Structural Observations of Heterometallic Uranyl Copper(II) Carboxylates and Their Solid-State Topotactic Transformation upon Dehydration

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Abstract: The hydrothermal reactions of uranyl nitrate and metallic copper with aromatic polycarboxylic acids gave rise to the formation of five heterometallic UO₂²⁺-Cu²⁺ coordination $(UO_2)Cu(H_2O)_2(1,2-bdc)_2$ polymers: (1; $1,2-bdc = phthalate), (UO_2)Cu (H_2O)_2(btec)\cdot 4H_2O$ (2) and $(UO_2)Cu$ btec=pyromellitate), (btec) (**2**'; $(UO_2)_2Cu(H_2O)_4(mel)$ (3; mel=mellitate), and $(UO_2)_2O(OH)_2Cu(H_2O)_2$ -(1,3-bdc)·H₂O (4; 1,3-bdc=isophthlalate). Single-crystal X-ray diffraction (XRD) analysis of compound 1 revealed 2D layers of chains of UO₈ and $CuO_4(H_2O)_2$ units that were connected through the phthalate ligands. In compound 2, these sheets were connected to each other through the two additional carboxylate arms of the pyromelli-

Introduction

Over the last few decades, there has been growing interest in the synthesis and structural characterization of actinidebased compounds by associating metallic centers with O- or N-donor organic ligands to generate multidimensional coordination polymers.^[1] Most of the contributions reported to date have involved the elaboration of uranium-containing solids, because this particular 5f element finds its main use as a fuel in nuclear power plants. Present in many natural minerals,^[2] the chemical reactivity of uranium has been intensively investigated in comparison with those of its neighboring 5f metals in the periodic table (except for thorium), which are characterized by highly radio-toxicity activity, thus making their handling more difficult. By using hexava-

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tate, thus resulting in a 3D open-framework with 1D channels that trapped water molecules. Upon heating, free and bonded water species (from Cu– OH_2) were evacuated from the structure. This thermal transition was followed by in situ XRD and IR spectroscopy. Heating induced a solid-state topotactic transformation with the formation of a new set of Cu–O interactions in the crystalline anhydrous structure (2'), in order to keep the square-planar environment around the copper centers. The structure of compound 3 was built up from trinuclear motifs, in

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which one copper center, $CuO_4(OH_2)_2$, was linked to two uranium units, UO₅- $(H_2O)_2$. The assembly of this trimer, "U₂Cu", with the mellitate generated a 3D network. Complex 4 contained a tetranuclear uranyl core of UO₅(OH)₂ and $UO_6(OH)$ units that were linked to two copper centers, CuO(OH)2- $(H_2O)_2$, which were then connected to each other through isophthalate ligands and U=O-Cu interactions to create a 3D structure. The common structural feature of these different compounds is a bridging oxo group of U=O-Cu type, which is reflected by apical Cu-O disthe range 2.350(3) tances in 2.745(5) Å. In the case of a shorter Cu-O distance, a slight lengthening of the uranyl bond (U=O) is observed (e.g., 1.805(3) Å in complex 4).

lent uranium (UO_2^{2+}) , which represents its most stable oxidation state under ambient conditions, a large number of coordination polymers have been reported that show different local environments around the cation (tetragonal, pentagonal, and hexagonal bipyramidal geometries), together with different dimensionalities of the hybrid network. Following the successful synthesis of metal-organic framework (MOF) materials,^[3] a wide variety of combinations of multi-topic carboxylate-based organic ligands have been tested with these uranyl species to create new atomic arrangements.^[1c] Besides the use of organic molecules with targeted functionalities, an alternative strategy involves the formation of assemblies of 5f elements with distinct heterometallic elements, such as lanthanides or transition metals. An interesting structural feature is observed in divalent copper, which usually possesses a specific environment that is defined by four short Cu-O bonds in a square plane and two long axial Cu-O bonds, thereby resulting in an elongated octahedral geometry, owing to the Jahn-Teller effect. In the various reported crystal structures (Inorganic Crystal Structure Database, FIZ Karlsruhe, Germany) of mixed uranyl copper oxides and their derived solids (phosphates, silicates, etc.), the uranyl-oxo group was often found to belong to the coordination sphere of copper through a long apical bond. This

group would correspond to a type of heterometallic bridging oxo group that is known as a cation–cation interaction $(CCI)^{[4]}$ and defines a bonding of the "yl" oxygen atom with neighboring metallic cations (usually U=O–U in uranyl). Indeed, the occurrence of contrasting Cu–O distances (equatorial/apical) seems to favor such U=O–Cu linkage, owing to the long bond of the apical group that is attached to the copper atom. The heterometallic bridging oxo group was only found in very few of the various reported uranyl– copper hybrid complexes,^[5] which implied the use of mixed N/O-donor ligands.^[1b,6]

Following our investigation into the preparation of mixed uranyl-lanthanide-carboxylate-based compounds,^[7] we continued our studies in the examination of the uranyl-copper chemical system under mild hydrothermal conditions. The origin of this work was the use of metallic copper as a starting reactant to analyze the redox behavior towards uranyl cations in aqueous solution under mild hydrothermal conditions. In fact, the hydrothermal oxidation of metallic copper into its divalent state was observed and gave rise to the formation of mixed uranyl-copper(II) coordination polymers. Herein, four distinct phases have been isolated in the presence of aromatic polycarboxylate linkers, such as phthalic acid: $((UO_2)Cu(H_2O)_2(1,2-bdc)_2$ (1)), pyromellitic acid $((UO_2)Cu(H_2O)_2(btec)\cdot 4H_2O$ (2)), mellitic acid $((UO_2)_2Cu$ - $(H_2O)_4$ (mel) (3)), and isophthalic acid $((UO_2)_2O(OH)_2Cu (H_2O)_2(1,3-bdc) \cdot H_2O$ (4)). Their synthesis and their singlecrystal structures have been established. The thermal behavior of compounds 1 and 2 has also been studied and special attention has been paid to U-Cu-pyromellitate compound 2, which exhibits a potentially porous tunnel-based framework with encapsulated water. Indeed, upon heating, water molecules are removed, thereby leading to the formation of an anhydrous crystalline phase, $(UO_2)Cu(btec)$ (2'). Its crystal structure and the topotactic phase transitions were characterized by both in-situ X-ray thermodiffraction and IR spectroscopy.

Results and Discussion

Structure description: Compounds **1–4** were synthesized hydrothermally from a mixture of uranyl nitrate hexahydrate and metallic copper in aqueous medium with different aromatic poly-carboxylate molecules. Single-crystal X-ray diffraction analysis revealed that copper(II) cations were incorporated into the final uranyl–organic networks, thus indicating the occurrence of an oxidization reaction during the hydrothermal treatment.

 $(UO_2)Cu(H_2O)_2(1,2-bdc)_2$ (1): The structure of compound 1 is composed of an asymmetric unit (Figure 1) that contains one uranyl cation and one copper(II) cation at special positions Ig and If (Wyckhoff position), respectively. The uranyl center is eightfold-coordinated with two short U=O double bonds (1.783(3) Å) in apical positions and six carboxy oxygen atoms in a hexagonal equatorial plane with U-

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Figure 1. Top: view of the coordination environments around the uranyl (dark gray) and copper cations (light gray) in $(UO_2)Cu(H_2O)_2(1,2-bdc)_2$ (1). Bottom: infinite ribbon with strict alternation of UO_8 and CuO_4 - $(H_2O)_2$ polyhedra (as indicated). A similar chain-like motif is observed in compound 2.

O distances from 2.380(3) to 2.504(4) Å. Four of the carboxy oxygen atoms correspond to two chelating carboxylate arms from two distinct phthalate ligands and are located in a trans geometry. The second type of carboxylate arms adopts a bidentate bridging mode between the uranyl cation and the copper cation. The latter atom is coordinated to two carboxy oxygen atoms (Cu-O 1.923(3) Å) and two terminal aquo species (Cu-O1W 1.973(3) Å), which occupy the corners of a square plane (bond-valence calculations^[8] give a value of 0.452, which is in agreement with the assignment of a terminal water molecule). Two additional oxo groups complete the coordination environment of the copper atom, with a quite-long axial Cu-O distance (Cu-O11U 2.517(3) Å), thereby resulting in an elongated octahedral geometry. This distorted octahedral polyhedron is quite common for divalent copper species (Jahn-Teller effect). The oxo species that results from significant axial lengthening of two of the copper-oxygen bonds is shared with the uranyl O=U=O entity, thus forming a μ_2 connection mode. The uranyl-oxo species is known to be quite chemically inert and rarely engages in bonding with other uranyl or other heterometallic cations. However, some rare cases of purely inorganic compounds or coordination complexes have reported such a U=O-U or U=O-M (M=metal) linkage, which is known as a cation-cation interaction^[4] and has been encountered in some uranyl carboxylates.^[9] With copper, this situation is not new and has been described in a few uranyl copper carboxylates.^[1b,6] The occurrence of such µ2-oxo bridges leads to the formation of infinite heterometallic chains (Figure 2) with a strict alternation of hexagonal UO_8 bipyramids and distorted $CuO_4(H_2O)_2$ octahedra along the [110] direction. These ribbons are then connected to each other through the carboxylate groups of the phthalate ligands, thereby creating mixed organic-uranyl-copper

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Figure 2. Views of the layered structure in $(UO_2)Cu(H_2O)_2(1,2-bdc)_2$ (1) along the *ac* plane (top) and the *ab* plane (bottom).

layers in the *ab* plane (Figure 2). The benzene rings of the phthalate molecules point up or down the plane of the sheet and are oriented along the c axis. The cohesion of the structure is ensured by π - π interactions between the aromatic rings, which are stacked along the a axis (C···C distances of about 3.7 Å). Thermogravimetric analysis (see the Supporting Information, S3a) indicated one weight loss from 180°C, which was assigned to the decomposition of compound 1. The observed weight loss was 52.8%, which agreed very well with a theoretical value (52.6%) based on the chemical formula UCuO₄. Evolution of the powder XRD patterns (see the Supporting Information, S4) showed the collapse of the structure from 180°C and the crystallization of CuU₃O₁₀ (PDF number: 44-0979) between 420 and 600°C, followed by the formation of the final product CuUO₄ (PDF number: 24-038).

(UO₂)Cu(H₂O)₂(btec)·4H₂O (2): The structure of coordination polymer **2** is closely related to that of compound **1**. In fact, the asymmetric units are identical (Figure 3), with one eightfold-coordinated uranyl center and one octahedrally coordinated copper center. The uranyl bond is 1.776(1) Å long and the U–O distances from the hexagonal equatorial plane range from 2.386(1) to 2.525(1) Å. The copper cation is surrounded by two carboxy oxygen atoms (Cu–O 1.969(1) Å), two terminal aquo species (Cu–OW1 1.937(1) Å), and two uranyl μ_2 -oxo groups, which correspond to the elongated Cu–O distances (2.437(1) Å). Bondvalence calculations^[8] give a value of 0.498 (for OW1),



Figure 3. Top: view of the coordination environments around the uranyl (dark gray) and copper cations (light gray) in $(UO_2)Cu(H_2O)_{2^-}$ (btec)-4H₂O (2), which represents a fragment of the infinite chains of alternating uranyl and copper centers, as in compound 1. Bottom: structural relationship between $(UO_2)Cu(H_2O)_2(1,2-bdc)_2$ (1) and $(UO_2)Cu(H_2O)_2(btec)$ -4H₂O (2), which shows a crystallographic shift of *a*/2 of the layers of compound 1 with respect to the 3D framework of compound 2, along with the elimination of phthalate groups, which are replaced by two additional carboxylates groups from the pyromellitate linker.

which is in agreement with the assignment of a terminal water molecule. The arrangement of the carboxylates arms at the 1,2 or 4,5 positions of the pyromellitate linker is identical to that of the two adjacent carboxylates groups in the phthalate groups in compound 1. For each pair, one group chelates to the uranyl center, whereas the other is a bidentate bridge between the uranyl and copper cations. This arrangement results in the generation of infinite heterometallic ribbons along the [110] direction, which are connected to each other through one pair of carboxylate groups to form uranyl-copper-carboxylate layers in the ab plane. The tetradentate character of the pyromellitate ligands induces the shift of the layer of compound **1** along the *a* axis (a/2 translation, Figure 3) to generate a 3D framework with the formation of channels that run along the *a* axis (Figure 4). In fact, the 3D network of compound 2 corresponds to a modified structure of compound 1, in which two carboxylate functions have been symmetrically added to the benzene ring to connect the hybrid uranyl-copper-organic layers to each other. In this operation, one phthalate group has been replaced by the two additional carboxylate functions. Free water molecules are encapsulated within the channels, which offer a free aperture window of 3.7×3.8 Å². These molecules can be easily removed upon heating and thermogravimetric analysis (see the Supporting Information, Figure S3b) indicated that two water molecules per UO₂ unit were evacuated between 50 and 120 °C. We also observed that the water species that were coordinated to copper atoms were also re-

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OU2

Figure 5. Top: representation of the coordination environment of the uranyl (dark gray) and copper cations (light gray) in a trinuclear building unit in $(UO_2)_2Cu(H_2O)_4(mel)$ (3). Bottom: scheme of the μ_8 -connection mode of the mellitate ligand in compound 3.

Figure 4. Views of the 3D structure of $(UO_2)Cu(H_2O)_2(btec)-4H_2O$ (2) along the *bc* plane (top) and the *ac* plane (bottom).

moved during the dehydration process, with a corresponding weight loss of 15.2%, which was in good agreement with the theoretical value (15.6%): $4H_2O$ (calcd: 10.4%)+ $2H_2O$ (from copper, calcd: 5.2%). The organic part decomposed from 320°C up to 380°C and the remaining final weight loss was 53.6%, which was in good agreement with the expected value (53.0%) based on CuUO₄. Powder XRD pattern of the residue at 800°C indicated a major CuUO₄ phase (PDF number: 24-038) and some weak Bragg peaks that were assigned to CuU₃O₁₀ (PDF number: 44-0979).

 $(UO_2)_2Cu(H_2O)_4(mel)$ (3): The crystal structure of compound 3 also shown heterometallic bridging oxo groups between the uranyl and copper centers. It consists of two independent crystallographic metallic centers, which are defined by a trinuclear motif in which one central copper-centered octahedron is linked to two peripheral uranyl-centered pentagonal bipyramids through a U=O-Cu bridge (Figure 5). The copper cations lie at a special position (2a) and are sixfold-coordinated to two carboxy oxygen atoms (Cu-O 1.918(2) Å) and two terminal water species (Cu-OW2 1.972(3) Å), which

are located in a square plane, as well as two axial uranyloxo groups (2.561(2) Å), thus resulting in an elongated octahedral geometry. The Cu-O_{uranyl} bond is slightly longer than those in previous phases 1 or 2 (Table 1). The uranyl cation (general position 4e) is sevenfold-coordinated to two axial oxo groups, with the expected short U=O bonds (U=O 1.769(2) and 1.772(2) Å), four carboxy oxygen atoms (U-O 2.308(2)-07(2) Å), and one terminal water species (U-OW1 2.465(3) Å). Bond-valence calculations^[10] (0.450) agree well with the attribution of water to this oxygen atom. The connection of one copper cation to two uranium centers through the uranyl-oxo groups generates a discrete trinuclear unit with a U/Cu ratio of 2:1 (Figure 5). Only one uranyl-oxo ligand (OU1) is shared between the UO_2^{2+} and Cu^{2+} cations, whereas the second ligand (OU2) is terminal; this latter configuration is commonly observed in most uranyl-based compounds. The remaining non-bonded oxo-

Table 1. U=O and Cu–O distances in different uranyl copper carboxylates that exhibit heterometallic cation–cation Cu–O=U interactions.

Compound	U=0 [Å]	Cu–O [Å]	Bond valence
			for $O_{(Cu-O)}$
$(UO_2)_2(OH)_2Cu(3,5-pdc)_2 \cdot 2H_2O^{[a,1b]}$	1.780(9)	2.593(11)	0.085
$(UO_2)Cu(nic)_2(NO_3)_2^{[b,6]}$	1.771(3)	2.504(2)	0.108
$(UO_2)Cu(H_2O)_2(1,2-bdc)_2$ (1)	1.783(3)	2.517(3)	0.104
$(UO_2)Cu(H_2O)_2(btec) \cdot 4H_2O(2)$	1.776(1)	2.437(1)	0.129
$(UO_2)Cu(btec)$ (2')	1.754(2)	2.745(5)	0.056
$(UO_2)_2Cu(H_2O)_4(mel)$ (3)	1.772(2)	2.561(2)	0.092
$(UO_2)_2O(OH)_2Cu(H_2O)_2(1,3-bdc)\cdot H_2O$ (4)	1.805(3)	2.350(3)	0.163
	1.783(3)	2.692(4)	0.065

[a] 3,5-pdc=3,5-Pyrazoledicarboxylate; [b] nic=nicotinate.

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uranyl group (OU2) prevents further condensation with additional copper cations to form infinite chains, as was observed in compounds 1 and 2. The " U_2Cu " blocks are then linked to each other through the mellitate molecules, which exhibit a quite-complex multidentate connection mode with the different cations. Indeed, two of the carboxylate arms (positions 1,4) act as a bidentate linkage in bridging two uranyl centers from two distinct trimers. Two other carboxylate arms (positions 2,5) also adopt a bidentate connection fashion, but bridge one uranyl center and one copper center. The last two carboxylate arms (positions 3,6) are monodentate with respect to the uranyl centers and there remains one terminal C=O bond (C6-O6B 1.224(4) Å). Therefore, the mellitate is an octadentate linker toward the UO_2^{2+} and Cu^{2+} cations, which generates a rather dense 3D network, without any voids (Figure 6).



Figure 6. Views of the structure of $(UO_2)_2Cu(H_2O)_4(mel)$ (3), which show the arrangement of the trinuclear building blocks in the *bc* plane (top) and the *ab* plane (bottom).

 $(UO_2)_2O(OH)_2Cu(H_2O)_2(1,3-bdc)\cdotH_2O$ (4): The structure of compound 4 exhibits a distinct type of connection mode of the uranyl groups with the copper cations. The asymmetric building unit consists of two inequivalent crystallographic uranyl centers (U1 and U2), in a tetranuclear motif, that are linked to two copper atoms (Figure 7). The uranium atoms



Figure 7. Representation of the building unit in $(UO_2)_2O(OH)_2Cu(H_2O)_2-(1,3-bdc)-H_2O$ (4), which shows the edge-sharing connection of four sevenfold-coordinated uranyl centers with two divalent copper cations.

are sevenfold-coordinated and describe a classical pentagonal bipyramidal geometry, with uranyl distances (U=O) in the range 1.764(4)-1.805(3) Å. For U1, the five oxygen atoms in the pentagonal plane correspond to one carboxy oxygen atom (U1-O5B 2.398(3) Å), two oxo groups (U1-O2 2.244(3)–2.284(3) Å), and two hydroxo groups (U1–O 2.448(3)-2.571(3) Å). For U2, the five oxygen atoms are comprised of three carboxy oxygen atoms (U2-O 2.358(3)-2.525(3) Å), one oxo group (U2–O2 2.225(3) Å), and one hydroxo group (U2-O1 2.363(3) Å). The uranyl cations are exclusively connected to each other through an edge-sharing mode, thereby generating a tetrameric motif, which has previously been encountered many times in several types of uranyl carboxylates.^[11] Copper cations are also linked through edge-sharing with the uranyl groups to two hydroxo groups (Cu-O1 1.977(3) Å and Cu-O3 1.912(3) Å). Two other oxygen atoms are located in a square plane and correspond to terminal aquo species (Cu1-O4 2.002(3) Å and Cu–O5 1.990(3) Å). As expected for divalent copper cation, two long Cu-O bonds are observed for the apical oxo groups; however, in compound 4, they are found in an asymmetric manner. One of these bonds is rather short, with a Cu-OU1B distance of 2.350(3) Å, whereas the second bond (Cu-OU2A) is quite long (2.692(4) Å). This particular contrast in Cu-O distances results in either a square-pyramidal geometry for the copper center or in a distorted octahedral geometry if the long Cu-O distance is considered. As previously observed in other mixed uranyl-copper phases (1-3), the apical oxygen atoms belong to the uranyl bonds (U=O). However, in compound 4, the quite-short Cu-O distance (2.350(3) Å) induces a slight lengthening of the U=O bond, with a U1=OU1B distance of 1.805(3) Å. In comparison, the neighboring U=O bond length is 1.783(3) Å for U1 and the U=O bond lengths are 1.764(4) and 1.786(3) Å for U2. Considering the average distance of 1.778 Å for the U=O bonds, which is not affected by the U=O-Cu bond, the shift in distance for the second U=O bond is +0.027 Å. Within the " U_4Cu_2 " brick, two of the oxygen atoms, which bridge the uranyl atom, are oxo groups (bond valence for O2: 2.042^[10]) and are shared between three uranium atoms (μ_3). Two other groups, which bridge two uranium atoms and one copper atom (μ_3), are hydroxo groups (bond valence for O1: 1.362^[8,10]). The last two oxygen atoms, which bridge one uranium atom and copper atom (μ_2) , are also hydroxo groups (bond valence for O1: 0.998^[8,10]). For the terminal oxygen atoms that are bonded to copper atoms, bond-valence calculations^[8] gave values of 0.431 for O5 and 0.418 for O4. The "U₄Cu₂" building units are linked to each other through the isophthalate ligands, with one chelating connection type for one carboxylate arm and a bidentate bridging connection type for the second carboxylate arm, with only uranyl centers. This type of connection generates infinite ribbons (Figure 8), which are then linked through uranyl-oxocopper bonds (U1=O-Cu), which involve the short apical Cu-O bonds to create layers (Figure 8). The 3D character of the structure is ensured by the connection of the remaining free second apical oxo group (OU2A) to a copper center, which has weak interactions with the uranyl U2 cations (Figure 8). Free water molecules are intercalated between the layers and show preferential hydrogen-bonding interactions with the μ_2 -hydroxo group (OW1...O3 2.941(9) Å) and carboxy oxygen atoms (OW1...O1B 2.817(8) Å).

In situ thermal studies of the dehydration of $(UO_2)Cu-(H_2O)_2(btec)\cdot 4H_2O$ (2): The dehydration of hydrated compound 2 was characterized by in situ X-ray diffraction (up to 800 °C) and by IR spectroscopy (up to 210 °C) as a function of temperature. We focused our attention on characterizing the thermal behavior of this specific phase because its structure possesses an open-framework with 1D channels that encapsulate free water molecules.

The thermodiffractogram of phase **2** (Figure 9) indicated the rapid disappearance of its Bragg peaks when heated to 100 °C. These peaks showed a progressive thermal transformation into a new set of Bragg peaks, which were visible up to 360 °C. Then, phase **2** transformed into an amorphous phase and a recrystallization process was observed from 500 °C, with the formation of CuU₃O₁₀ (PDF number: 44-

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Figure 8. Top: view of the connection mode of the heterometallic "U₄Cu₂" building blocks through the isophthalate moiety, thereby generating infinite ribbons in $(UO_2)_2O(OH)_2Cu(H_2O)_2(1,3-bdc)-H_2O$ (4). Middle: connection of the $[U_4Cu_2-1,3-bdc]$ ribbons with copper cations through uranyl-oxo bonds (U=O-Cu, with C-O=2.350(3) Å). Bottom: 3D cohesion of the structures that are connected through long U=O-Cu linkages (2.692(4) Å).



Figure 9. X-ray thermodiffractograms of $(UO_2)Cu(H_2O)_2(btec)$ -4 H_2O (2) in air $(Cu_{K\alpha} \text{ radiation})$.

0979), followed by the formation of CuUO₄ (PDF number: 24-038) from 620 °C. The powder XRD pattern of the solid that crystallized between 100 and 360 °C can be indexed in a triclinic cell (a=5.0092, b=6.9847, c=8.5309 Å; a=97.286, β =106.280, γ =92.041°; V=283.40 Å³), with a good figure of merit M_{20} =51 (by using the DICVOL06^[12] program). These cell parameters were drastically different to those of the as-synthesized solid **2** (Table 2). From the TGA observa-

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	1	2	2'	3	4
formula	C16H8CuO12U	$C_{10}H_{14}CuO_{16}U$	$C_{10}H_2CuO_{10}U$	$C_{12}H_8CuO_{20}U_2$	$C_8H_{12}CuO_{14}U_2$
formula weight	693.8	691.78	583.7	1011.8	871.78
T [K]	296(2)	293(2)	293(2)	293(2)	293(2)
crystal type	green block	green block	blue-green block	green needle	green block
crystal size [mm]	$0.53 \times 0.51 \times 0.40$	$0.07 \times 0.05 \times 0.03$	$0.05 \times 0.02 \times 0.02$	$0.31 \times 0.14 \times 0.13$	$0.21 \times 0.07 \times 0.05$
crystal system	triclinic	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_{1}/c$	$P\bar{1}$
a [Å]	6.9898(5)	7.1070(2)	4.9959(3)	7.9835(2)	8.5643(1)
<i>b</i> [Å]	7.0913(5)	7.2234(2)	6.9710(4)	11.5456(2)	8.7504(1)
c [Å]	10.0712(11)	9.2050(2)	8.5143(5)	10.9719(2)	12.4227(2)
α [°]	100.537(4)	95.377(1)	97.310(3)	90	84.916(1)
β[°]	96.433(4)	91.256(1)	106.420(3)	105.350(1)	77.175(1)
γ [°]	114.224(3)	114.893(1)	91.960(4)	90	61.926(1)
V [Å ³]	437.71(6)	425.78(2)	281.35(3)	975.25(3)	800.80(2)
$Z, \rho_{\text{calcd}} [\text{g cm}^{-3}]$	1, 2.658	1, 2.698	1, 3.439	2, 3.445	2, 3.590
$\mu [{ m mm}^{-1}]$	10.526	10.833	16.322	17.754	21.56
θ range [°]	2.10-29.99	2.23-36.67	2.95-36.36	2.65-30.56	1.68-36.41
limiting indices	$-9 \leq h \leq 9$	$-11 \le h \le 11$	$-8 \le h \le 8$	$-11 \le h \le 11$	$-14 \le h \le 14$
	$-9 \leq k \leq 9$	$-12 \leq k \leq 12$	$-11 \le k \le 11$	$-16 \le k \le 16$	$-14 \le k \le 14$
	$-14 \le l \le 14$	$-16 \le l \le 16$	$-13 \le l \le 14$	$-15 \le l \le 15$	$-20 \le l \le 20$
total reflns	11275	19546	10041	23419	37605
unique reflns	2547 [R(int)=0.0435]	4209 [R(int)=0.0215]	2734 [R(int)=0.0592]	2988 [R(int)=0.0340]	7809 [R(int) = 0.0462]
parameters	139	125	103	160	221
GOF on F^2	1.136	1.0176	0.956	1.110	1.186
final R indices $[I > 2\sigma(I)]$	R1 = 0.0278	R1 = 0.0176	R1 = 0.0267	R1 = 0.0185	R1 = 0.0239
	wR2 = 0.0713	wR2 = 0.0421	wR2 = 0.0497	wR2 = 0.0491	wR2 = 0.0571
R indices (all data)	R1 = 0.0289	R1 = 0.0176	R1 = 0.0278	R1 = 0.0193	R1 = 0.0325
	wR2 = 0.0789	wR2 = 0.0422	wR2 = 0.0502	wR2 = 0.0495	wR2 = 0.0718
largest diff. peak/hole $[e \text{ Å}^{-3}]$	2.467/-4.931	1.745/-0.950	1.606/-2.648	1.837/-1.907	3.136/-3.695

tions, this new crystallized phase (denoted 2') could be assigned to the dehydrated form of phase 2, with the chemical formula (UO₂)Cu(btec). To obtain single crystals of the dehydrated phase 2', we attempted to synthesize it at higher temperatures from the mixture of reactants that was used for the formation of compound 2. After hydrothermal treatment at 200°C, a new compound was successfully isolated with single crystals that were suitable for XRD structure determination. Indeed, the cell parameters of the sample that was prepared hydrothermally at 200°C were similar to those that were obtained by the dehydration of phase 2.

The crystal structure of $(UO_2)Cu(btec)$ (2') reveals a new type of connection mode between the uranyl and copper cations, which reflects a structural transition that involved water elimination, together with the formation of Cu-O-U bonds, during the dehydration of compound 2. The structure is composed of an asymmetric unit that contains one eightfold-coordinated uranyl center and one copper cation with a surrounding square plane (Figure 10). The uranium-oxygen distances are 1.754(2) Å for the two uranyl bonds and range from 2.360(2) to 2.622(2) Å for the other bonds in the hexagonal plane of the uranyl-centered polyhedron. The copper atom is coordinated to four oxygen atoms in a square plane, with two sets of Cu-O distances of 1.922(2) (O1B) and 1.969(2) Å (O4A). Apical oxygen atoms that lead to an elongated octahedral geometry could be considered around the divalent cation, but are located quite far (2.745(5) Å)from the copper centers. The uranyl atom is linked to the copper center through one carboxy oxygen atom (O4A) and



Figure 10. Representation of the asymmetric unit in $(UO_2)Cu(btec)$ (2'). The copper environment is indicated by a square plane and the uranyl environment us indicated by a hexagonal bipyramid.

through a second carboxylate arm, thereby adopting a bidentate bridging mode. This mode results in the formation of infinite chains of alternating uranyl and copper cations along the [110] direction. These chains are then connected to each other through the carboxylate arms of the pyromellitate ligands to form a 3D network (Figure 11).

In fact, the structure of phase 2' is closely related to that of its hydrated form (2) and only differs in the water-molecule content. In the hydrated phase (2), water species are present within 1D tunnels, as well as coordinated ligands that are attached to the copper atoms. Upon heating, the water molecules are removed, which modifies the local coordination environment around the copper cations. A new type of copper-oxygen bond is formed to satisfy the squareplanar coordination around the copper atom and a possible

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Figure 11. Views of the structure of $(UO_2)Cu(btec)$ (2') in the *ac* and *bc* planes.

transition pathway can be proposed regarding the relationship between the two structures (2 and 2'). This pathway involves the shift of some carboxy oxygen atoms in equatorial U-O bonds toward the copper centers (Figure 12), which induces a rotation of 45° of the equatorial plane of the uranylcentered bipyramids with respect to the plane of the benzene rings of the tetracarboxylate molecules. Thus, a new square-planar environment is obtained at the copper center from this topotactic transition and longer Cu-O_{apical} distances are observed (2.745(5) Å in phase 2' instead of 2.437(1) Å in **2**). This result implies the irreversible shrinkage of the network channels, without any modification of the uranyl environment. The cell volume is reduced to 34% compared to that of phase 2 and this structural transformation prevents any re-adsorption of water molecules from, for instance, the ambient atmosphere. Such a thermal solid-state transition has only scarcely been reported in other metal-organic-framework-type metal carboxylates, which showed network flexibility upon dehydration.^[13]

This structural transition was also followed by in situ IR spectroscopy. At room temperature, the hydration state of



Figure 12. Top: detailed view of the structural relationship that reflects the possible transition pathway from a hydrated ribbon fragment, $[(UO_2)Cu(H_2O)_2(btec)]$, in compound **2** into the dehydrated ribbon, $[(UO_2)Cu(btec)]$, in compound **2'**. Black arrows indicate the formation of μ_3 -oxo bonds, in which the carboxy oxygen atoms are linked to the uranyl cations, owing to the elimination of coordinated water molecules upon heating. Bottom: representation of the structural transition that is involved in the dehydration of phase **2** into anhydrous phase **2'** and the irreversible shrinkage of the framework.

phase 2 was confirmed by IR spectroscopy, which showed a very broad absorption band within the range 3650- 2500 cm^{-1} , which corresponded to the stretching vibrations of water (see the Supporting Information, S7). We observed the asymmetric stretch ($v_{asym}(OH)$) at 3530 cm⁻¹, as well as the symmetric stretch ($v_{sym}(OH)$) at 3386 cm⁻¹; the broad band that was centered at 2500 cm⁻¹ is typical of intermolecular hydrogen-bonding interactions. Furthermore, the peak at 1651 cm⁻¹ was attributed to the deformation $\delta(H_2O)$. The IR spectrum of the parent structure of compound 1, which only possessed terminal bonded water molecules, did not show any sharp band at around 3500 cm⁻¹ (only a broad signal was visible in the range 3000–3500 cm⁻¹, for bonded water). Therefore, the resonance at 3530 cm⁻¹ for compound 2 can be easily assigned to free water species that are trapped within the structure channels. The sharpness of this band confirms the relative confinement of these molecules. Between 1600 and 1140 cm⁻¹, the IR spectrum displayed very intense bands, owing to the carboxylate groups and phenyl-ring deformations, which could not be precisely determined. Among the numerous bands that characterize metal-oxygen vibrations at lower wavenumbers, we assigned the peaks at 904 cm⁻¹ and 874 cm⁻¹ to v_{asym} (U=O) and v_{svm} (U=O), respectively. Indeed, the calculated uranyl bond length, from asymmetric vibration by using the empirical relationship defined by Bartlett and Cooney,^[14] (d_{calcd} (U=O) 1.781 Å) is in good agreement with that found in the XRD data (*d*_{obs}(U=O) 1.776(1) Å).

Upon heating, we analyzed the evolution of the vibration bands that were related to the water molecules and to the uranyl bonds because they appeared to be the most relevant for examining the thermal dehydration of compound 2 and its in situ transformation into compound 2' (Figure 13). Up



Figure 13. Evolution of the in situ IR spectra as a function of temperature, which represents the structural transition of compound **2** into compound **2'**, between 22–210 °C in the range 3600–3200 cm⁻¹ (top) and 960– 830 cm⁻¹ (bottom), with an interval of 4.5 °C between two consecutive spectra. Absorbance is represented in arbitrary units on the right-hand side.

to 100°C, we observed a significant decrease in intensity and the disappearance of the bands that were assigned to water. Unfortunately, this process did not show any differentiation between the water molecules that were linked to the copper centers and those that were trapped within the tunnels. This phenomenon is in perfect agreement with the TGA results, which did not show any specific weight-loss events owing to the successive evacuation of free and bonded water molecules. By analogy with the departure of water, the rearrangement of the uranium environment is highlighted by the continuous shift of the $v_{asym}(U=O)$ and $v_{sym}(U=O)$ bands up to 916.5 cm⁻¹ and 893 cm⁻¹ at 210°C, respectively, thus indicating a shortening of the uranyl bond during the topotactic transition (U=O 1.754(2) Å).

Conclusion

This study showed the association of uranyl cations with divalent copper cations in combination with aromatic polycarboxylate linkers. After a hydrothermal reaction in aqueous solvent, five distinct heterometallic coordination compounds were isolated with phthalate (1), pyromellitate (2, 2'), mellitate (3), and isophthalate ligands (4). A diverse range of inorganic building blocks have been structurally identified as discrete trinuclear units, "UCu₂", hexanuclear units, "U₄Cu₂", or infinite chains of alternating uranyl and copper centers. Despite the observed structural diversity in this series of organic–inorganic assemblies, a common feature was observed between them, that is, the occurrence of heterometallic bridging oxo groups between the uranyl and copper atoms. The copper cations are typically surrounded by four oxo groups that are located in a square plane (Cu-O=1.90-2.00 Å) whilst the two remaining oxo groups occupy the apical positions, with quite long Cu-O_{apical} distances, thus resulting in an elongated octahedral polyhedron. For compounds 1-4, the apical oxygen atoms also bridge the uranium centers through short U=O bonds, which correspond to a U=O-Cu-type linkage. The relatively long Cu-O_{apical} distances, which range from 2.350(3) to 2.745(5) Å (Table 1), are in agreement with those previously found in other mixed uranyl copper carboxylates and do not strongly affect the U-O distances. The uranyl bond lengths were within the expected range but we did observe that a shortening of the Cu–O_{apical} distance (2.350(3) Å in compound **4**) induced a slight lengthening of the U=O distance (1.805(3) Å). In contrast, the longer Cu-O_{apical} bond in the anhydrous form (2') is quite long (2.745(5) Å) and the corresponding U=O bond is rather short (1.754(2) Å). These different examples illustrate the amplitude of the elongated apical Cu–O bond (about 0.4 Å), thus reflecting a relative structural flexibility of this U=O-Cu interaction, which is adopted in the different uranyl-copper-organic assemblies. The uranyl bond length is not affected so much by the neighboring copper cation, except in the case of shorter Cu-O_{apical} distances.

The second aspect of this study concerned the possibility of designing different structural arrangements from a given building motif and their solid-state structural transformations upon heating. In our study, 3D open-framework 2 is formed from a 2D network (1) by increasing the number of carboxylate connectors on going from phthalate groups (1,2benzenedicarboxylate) to pyromellitate groups (1,2,4,5-benzenetetracarboxylate). The topological arrangement of the structural "uranyl-copper-carboxylate" entity is identical for compounds 1 and 2, but, in one case, a layered compound is obtained (1) whereas, in the second case, it is a 3D framework (2). This potentially porous structure encapsulates the water species within its channels, which could be removed upon heating. In situ thermodiffraction and IR spectroscopy showed that the water molecules that were coordinated to copper centers followed the same process and no distinct step of evacuation of such bonded water species was visible. Heating resulted in a topotactic transformation into a new crystalline anhydrous structure (2'), in which the eightfold-coordinated uranyl environment was identical, but the equatorial hexagonal plane was shifted to satisfy the square-planar coordination of copper, with the formation of a new set of U-O-Cu linkages from a µ₃-oxo bridge (belonging to a carboxylate arm). The dehydration transition implied the irreversible shrinkage of the structure and prevented any rehydration process. This thermal transformation gave another illustration of the flexibility of the weak Cu-O_{apical} bond that was involved in U=O-Cu bonding, which seemed to favor such structural transitions.

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Experimental Section

Synthesis: Caution! Uranyl nitrate $UO_2(NO_3)_2$ ·6H₂O is a radioactive and chemically toxic reactant and precautions, with suitable care and protection for handling such substances, should be followed.

The compounds described herein were synthesized hydrothermally under autogenous pressure by using Teflon-lined Parr-type autoclaves from a mixture of uranyl nitrate hexahydrate (UO₂(NO₃)₂·6H₂O, Merck, 99%), powdered copper metal (Aldrich, \geq 99.5%), phthalic acid (1,2-benzenedicarboxylic acid or 1,2-H₂bdc, Acros Organics, 99%), pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid or H₄btec, Aldrich, 96%), mellitic acid (1,2,3,4,5,6-benzenehexacarboxylic acid or 1,3-H₂bdc, Aldrich, 99%), isophthalic acid (1,3-benzenedicarboxylic acid or 1,3-H₂bdc, Aldrich, 99%), and deionized water. The starting chemical reactants were commercially available and were used without any further purification.

 $(UO_2)Cu(H_2O)_2(1,2-bdc)_2$ (1): A mixture of $UO_2(NO_3)_2\cdot 6H_2O$ (250 mg, 0.5 mmol), copper metal (31 mg, 0.5 mmol), phthalic acid (100 mg, 0.6 mmol), and water (5 mL, 277 mmol) was placed in a Parr bomb and then heated statically at 150 °C for 24 h. The pH value of the solution was 1 at the end of the reaction. The resulting green product was then filtered off, washed with water, and dried at RT. Compound **1** was analyzed by SEM (Hitachi S-3400N) and showed typical large truncated parallele-piped-like crystals of size 100–800 µm (see the Supporting Information, S1).

 $(UO_2)Cu(H_2O)_2(btec)\cdot 4H_2O$ (2): A mixture of $UO_2(NO_3)_2\cdot 6H_2O$ (250 mg, 0.5 mmol), copper metal (31 mg, 0.5 mmol), pyromellitic acid (150 mg, 0.59 mmol), and water (5 mL, 277 mmol) was placed in a Parr bomb and then heated statically at 150 °C for 24 h. The pH value of the solution was 1 at the end of the reaction. The resulting green product was then filtered off, washed with water, and dried at RT. Compound **2** was analyzed by SEM and showed typical elongated crystals of size 20–50 µm (see the Supporting Information, S1).

(UO₂)Cu(btec) (2'): This compound, which corresponds to the anhydrous form of compound **2**, was obtained upon heating phase **2** from 100 °C. Compound **2'** is also prepared from a mixture of UO₂(NO₃)₂·6H₂O (250 mg, 0.5 mmol), copper metal (31 mg, 0.5 mmol), pyromellitic acid (150 mg, 0.59 mmol), and water (5 mL, 277 mmol), which was placed in a Parr bomb and then heated statically at 200 °C for 24 h. The pH value of the solution was 1 at the end of the reaction. The resulting blue–green product was then filtered off, washed with water, and dried at RT. Compound **2'** was analyzed by SEM and showed typical elongated crystals of size 20–50 µm (see the Supporting Information, S1).

 $(UO_2)_2Cu(H_2O)_2(mel)$ (3): A mixture of $UO_2(NO_3)_2$ -6H₂O (180 mg, 0.36 mmol), copper metal (20 mg, 0.3 mmol), mellitic acid (80 mg, 0.23 mmol), and water (5 mL, 277 mmol) was placed in a Parr bomb and then heated statically at 150 °C for 24 h. The resulting green product was then filtered off, washed with water, and dried at RT. However, optical microscopy clearly showed the presence of different colored phases (yellow and green). Green crystals, which corresponded to phase 3, were selected for X-ray diffraction analysis. Different attempts (by changing the concentrations of the starting reactants, reaction time, or temperature) were made to isolate and obtain the pure phase (3), but were unsuccessful.

 $(UO_2)_2O(OH)_2Cu(H_2O)_2(1,3-bdc)-H_2O$ (4): A mixture of UO₂-(NO₃)₂-6 H₂O (250 mg, 0.5 mmol), copper metal (31 mg, 0.5 mmol), isophthalic acid (100 mg, 0.6 mmol), and water (5 mL, 277 mmol) was placed in a Parr bomb and then heated statically at 170 °C for 24 h. The resulting product was then filtered off, washed with water, and dried at RT. However, optical microscopy clearly showed the presence of different colored phases (yellow, green, or unreacted copper powder). Green crystals, which corresponded to phase 4, were selected for X-ray diffraction analysis. Different attempts (by changing the concentrations of the starting reactants, reaction time, or temperature) were made to isolate and obtain the pure phase (4), but were unsuccessful.

Single-crystal X-ray diffraction: Crystals of compounds **1–4** and **2'** were selected under a polarizing optical microscope and glued onto a glass fiber for a single-crystal X-ray diffraction analysis. X-ray intensity data

were collected on a Bruker X8-APEX2 CCD area-detector diffractometer by using Mo_{Ka} radiation ($\lambda = 0.71073$ Å) with optical fiber as a collimator. Several sets of narrow data frames (20 s per frame) were collected at different values of θ for two initial values of ϕ and ω , respectively, by using 0.3° increments of ϕ or ω . Data reduction was accomplished by using SAINT V7.53a.^[15] The substantial redundancy in data allowed a semi-empirical absorption correction (SADABS V2.10)^[16] to be applied, on the basis of multiple measurements of equivalent reflections. The structures were solved by using direct methods, which were developed by successive difference Fourier syntheses, and were refined by full-matrix least-squares on all F^2 data by using the SHELX^[17] program suite with the WINGX^[18] interface. Hydrogen atoms on the benzene rings were included at calculated positions and were allowed to ride on their parent atoms. However, the hydrogen atoms on the aquo or hydroxo groups were not located and not included in the calculations. The final refinements included anisotropic thermal parameters of all non-hydrogen atoms. The crystal data are given in Table 2. CCDC-906140 (1), CCDC-906141 (2), CCDC-906142 (2'), CCDC-906143 (3), CCDC-906144 (4) 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.

Thermogravimetric analysis: The thermogravimetric experiments were carried out on a TGA 92 SETARAM thermoanalyzer in air with a heating rate of 5°Cmin⁻¹ from RT up to 800°C. X-ray thermodiffractometry was performed under a flow of air (rate: 5 Lh^{-1}) in an Anton Paar HTK1200N of a D8 Advance Bruker diffractometer (θ – θ mode, Cu_{Ka} radiation) that was equipped with a Vantec1 linear position-sensitive detector (PSD). Each powder pattern was recorded in the range 2θ =5–60° (at intervals of 20°C up to 800°C) with a 0.5 s/step scan, which corresponded to an approximate duration of 30 min. The temperature ramp rate between the two patterns were 0.08°Cs⁻¹ up to 800°C.

Infrared spectroscopy: IR spectra of compounds 1 and 2 were measured on a Perkin–Elmer Spectrum Two spectrometer that was equipped with a diamond attenuated total reflectance (ATR) accessory between 4000 and 400 cm⁻¹ (see the Supporting Information). Dehydration of compound 2 was characterized by in situ IR spectroscopy in air with a heating rate of $10 \,^{\circ}$ Cmin⁻¹ from RT up to 210 $^{\circ}$ C. During this period, 195 spectra were recorded in the range 4000–400 cm⁻¹, with a resolution of 4 cm⁻¹, on a Perkin–Elmer Spectrum Two spectrometer that was equipped with a Pike Special-IR GladiATR accessory.

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