 41.57, H 2.88, N 5.10; found C 41.51, H 2.82, N 5.19.

[UO_2(cpa)$_2$Ni(*R,S*-Me_6cyclam)] (4): cpaH_2 (18 mg, 0.10 mmol), [$UO_2(NO_3)_2(H_2O)_2$]·4H_2O (35 mg, 0.07 mmol), and [Ni(*R,S*-Me_6cyclam)$(NO_3)_2$] (23 mg, 0.05 mmol) were dissolved in a mixture of water (0.6 mL) and DMF (0.2 mL), giving yellow crystals of complex **4** overnight (21 mg, 31% yield based on U). $C_{34}H_{48}N_4NiO_{10}U$ (969.5): calcd. C 42.12, H 4.99, N 5.78; found C 42.14, H 4.79, N 5.89.

[dmaepH_2][(UO_2)$_2$(1,2-pda)$_3$]·3H_2O (5): 1,2-pdaH_2 (20 mg, 0.10 mmol), $UO_2(NO_3)_2$·6H_2O (35 mg, 0.07 mmol), and (Me_6trien)$(HCF_3SO_3)_4$ (30 mg, 0.04 mmol) were dissolved in a mixture of water (0.8 mL) and DMF (0.2 mL), giving a few yellow crystals of complex **5** within one week.

[QH]$_2$[(UO_2)$_2$(1,2-pda)$_3$]·3CH_3CN (6): 1,2-pdaH_2 (20 mg, 0.10 mmol), $UO_2(NO_3)_2$·6H_2O (35 mg, 0.07 mmol), and QHCl (15 mg, 0.10 mmol) were dissolved in a mixture of water (0.7 mL) and acetonitrile (0.2 mL), giving a few yellow crystals of complex **6** within three weeks.

[QH]$_2$[(UO_2)$_2$(1,4-pda)$_3$]·2CH_3CN (7): 1,4-pdaH_2 (20 mg, 0.10 mmol), $UO_2(NO_3)_2$·6H_2O (35 mg, 0.07 mmol), and QHCl (30 mg, 0.20 mmol) were dissolved in a mixture of water (0.7 mL) and acetonitrile (0.2 mL), giving a few yellow crystals of complex **7** within one week.

Crystallography: The data were collected at 100(2) K 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.[40] The crystals were mounted on Mitegen micromounts with a protective coating of Paratone-N oil (Hampton Research). The data were processed with SAINT,[41] and absorption effects were corrected for empirically with SADABS.[42] The structures were solved by intrinsic phasing with SHELXT,[43] expanded by subsequent difference Fourier synthesis and refined by full-matrix least-squares on F^2 with SHELXL,[44] using the ShelXle interface.[45] All non-hydrogen atoms were refined with anisotropic displacement parameters. When present, the hydrogen atoms bound to oxygen and nitrogen atoms were found on difference Fourier maps in most cases, and they were either fully refined isotropically with restraints, or refined with an isotropic displacement parameter equal to 1.2 or 1.5 (for water) times that of the attached atom. In complexes **3** and **5**, one water molecule has been given an occupancy factor of 0.5 in order to retain an acceptable displacement parameter and another one in **3** is disordered over two positions (and its hydrogen atoms were not found). 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 0.422(11) (inversion twin), and that for complex **6** was 0.021(4). Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with ORTEP-3[46] and the polyhedral representations with VESTA.[47] Topological analyses were conducted with ToposPro.[48]

CCDC 2065099 (for **1**), 2065100 (for **2**), 2065101 (for **3**), 2065102 (for **4**), 2065103 (for **5**), 2065104 (for **6**), and 2065105 (for **7**) 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 1. Crystal data and structure refinement details.

	1	**2**	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_9H_6O_6U$	$C_{21}H_{14}N_2O_6U$	$C_{57}H_{47}N_6NiO_{18.5}U_2$	$C_{34}H_{48}N_4NiO_{10}U$	$C_{42}H_{60}N_4O_{19}U_2$	$C_{50}H_{61}N_5O_{16}U_2$	$C_{48}H_{58}N_4O_{16}U_2$
M (g mol^{-1})	448.17	628.37	1646.77	969.50	1401.00	1464.09	1423.04
Crystal system	triclinic	orthorhombic	monoclinic	triclinic	monoclinic	trigonal	triclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$	$C2/c$	$P3_1$	$P\bar{1}$
a (Å)	5.8032(2)	7.1514(3)	12.2376(4)	10.2024(6)	27.8579(11)	14.1572(5)	10.2002(4)
b (Å)	8.1714(3)	15.5927(8)	32.4606(10)	11.3579(7)	14.6046(5)	14.1572(5)	10.7472(4)
c (Å)	10.7204(4)	16.3607(9)	14.2062(4)	16.4720(10)	13.2707(5)	22.6156(9)	13.1019(5)
α (°)	95.3644(16)	90	90	73.035(3)	90	90	103.2498(18)
β (°)	98.4453(16)	90	97.5541(14)	72.944(3)	114.558(2)	90	99.8555(19)
γ (°)	102.6684(15)	90	90	86.054(3)	90	120	116.2206(17)
V (Å^3)	486.43(3)	1824.38(16)	5594.3(3)	1745.09(19)	4910.8(3)	3925.5(4)	1191.59(8)
Z	2	4	4	2	4	3	1
Reflections collected	49591	47578	201948	110417	122640	254395	195051
Independent reflections	2941	3455	10616	6617	7507	15959	7293
Observed reflections [$I > 2\sigma(I)$]	2896	3392	9775	6241	6729	15380	6981
R_{int}	0.047	0.059	0.040	0.079	0.047	0.065	0.053
Parameters refined	145	272	788	472	319	670	321
R_1	0.012	0.021	0.018	0.029	0.018	0.020	0.017
wR_2	0.027	0.052	0.036	0.075	0.039	0.043	0.047
S	1.082	1.054	1.068	1.065	1.078	1.046	1.043
$\Delta\rho_{min}$ (e Å^{-3})	−0.66	−1.09	−0.73	−1.63	−1.07	−0.62	−0.71
$\Delta\rho_{max}$ (e Å^{-3})	1.07	2.41	1.20	2.28	1.42	1.25	3.60

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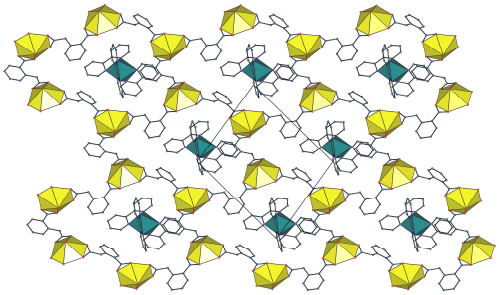
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Table of Contents Entry

Stepwise Introduction of Flexibility into Aromatic Dicarboxylates Forming Uranyl Ion Coordination Polymers: a Comparison of 2-Carboxyphenylacetate and 1,2-Phenylenediacetate

Pierre Thuéry, Jack Harrowfield

Key Topic: Uranyl complexes



While 2-carboxyphenylacetate gives mono-or diperiodic coordination polymers with the uranyl cation, depending on the additional ligands and counterions present, 1,2-phenylenediacetate yields the first triperiodic framework in the uranyl–phenylenediacetate family, in the presence of quinuclidinium cations. The results are discussed in terms of ligand flexibility and ability to form large chelate rings.