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Pierre Thuéry, Jack Harrowfield. Three Different Modes of Association Between Metal Cations in Heterometallic Uranyl-Co<sup>III</sup> and Uranyl-Mn<sup>II</sup> Species. *European Journal of Inorganic Chemistry*, 2018, 2018 (40), pp.4465-4471. 10.1002/ejic.201800873 . cea-01878578

**HAL Id: cea-01878578**

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Submitted on 21 Sep 2018

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# Three Different Modes of Association Between Metal Cations in Heterometallic Uranyl–Co<sup>III</sup> and Uranyl–Mn<sup>II</sup> Species

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**Abstract.** Three heterometallic complexes including uranyl and either Co<sup>III</sup> or Mn<sup>II</sup> cations were crystallized under hydrothermal conditions. Complexes [Co(bipy)<sub>3</sub>]<sub>2</sub>[UO<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>]<sub>2</sub>[(UO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>] (**1**) and [UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>Co(bipy)<sub>2</sub>(OH)<sub>2</sub>]<sub>2</sub>·NO<sub>3</sub>·H<sub>2</sub>O (**2**) (bipy = 2,2'-bipyridine) were obtained from the same solution. UO<sub>2</sub><sup>2+</sup> and Co<sup>3+</sup> are part of separate anions and cations, respectively, in complex **1**, the uranyl ion being present in both a mononuclear dianion with two chelating and two monodentate nitrates in *cis* positions, and in a dinuclear, bis-hydroxo-bridged dianion. In contrast, both metal cations are part of a monocationic heterometallic bis-hydroxo-bridged complex in **2**, UO<sub>2</sub><sup>2+</sup> retaining two nitrate and Co<sup>III</sup> two bipy ligands. This is the third example only of a hydroxo-bridged heterometallic uranyl complex, and the first to involve Co<sup>III</sup>. The complex [(UO<sub>2</sub>)<sub>6</sub>Mn(O)<sub>4</sub>(OH)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>]<sub>2</sub>·5H<sub>2</sub>O (**3**), synthesized in the absence of any added ligand, crystallizes as a three-dimensional framework in which anionic uranyl oxyhydroxide layers with the α-U<sub>3</sub>O<sub>8</sub>-type polyhedral arrangement are connected to one another by Mn(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> cations axially bound to two uranyl oxo atoms. These very simple systems thus display a large range of possible intermetallic associations, that involving bis-oxo-bonding to uranyl enabling formation of a framework through pillaring of sheets.

## Introduction

Studies of uranyl–organic frameworks or coordination polymers frequently use additional metal cations, particularly from d-block elements, so as to provide extra connectivity, when the latter cations are part of the polymeric unit, or to exert structure-directing effects when they are isolated counterions.<sup>[1]</sup> Many such complexes have been reported over the years,<sup>[2]</sup> particularly in the case of carboxylate ligands, for which about 200 crystal structures of heterometallic uranyl complexes involving d-block metal cations are reported in the Cambridge Structural Database (CSD, version 5.39<sup>[3]</sup>). We have recently been interested in the use of the bulky spherical cations  $[M(L)_3]^{2+}$ , in which M is a 3d-block metal cation and L is either 2,2'-bipyridine or 1,10-phenanthroline, as structure-inducing species, and this has enabled isolation of several uranyl carboxylate compounds with original geometry, such as triple-stranded helicates<sup>[4]</sup> and entangled networks,<sup>[5]</sup> as well as three-dimensional (3D) frameworks.<sup>[6]</sup> Our work has been based on the use of solvothermal synthesis to obtain crystalline materials suitable for X-ray diffraction studies. While this is a procedure which has been used by many groups with great success, the lack of detailed kinetic and thermodynamic data on mixed-solvent systems at high temperatures and under pressure is a considerable handicap to the rational design of solvothermal syntheses. Thus, in seeking to explore what might be considered as the background chemistry to more sophisticated syntheses, we have commenced investigation of the crystalline species formed, under hydrothermal conditions, from uranyl cations, 3d-block cations and *N*-chelators, in the absence of carboxylate ligands. Surprisingly, while carboxylate complexes crystallize rather readily, obtaining crystalline complexes in the absence of carboxylic acids has proven much more

difficult and we report herein just our initial results involving two different species in which  $\text{Co}^{\text{III}}$  is bound to 2,2'-bipyridine, as well as a  $\text{Mn}^{\text{II}}$  complex produced in the absence of this *N*-chelator. Together, these three species illustrate the three different association modes that may exist in such compounds: separation of the two metal cations as an ion pair, formation of a heterometallic complex with common ligands, and association through bonding of the 3d metal to a uranyl oxo group. The latter oxo bonding is a widespread phenomenon<sup>[1]</sup> and is a particular case of interaction of the oxo groups with Lewis acids.<sup>[7]</sup> The numerous purely inorganic compounds and natural minerals containing both uranyl and d-block metal cations<sup>[8]</sup> provide examples of such bonding, some of them among the earliest which have been reported.<sup>[9]</sup>

## Results and Discussion

### Synthesis

Reaction of uranyl nitrate, cobalt(II) nitrate and 2,2'-bipyridine (bipy) under hydrothermal conditions at a temperature of 140 °C gave a mixture of two diamagnetic complexes,  $[\text{Co}(\text{bipy})_3]_2[\text{UO}_2(\text{NO}_3)_4]_2[(\text{UO}_2)_2(\text{NO}_3)_4(\text{OH})_2]$  (**1**) and  $[\text{UO}_2(\text{NO}_3)_2\text{Co}(\text{bipy})_2(\text{OH})_2] \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$  (**2**), the crystals of which differ in color, yellow for **1** and dark orange for **2**. Whilst it is not surprising to find that  $\text{Co}^{\text{II}}$  has undergone oxidation to  $\text{Co}^{\text{III}}$  in the presence of 2,2'-bipyridine, this is not the case in otherwise similar reactions where a dicarboxylate is present<sup>[10]</sup> and is possibly a consequence of the rather prolonged reaction times in the present work or quite simply of solubility differences, especially given that the yield is low. The oxidants present include uranyl ion, dissolved oxygen, nitrate and possibly peroxide, since it is known that uranyl-peroxo complexes can form when solutions are exposed to light and/or heat.<sup>[11]</sup> Hydrogen peroxide is the

oxidant most commonly used for the preparation of  $[\text{Co}(\text{bipy})_3]^{3+}$ ,<sup>[12]</sup> but in the present work, all possibilities remain open.

Reaction between uranyl nitrate and manganese(II) nitrate in aqueous methanol at 140 °C under pressure gave the complex  $[(\text{UO}_2)_6\text{Mn}(\text{O})_4(\text{OH})_6(\text{H}_2\text{O})_4]\cdot 5\text{H}_2\text{O}$  (**3**) in which the uranyl ions form a two-dimensional (2D) hydrolytic polymer but the  $\text{Mn}^{\text{II}}$  ions are bound to water and uranyl oxo groups, this lack of hydrolysis of the  $\text{Mn}^{\text{II}}$  aqua ion being consistent with its much weaker acidity ( $\text{p}K_a \sim 10.6$ <sup>[13]</sup>) compared to the pentaquauranyl ion ( $\text{p}K_a \sim 5.6$ <sup>[14]</sup>) if just values at room temperature are considered. It is notable that  $\text{Mn}^{\text{II}}$  does not undergo oxidation, although such a reaction occurs very readily under ambient conditions when a  $\text{Mn}^{\text{II}}$  solution is made appreciably basic.<sup>[15]</sup> The long reaction time necessary for the deposition of complex **3** is consistent with slow polymerization of lower-nuclearity hydroxo-uranium(VI) species present initially, but although acidity constant measurements for uranyl ion have been extended to quite high temperatures,<sup>[14b]</sup> the equilibria involved under the conditions used herein are unknown.

### Crystal Structures

The complex  $[\text{Co}(\text{bipy})_3]_2[\text{UO}_2(\text{NO}_3)_4]_2[(\text{UO}_2)_2(\text{NO}_3)_4(\text{OH})_2]$  (**1**) crystallizes in the monoclinic space group  $P2_1/c$ , with an asymmetric unit corresponding to half the formula content (Figure 1).  $\text{Co}^{\text{III}}$  is tris-chelated by bipy, with Co–N bond lengths in the range 1.928(3)–1.954(3) Å [average 1.939(8) Å], these values being consistent with those for the 25  $[\text{Co}(\text{bipy})_3]^{3+}$  groups reported in the CSD, which are in the range 1.894–1.981 Å [average 1.936(2) Å], while the bonds in  $[\text{Co}(\text{bipy})_3]^{2+}$  cations tend to be somewhat longer, although with a larger dispersion [1.904–2.199 Å; average 2.08(8)

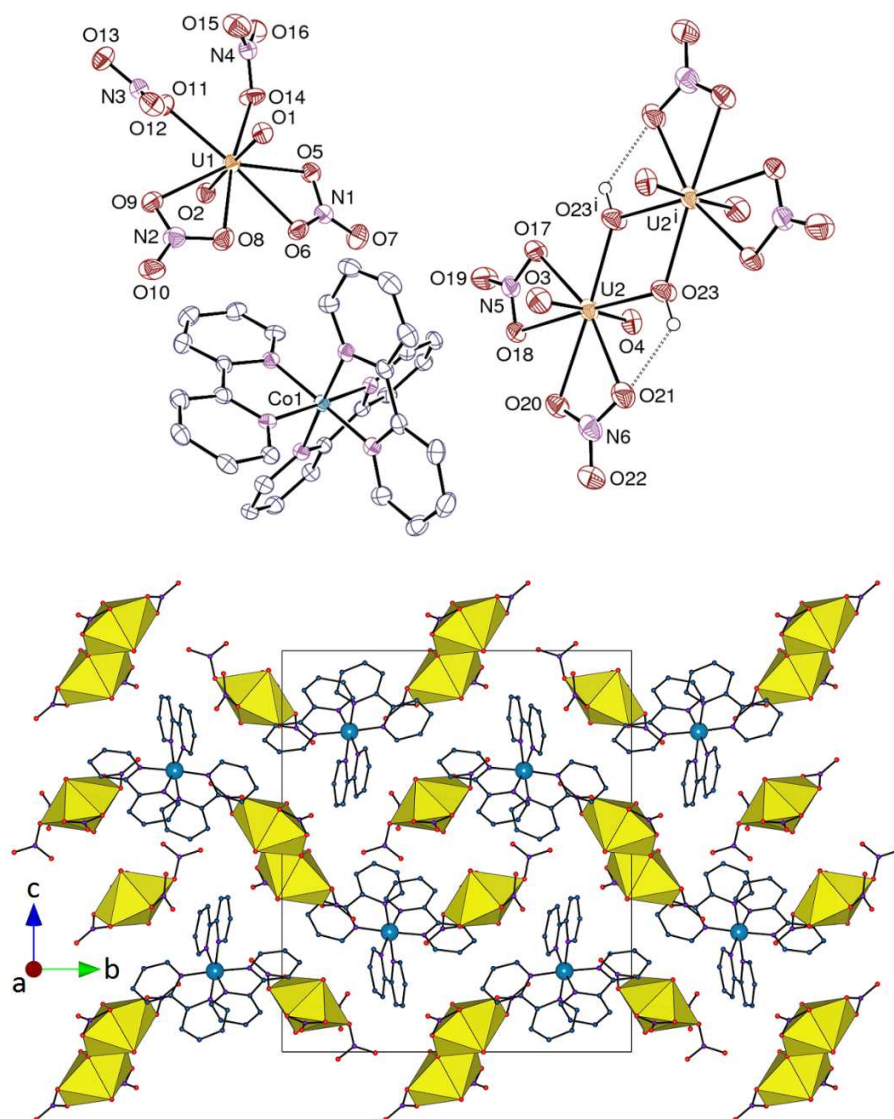


Figure 1. Top: view of compound **1**. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code:  $i = 2 - x, -y, 1 - z$ . Bottom: view of the packing with uranium coordination polyhedra colored yellow and cobalt atoms shown as blue spheres.

Å], such that the difference is not statistically significant. Both enantiomers of the chiral cation are present in the lattice, with individual columns down  $a$  being homochiral but columns along  $c$  being heterochiral. The uranium atoms are found in two different moieties, both of them being heterochiral. The uranium atoms are found in two different moieties, both of them being dianionic. One of them is the tetra-nitrato complex  $[\text{UO}_2(\text{NO}_3)_4]^{2-}$  with two chelating and two

monodentate nitrate anions, of which 10 occurrences are reported in the CSD. However, in all previous cases, the two identically coordinated nitrates are in *trans* positions, while they are *cis* here, this being seemingly the first instance of this geometry. The U–O bond lengths for the monodentate [2.375(3) and 2.421(2) Å] and the chelating nitrates [2.498(3)–2.576(2) Å, average 2.54(3) Å] are in agreement with the averages from the CSD [2.43(2) and 2.52(2) Å, respectively]. The other dianion, [(UO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup>, is a centrosymmetric, bis(hydroxo)-bridged unit of which 13 other examples are given in the CSD. The U–O(hydroxo) bond lengths [2.339(2) and 2.348(3) Å] and U–O–U angle [115.26(12)°], and the U–O(nitrate) bond lengths [2.535(3)–2.558(2) Å, average 2.544(9) Å] are comparable to those from the CSD [average values 2.33(2) Å, 113.6(12)° and 2.55(2) Å, respectively]. The two hydroxide ions form two intramolecular hydrogen bonds with the proximal nitrate oxygen atoms [O23...O21 2.712(4) Å, H...O21 2.20 Å, O23–H...O21 114°]. Apart from the dominant Coulombic forces, the other notable interactions between the three components are several possible CH...O hydrogen bonds<sup>[16]</sup> involving both dianions [C...O distances 2.992(5)–3.397(4) Å, C–H...O angles 111–160°]. These interactions appear prominently on the Hirshfeld surfaces (HSs)<sup>[17]</sup> calculated with CrystalExplorer,<sup>[18]</sup> and they account for 52% of the HS of [Co(bipy)<sub>3</sub>]<sup>3+</sup>, and ca. 63% of the HS of each anion. The packing is quite compact, with a Kitaigorodski packing index (KPI, estimated with PLATON<sup>[19]</sup>) of ~0.73.

The complex [UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>Co(bipy)<sub>2</sub>(OH)<sub>2</sub>]·NO<sub>3</sub>·H<sub>2</sub>O (**2**) was obtained together with **1**, from which it differs by its color (see above). It crystallizes in the orthorhombic space group *Pbcn*, with the asymmetric unit matching the formula content (Figure 2). Both uranyl and cobalt(III) cations pertain to the same monocationic complex unit, being bridged by two hydroxo anions [U–O bond lengths 2.329(3) and 2.357(3) Å, Co–O bond lengths 1.874(3) and 1.891(3) Å, and U–O–Co angles

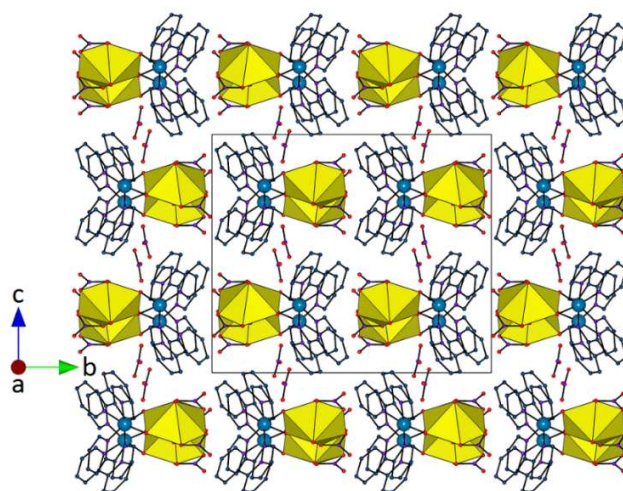
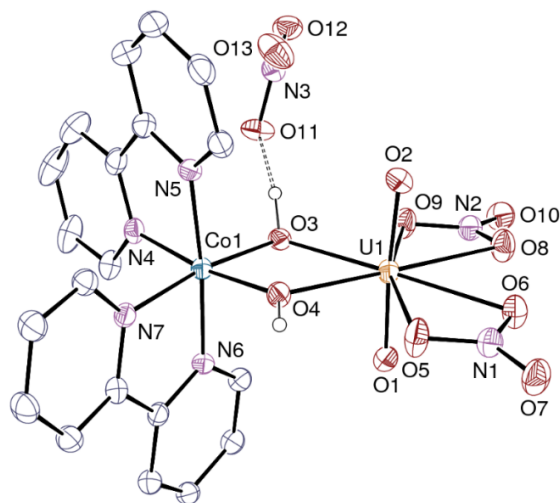


Figure 2. Top: view of compound **2**. Carbon-bound hydrogen atoms are omitted and the hydrogen bond is shown as a dashed line. Displacement ellipsoids are drawn at the 30% probability level. Bottom: view of the packing with uranium coordination polyhedra colored yellow and cobalt atoms shown as blue spheres, and solvent molecules excluded.

105.49(12) and 107.16(13)°]. Examples of uranyl cations hydroxo-bridged to other metallic cations are exceedingly rare since only two are reported in the CSD and both involve  $\text{Cu}^{\text{II}}$  cations and single hydroxo bridges,<sup>[2e,2m]</sup> while homometallic hydroxo-bridged complexes of  $\text{Co}^{\text{III}}$ , in contrast, are relatively common.<sup>[20]</sup> The  $\text{Co}^{\text{III}}$  cation is also chelated by two bipy molecules and is



thus in an  $N_4O_2$  octahedral environment with the oxygen atoms in *cis* positions, while the uranium atom is chelated by two nitrate anions [U–O bond lengths 2.534(3)–2.549(3) Å, average 2.541(6) Å] and is thus in a hexagonal bipyramidal environment. The bimetallic complex unit is chiral but enantiomers alternate in columns down *b*, so that once again the crystal is achiral. Both hydroxo groups are hydrogen bonded to the uncoordinated nitrate ion [O3···O11 2.748(4) Å, H···O11 1.89 Å, O3–H···O11 153°; O4···O12<sup>i</sup> 2.745(5) Å, H···O12<sup>i</sup> 1.94 Å, O4–H···O12<sup>i</sup> 166°, symmetry code:  $i = 1/2 - x, 3/2 - y, z + 1/2$ ], thus generating chains directed along the *c* axis. These columns are stacked in the (1 0 0) plane so that the bipy groups of one column are close to the nitrate ligands of its neighbour along the *b* axis. Here also, the interactions between ions, apart from the Coulombic ones, are essentially CH···O hydrogen bonds, as shown by examination of the Hirshfeld surface (Figure 3). These interactions involve uranyl oxo groups or nitrate anions as acceptors

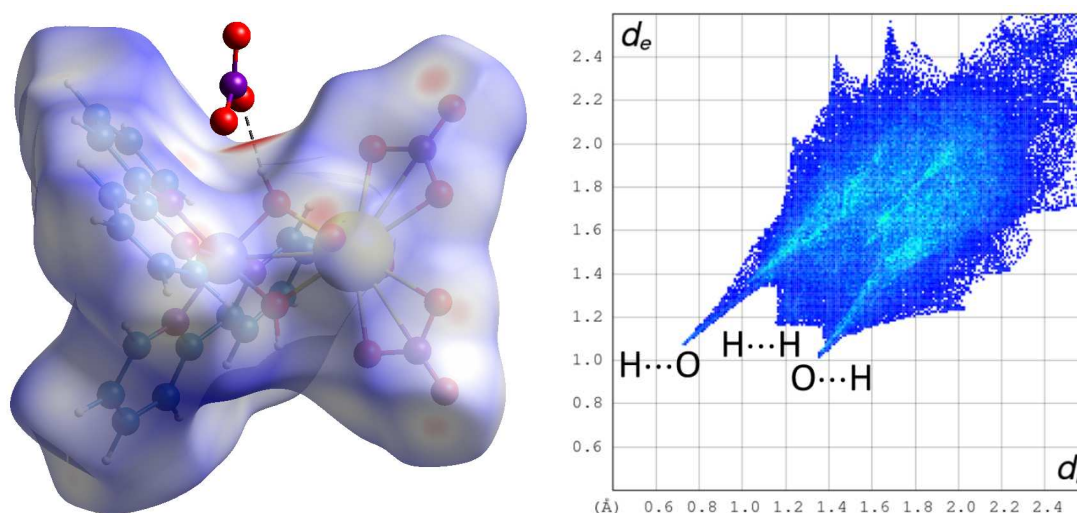


Figure 3. Left: Hirshfeld surface mapped with  $d_{norm}$  calculated for the cationic part of complex **2**. The hydrogen bond is shown as a dashed line; the red spots on the HS correspond to distances shorter than the sum of van der Waals radii and indicate the positions of CH···O hydrogen bonds with neighbouring units. Right: Fingerprint plot corresponding to the HS of the cation. The nature of the interactions associated with the three main features is indicated with the atom located inside the HS first.

[C...O distances 3.090(5)–3.441(6) Å, H...O 2.47–2.57 Å, C–H...O angles 123–153°], and they generate a weakly bonded 3D assembly. With a KPI of 0.71, the packing does not contain significant free spaces (apart from that occupied by the water molecule).

In contrast to **1** and **2**, complex **3**, [(UO<sub>2</sub>)<sub>6</sub>Mn(O)<sub>4</sub>(OH)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>].5H<sub>2</sub>O, does not include bipy molecules. It crystallizes in the orthorhombic space group *Pnmm*, with two uranium atoms located on mirror planes (Wyckoff position 4*g*) and one Mn<sup>II</sup> cation on site 2*a* with 2/*m* symmetry in the asymmetric unit (Figure 4). Uranium centres are part of a 2D assembly parallel to (0 1 0) with oxo and hydroxo bridges. Both U1 and U2 are bound to two oxo anions (O5 and its images by symmetry) and three hydroxo anions (O6, located on a mirror plane, and O7 and its images by symmetry), all the oxo and hydroxo anions being bound to three metal atoms. The U–O(oxo) bond lengths are in the range 2.190(6)–2.281(6) Å and the U–O(oxo)–U angles in the range 117.4(3)–124.4(3)° (with a sum of 359.3° indicating near planarity), while the corresponding values for the hydroxo bridges, which display much larger dispersion, are 2.387(5)–2.830(8) Å and 96.7(2)–148.2(4)°. The value of 2.830(8) Å for U1–O6 is particularly large, so that this uranium atom is borderline between pentagonal and square bipyramidal coordination. There are 67 examples of μ<sub>3</sub>-oxo anions in uranyl complexes reported in the CSD, with an average bond length of 2.26(6) Å and an average U–O–U angle of 119(10)°, and a smaller number of 14 structures with μ<sub>3</sub>-hydroxo anions, also with very large dispersion in bond lengths and angles. There seems to be only three cases of uranyl complexes in which μ<sub>3</sub>-oxo and μ<sub>3</sub>-hydroxo anions coexist.<sup>[2q,21]</sup> In the layers

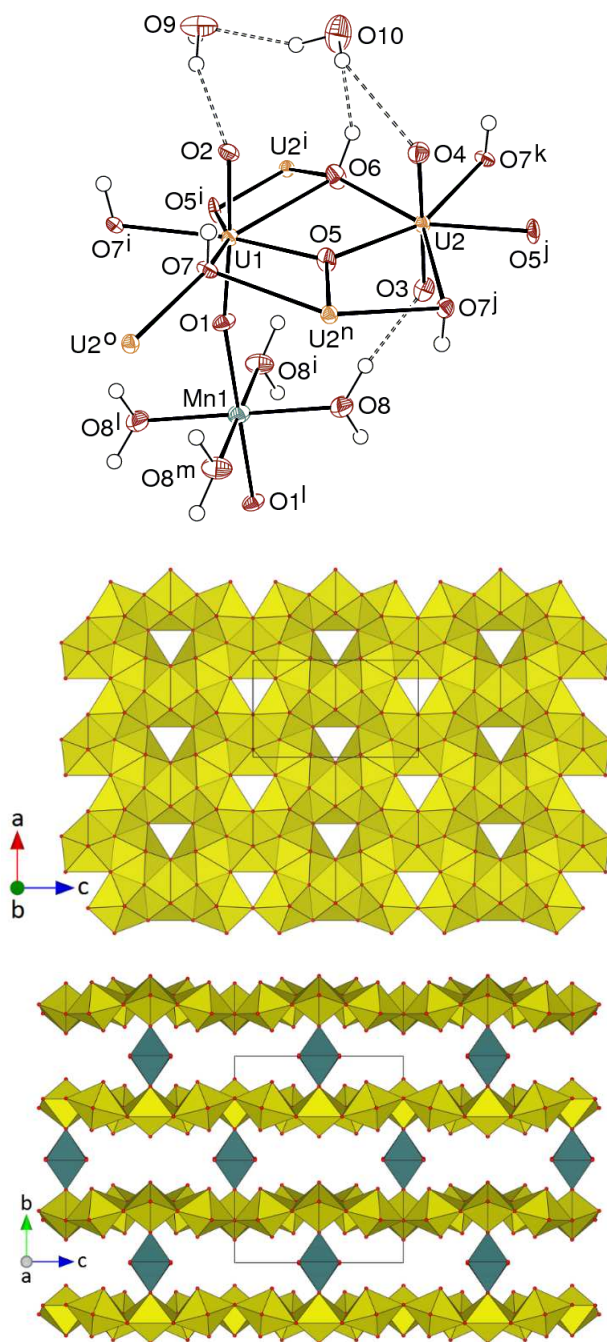


Figure 4. Top: view of compound **3**. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes:  $i = x, y, 1 - z$ ;  $j = x + 1/2, 3/2 - y, 1/2 - z$ ;  $k = x + 1, y, z$ ;  $l = 1 - x, 2 - y, 1 - z$ ;  $m = 1 - x, 2 - y, z$ ;  $n = x - 1/2, 3/2 - y, 1/2 - z$ ;  $o = x - 1, y, z$ . Middle: view of the 2D subunit. Bottom: view of the 3D framework with uranyl-based sheets viewed edge-on. Uranium coordination polyhedra are colored yellow and those of manganese green. Solvent molecules and hydrogen atoms are omitted.

formed in **3**, all uranium atoms are in pentagonal bipyramidal environments (if the longest U1–O6 bond is considered significant, see above), and each pentagon shares four edges with its neighbours, thus creating isolated triangular voids in the array, all pointing in the same direction and with the hydroxo anions as apexes (Figure 4). This  $\alpha$ - $\text{U}_3\text{O}_8$ -type polyhedral arrangement is found in several uranyl oxide hydrate minerals and synthetic phases, in which the charge of the sheet varies depending on the number of hydroxo anions present.<sup>[8]</sup> If U1 is considered to be in a square bipyramidal environment, the corresponding array is of  $\beta$ - $\text{U}_3\text{O}_8$ -type, with a tessellation of pentagons and squares, and triangular voids.<sup>[22]</sup> In the known examples of  $\alpha$ - $\text{U}_3\text{O}_8$ -type polyhedral arrangements, various counterions, either alkali, alkaline-earth or  $\text{Pb}^{\text{II}}$ , are found in the interlayer spaces and are bound to oxygen atoms of the sheets. The same  $\text{UO}_2^{2+}/\text{O}^{2-}/\text{OH}^-/\text{M}^{2+}$  3:2:3:0.5 stoichiometry is found in the two minerals billietite and becquerelite, with  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$  as counterions, respectively.<sup>[22]</sup> It is notable that, in billietite, there are two long U–O bond lengths of 3.02(7) and 2.81(6) Å, making this structure also intermediate between the  $\alpha$ - and  $\beta$ - $\text{U}_3\text{O}_8$ -types. In **3**, the  $\text{Mn}^{2+}$  counterions are bound to two uranyl oxo groups from two different sheets (O1 and its image by inversion), with a bond length of 2.187(9) Å, which lies between the values of 2.170(4) and 2.199(4) Å in the only other examples of manganese oxo bonding to uranyl reported in the CSD<sup>[23]</sup> (excluding cases in which uranium is pentavalent instead of hexavalent); as in these other cases, the two U=O bonds of the uranyl ion bound to  $\text{Mn}^{\text{II}}$  in **3** are slightly longer than those of the other uranyl ion [1.826(9) and 1.812(8) Å, *versus* 1.798(6) and 1.785(6) Å], but the difference is not quite statistically significant. The manganese cation is also bound to four water molecules (O8 and its images by symmetry) with a bond length of 2.176(6) Å, and it is thus in a slightly distorted octahedral environment [O1–Mn1–O8 90°, O8–Mn1–O8<sup>i</sup> 84.4°, O8–Mn1–

O8<sup>m</sup> 95.6(4)°, symmetry codes: see Figure 4]. The Mn<sup>II</sup> cations assemble the sheets into a 3D framework by acting as pillars offset from one layer to the next, such pillaring being a common feature of the structures of layered metal hydroxides and an important determinant of their properties.<sup>[24]</sup> The interlayer spaces are occupied by the free water molecules (one of them located at a site with 2/*m* symmetry and with its hydrogen atoms disordered), and hydrogen bonding unites hydroxo and water donors to uranyl oxo and water acceptors. The hydrogen bonding pattern is represented in Figure 5, as seen down the *a* and *c* axes. Each water ligand (O8) is a donor in two hydrogen bonds with one uranyl oxo atom in each of the neighbouring layers [O⋯O 2.828(8) and 2.994(9) Å, H⋯O 1.93 and 2.01 Å, O–H⋯O 155 and 172°]. The hydroxo anions (O6 and O7) are hydrogen bond donors to the solvent water molecules [O⋯O 2.694(9) and 3.068(10) Å, H⋯O 1.83 and 2.22 Å, O–H⋯O 166 and 144°]. The free water molecules (O9 and O10) are hydrogen bond donors to uranyl oxo groups and coordinated water molecules, as well as

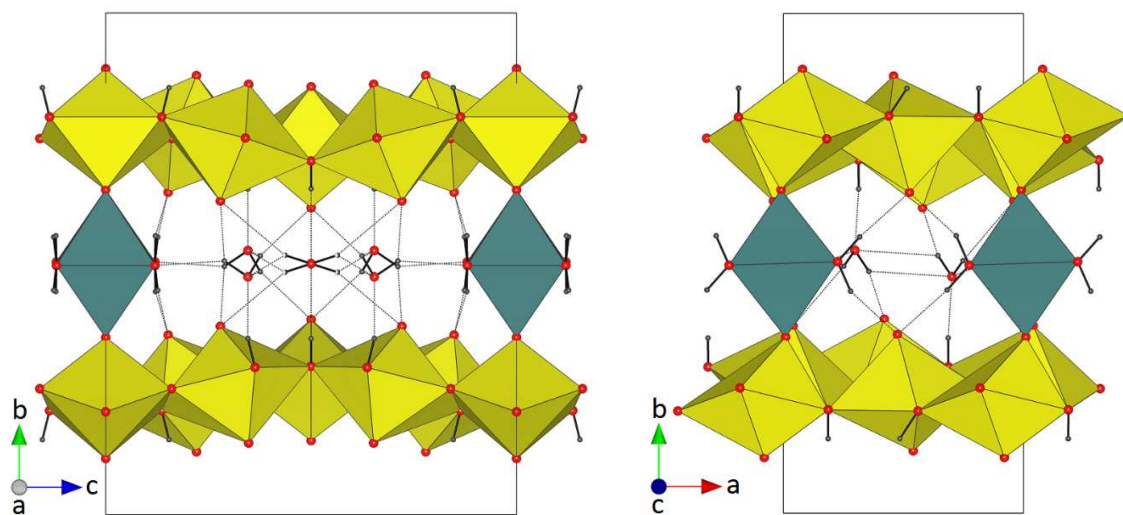


Figure 5. The hydrogen bonding array within the framework in compound **3**, seen down the *a* (left) and *c* (right) axes. Hydrogen bonds are shown as dashed lines.

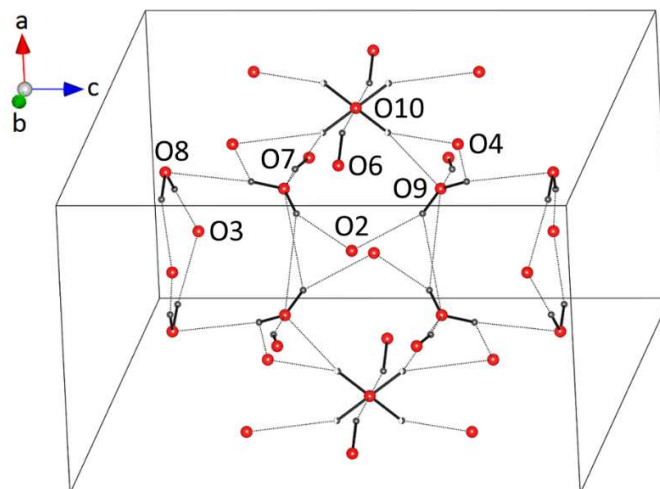


Figure 6. The hydrogen bonding array in compound **3**. Hydrogen bonds are shown as dashed lines. The hydrogen atoms bound to O10 are disordered and shown as parti-colored spheres. Only one of the equivalent positions of each atom is labelled.

forming bonds between themselves [O...O 2.827(10)–3.282(6) Å, H...O 2.04–2.51 Å, O–H...O 118–157°]. Figure 6 shows this hydrogen bonding pattern, which is continuous along the *a* axis, and in which rings corresponding to the graph set descriptors<sup>[25]</sup>  $R_4^2(8)$  (atoms O3, O8 and their symmetry equivalents) and  $R_2^2(4)$  (O9 and its symmetry equivalent, and O4, O9 and O10) can be discerned. The KPI with solvent excluded is 0.68, in keeping with the presence of small solvent-accessible channels.

## Conclusions

We have reported the crystal structure of three heterometallic complexes involving uranyl and 3d-block metal cations (Co<sup>III</sup>, Mn<sup>II</sup>), obtained under hydrothermal conditions in the absence of added ligands, except for 2,2'-bipyridine in the case of Co<sup>III</sup>. In complexes **1** and **2**, crystallized

from the same solution, the uranyl and  $\text{Co}^{\text{III}}$  cations are either separated into different ionic moieties,  $[\text{Co}(\text{bipy})_3]^{3+}$  and both a mononuclear and a bis-hydroxo-bridged dinuclear uranyl nitrate anions, or united in a heterometallic bis-hydroxo-bridged dinuclear complex in which  $\text{Co}^{\text{III}}$  retains two bipy ligands. In contrast, in complex **3**,  $\text{Mn}^{\text{II}}$  cations act as pillars uniting uranyl oxyhydroxide sheets of  $\alpha\text{-U}_3\text{O}_8$  type into a 3D framework through bonding to uranyl oxo groups. Thus, three different association modes between the metal cations are found in these very simple systems, the third case in particular showing the ability of d-block metal ions to turn into frameworks what are essentially planar uranyl-containing sheets.<sup>[1,8]</sup> The formation of hydroxo-bridged oligomers and polymers in the present instances provides further illustration of the well-known tendency of uranyl ion to undergo hydrolytic condensation in neutral media. Clearly, in the presence of carboxylic acids, this tendency is partially inhibited but under ambient conditions this would not be expected to lead to the formation of the carboxylate complexes of mononuclear uranyl ion (since the carboxylic acid group retains its proton), so that an advantage of solvo-hydrothermal synthesis is that it provides conditions where the solution remains acidic while free carboxylate levels are high. The implication of this, of course, is that the  $\text{pK}_a$  of the carboxylic acid is significantly smaller under solvothermal conditions than at 298 K and 101 kPa pressure, even though in general the temperature dependence of such constants is expected to be slight.<sup>[26]</sup> It would also appear that the acid is strong enough to inhibit dissociation of  $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ , which is known to become a stronger acid as the temperature is increased.<sup>[14b]</sup> Another interesting feature of the present study is that crystallisation of the hydroxo-bridged products required exceptionally long reaction periods, possibly consistent with slow second-order condensation reactions in the

solution phase, indicating that alternative reaction pathways in the presence of carboxylic acids could be kinetically favoured.

## Experimental Section

**General:**  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (depleted uranium, R. P. Normapur, 99%) was purchased from Prolabo,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  were from Sigma-Aldrich, and 2,2'-bipyridine was from Fluka.

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

**[Co(bipy)<sub>3</sub>]<sub>2</sub>[UO<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>]<sub>2</sub>[(UO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>] (1) and [UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>Co(bipy)<sub>2</sub>(OH)<sub>2</sub>]·NO<sub>3</sub>·H<sub>2</sub>O (2):**

$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (50 mg, 0.10 mmol),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (29 mg, 0.10 mmol), 2,2'-bipyridine (32 mg, 0.21 mmol), and demineralized water (0.4 mL) were placed in a 10 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, giving a mixture of yellow crystals of **1** and dark orange crystals of **2** in low yield within two months.

**[(UO<sub>2</sub>)<sub>6</sub>Mn(O)<sub>4</sub>(OH)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>]·5H<sub>2</sub>O (3).**  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (50 mg, 0.10 mmol),  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (25 mg, 0.10 mmol), methanol (0.3 mL), and demineralized water (0.6 mL) were placed in a 10 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, giving orange crystals of **3** in low yield within one month.

## Crystallography

The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer<sup>[27]</sup> 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  $\varphi$ - and  $\omega$ -scans with a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.<sup>[28]</sup> Absorption effects were corrected for empirically with the program SCALEPACK.<sup>[28]</sup> The structures were solved by intrinsic phasing with SHELXT,<sup>[29]</sup> expanded by subsequent difference Fourier synthesis and refined by full-matrix least-squares on  $F^2$  with SHELXL-2014.<sup>[30]</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen atoms were found on difference Fourier maps, except for those of the water molecule in **2**, 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. Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with ORTEP-3<sup>[31]</sup> and the polyhedral representations with VESTA.<sup>[32]</sup>

CCDC-1855235–1855237 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](http://www.ccdc.cam.ac.uk/data_request/cif).

Table 1. Crystal data and structure refinement details.

	1	2	3
Empirical formula	C <sub>60</sub> H <sub>50</sub> CO <sub>2</sub> N <sub>24</sub> O <sub>46</sub> U <sub>4</sub>	C <sub>20</sub> H <sub>20</sub> CoN <sub>7</sub> O <sub>14</sub> U	H <sub>24</sub> MnO <sub>31</sub> U <sub>6</sub>
<i>M</i> (g mol <sup>-1</sup> )	2913.22	879.39	2003.31
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	<i>P2<sub>1</sub>/c</i>	<i>Pbcn</i>	<i>Pnnm</i>
<i>a</i> (Å)	9.4494(3)	16.7417(7)	7.1353(2)
<i>b</i> (Å)	19.2962(6)	19.3777(9)	14.8384(8)
<i>c</i> (Å)	22.4283(5)	16.5427(7)	12.1889(7)
$\beta$ (°)	99.184(2)		
<i>V</i> (Å <sup>3</sup> )	4037.1 (2)	5366.7 (4)	1290.52 (11)
<i>Z</i>	2	8	2
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	8.52	6.73	38.10
Reflections collected	140685	198807	29548
Independent reflections	12327	6936	1277
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	9045	5094	1152
<i>R</i> <sub>int</sub>	0.068	0.037	0.021
Parameters refined	613	388	96
<i>R</i> <sub>1</sub>	0.032	0.037	0.027
w <i>R</i> <sub>2</sub>	0.060	0.090	0.069
<i>S</i>	0.96	1.04	1.16
$\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	-1.75	-1.00	-2.62
$\Delta\rho_{\max}$ (e Å <sup>-3</sup> )	1.19	1.90	1.26

**Keywords:** Heterometallic complexes / Hirshfeld surface / Structure elucidation / Uranium(VI) / Uranyl oxyhydroxide

## References

- [1] a) K. X. Wang, J. S. Chen, *Acc. Chem. Res.* **2011**, *44*, 531–540; b) M. B. Andrews, C. L. Cahill, *Chem. Rev.* **2013**, *113*, 1121–1136; c) T. Loiseau, I. Mihalcea, N. Henry, C. Volkringer, *Coord. Chem. Rev.* **2014**, *266–267*, 69–109; d) J. Su, J. S. Chen, *Struct. Bond.* **2015**, *163*, 265–296; e) P. Thuéry, J. Harrowfield, *Dalton Trans.* **2017**, *46*, 13660–13667.
- [2] See, for selected examples: a) W. Chen, H. M. Yuan, J. Y. Wang, Z. Y. Liu, J. J. Xu, M. Yang, J. S. Chen, *J. Am. Chem. Soc.* **2003**, *125*, 9266–9267; b) Z. T. Yu, Z. L. Liao, Y. S. Jiang, G. H. Li, G. D. Li, J. S. Chen, *Chem. Commun.* **2004**, 1814–1815; c) T. Y. Shvareva, T. E. Albrecht-

- Schmitt, *Inorg. Chem.* **2006**, *45*, 1900–1902; d) G. G. Luo, L. R. Lin, R. B. Huang, L. S. Zheng, *Dalton Trans.* **2007**, 3868–3870; e) A. N. Alsobrook, W. Zhan, T. E. Albrecht-Schmitt, *Inorg. Chem.* **2008**, *47*, 5177–5183; f) P. Thuéry, *Inorg. Chem. Commun.* **2009**, *12*, 800–803; g) K. E. Knope, C. L. Cahill, *Eur. J. Inorg. Chem.* **2010**, 1177–1185; h) A. N. Alsobrook, B. G. Hauser, J. T. Hupp, E. V. Alekseev, W. Depmeier, T. E. Albrecht-Schmitt, *Chem. Commun.* **2010**, *46*, 9167–9169; i) A. N. Alsobrook, B. G. Hauser, J. T. Hupp, E. V. Alekseev, W. Depmeier, T. E. Albrecht-Schmitt, *Cryst. Growth Des.* **2011**, *11*, 1385–1393; j) J. Olchowka, C. Falaise, C. Volkringer, N. Henry, T. Loiseau, *Chem.–Eur. J.* **2013**, *19*, 2012–2022; k) J. Olchowka, C. Volkringer, N. Henry, T. Loiseau, *Eur. J. Inorg. Chem.* **2013**, 2109–2114; l) P. Thuéry, *CrystEngComm* **2013**, *15*, 6533–6545; m) P. Thuéry, E. Rivière, *Dalton Trans.* **2013**, *42*, 10551–10558; n) P. Thuéry, *Cryst. Growth Des.* **2014**, *14*, 901–904; o) P. Thuéry, J. Harrowfield, *Cryst. Growth Des.* **2014**, *14*, 1314–1323; p) Z. Weng, Z. H. Zhang, T. Olds, M. Sterniczuk, P. C. Burns, *Inorg. Chem.* **2014**, *53*, 7993–7998; q) P. Thuéry, E. Rivière, J. Harrowfield, *Cryst. Growth Des.* **2016**, *16*, 2826–2835; r) P. Thuéry, J. Harrowfield, *Eur. J. Inorg. Chem.* **2018**, 1016–1027.
- [3] C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, *Acta Crystallogr., Sect. B* **2016**, *72*, 171–179.
- [4] P. Thuéry, J. Harrowfield, *Inorg. Chem.* **2015**, *54*, 10539–10541.
- [5] a) P. Thuéry, J. Harrowfield, *Inorg. Chem.* **2015**, *54*, 8093–8102; b) P. Thuéry, *Cryst. Growth Des.* **2016**, *16*, 546–549.
- [6] P. Thuéry, J. Harrowfield, *Inorg. Chem.* **2017**, *56*, 13464–13481.

- [7] a) S. Fortier, T. W. Hayton, *Coord. Chem. Rev.* **2010**, *254*, 197–214; b) R. J. Baker, *Chem.–Eur. J.* **2012**, *18*, 16258–16271.
- [8] P. C. Burns, *Can. Mineral.* **2005**, *43*, 1839–1894.
- [9] See, for example: a) S. Siegel, H. R. Hoekstra, *Acta Crystallogr., Sect. B* **1968**, *24*, 967–970; b) J. P. Legros, Y. Jeannin, *Acta Crystallogr., Sect. B* **1975**, *31*, 1133–1139.
- [10] P. Thuéry, E. Rivière, J. Harrowfield, *Inorg. Chem.* **2015**, *54*, 2838–2850.
- [11] a) B. T. McGrail, L. S. Pianowski, P. C. Burns, *J. Am. Chem. Soc.* **2014**, *136*, 4797–4800; b) S. G. Thangavelu, C. L. Cahill, *Inorg. Chem.* **2015**, *54*, 4208–4221; c) P. Thuéry, J. Harrowfield, *CrystEngComm* **2016**, *18*, 3905–3918 and references therein.
- [12] F. H. Burstall, R. S. Nyholm, *J. Chem. Soc.* **1952**, 3570–3579.
- [13] R. Sharma, J. Zhang, C. A. Ohlin, *Dalton Trans.* **2015**, *44*, 19068–19071.
- [14] a) U. Scheddin, M. Frydman, *Acta Chem. Scand.* **1968**, *22*, 115–127; b) P. L. Zanonato, P. Di Bernardo, A. Bismondo, G. Liu, X. Chen, L. Rao, *J. Am. Chem. Soc.* **2004**, *126*, 5515–5522.
- [15] D. C. Weatherburn, S. Mandal, S. Mukhopadhyay, S. Bhaduri, L. F. Lindoy, *Manganese*, in *Comprehensive Coordination Chemistry II*, J. A. McCleverty, T. J. Meyer, Eds., Vol. 5, Ch. 1, pp. 1–125, Elsevier Ltd., **2003**.
- [16] a) R. Taylor, O. Kennard, *J. Am. Chem. Soc.* **1982**, *104*, 5063–5070; b) G. R. Desiraju, *Acc. Chem. Res.* **1996**, *29*, 441–449.
- [17] M. A. Spackman, D. Jayatilaka, *CrystEngComm* **2009**, *11*, 19–32, and references therein.
- [18] S. K. Wolff, D. J. Grimwood, J. J. McKinnon, M. J. Turner, D. Jayatilaka, M. A. Spackman, *CrystalExplorer*, University of Western Australia, 2012.
- [19] A. L. Spek, *Acta Crystallogr., Sect. D* **2009**, *65*, 148–155.

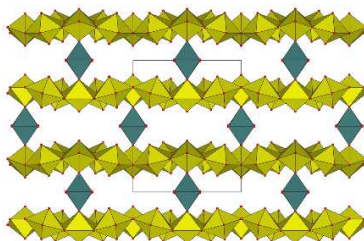
- [20] J. Springborg, *Adv. Inorg. Chem.* **1988**, *32*, 55–169.
- [21] a) P. Thuéry, *Cryst. Growth Des.* **2011**, *11*, 3282–3294; b) J. de Groot, B. Cassell, M. Basile, T. Fetrow, T. Z. Forbes, *Eur. J. Inorg. Chem.* **2017**, 1938–1946.
- [22] M. K. Pagoaga, D. E. Appleman, J. M. Stewart, *Amer. Miner.* **1987**, *72*, 1230–1238.
- [23] A. N. Alsobrook, E. V. Alekseev, W. Depmeier, T. E. Albrecht-Schmitt, *Cryst. Growth Des.* **2011**, *11*, 2358–2367.
- [24] H. Yin, Z. Tang, *Chem. Soc. Rev.* **2016**, *45*, 4873–4891.
- [25] a) M. C. Etter, J. C. MacDonald, J. Bernstein, *Acta Crystallogr., Sect. B* **1990**, *46*, 256–262; b) J. Bernstein, R. E. Davis, L. Shimoni, N. L. Chang, *Angew. Chem. Int. Ed.* **1995**, *34*, 1555–1573.
- [26] J. C. Reijenga, L. G. Gagliardi, E. Kenndler, *J. Chromatogr. A* **2007**, *1155*, 142–145.
- [27] R. W. W. Hooft, *COLLECT*, Nonius BV: Delft, The Netherlands, 1998.
- [28] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326.
- [29] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2015**, *71*, 3–8.
- [30] G. M. Sheldrick, *Acta Crystallogr., Sect. C* **2015**, *71*, 3–8.
- [31] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, p. 565.
- [32] K. Momma, F. Izumi, *J. Appl. Crystallogr.* **2008**, *41*, 653–658.

## Table of Contents Entry

### Three Different Modes of Association Between Metal Cations in Heterometallic Uranyl–Co<sup>III</sup> and Uranyl–Mn<sup>II</sup> Species

Pierre Thuéry and Jack Harrowfield

Key Topic: Heteronuclear Uranyl Complexes



In the three simple compounds reported, synthesized under hydrothermal conditions in the absence of any added ligand except 2,2'-bipyridine in two cases, uranyl and 3d-block metal cations (Co<sup>III</sup>, Mn<sup>II</sup>) are either separated into discrete ionic units, connected to one another through hydroxo ligands, or bonded to one another through the uranyl oxo atoms. In the last case, uranyl oxyhydroxide layers are united into a three-dimensional framework by Mn<sup>II</sup> pillars.