

# Uranyl Ion Complexation by Citric and Citramalic Acids in the Presence of Diamines

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Uranyl nitrate reacts with citric ( $H_4cit$ ) or D-(–)-citramalic ( $H_3citml$ ) acids under mild hydrothermal conditions and in the presence of diamines to give different complexes which are all characterized by the presence of 2:2 uranyl/polycarboxylate dianionic dimers or of polymeric chains based on the same dimeric motif. Each uranium ion is chelated by the two ligands through the alkoxide and the  $\alpha$ - or  $\beta$ -carboxylate groups, the second  $\beta$ -carboxylic group in citrate being uncoordinated. The uranium coordination sphere is completed by either a water molecule or the  $\beta$ -carboxylate group of a neighboring unit, thus giving zero- or one-dimensional assemblages, respectively. The evidence for  $[UO_2(Hcit)]_2$  dimers in the solid state confirms previous results from potentiometric and EXAFS measurements on solutions. Depending on the diamine used (DABCO, 2,2'- and 4,4'-bipyridine, [2.2.2]cryptand) and its ability to form divergent hydrogen bonds or not, different uranyl/polycarboxylate topologies are obtained, thus evidencing template effects, and extended hydrogen bonding gives two- or three-dimensional assemblages. These results, together with those previously obtained with NaOH as a base, add to the knowledge of the uranyl/citrate system, which is much investigated for its environmental relevance.

## Introduction

The investigation of uranyl ion complexation by citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) is appealing in the context of several different research fields. From the viewpoint of decontamination technology, citric acid is a versatile, environmentally friendly natural agent which has been studied extensively in recent years. As a uranium extractant giving bio- or photodegradable complexes, it may have possible applications either for the treatment of nuclear wastes or for the remediation of contaminated soils.<sup>1</sup> The latter may also benefit from its significant effect on uranium accumulation in plants and the possibility to use it to enhance the efficiency of phytoremediation methods.<sup>2</sup> Further, citric acid is present in the natural environment as well as in nuclear wastes such as those stored in the Hanford tanks,<sup>3</sup> and its effect on radionuclide mobility is a critical parameter

to be taken into account.<sup>4</sup> Also in the field of speciation studies, citric acid has been used for calibration of experimental and modeling studies of uranyl complexation by humic and fulvic acids.<sup>5</sup> Much effort has been devoted to the elucidation of the behavior of the uranyl/citric acid system<sup>6</sup> and of the structures of the complexes formed in solution,<sup>7</sup> but the crystal structure of a complex, obtained under hydrothermal conditions and in the presence of NaOH, was reported only recently.<sup>8</sup> The studies in solution concur

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to evidence the existence, at low pH values ( $\sim 2-4$ ), of a 2:2 dinuclear dimeric species with uranium coordination to both hydroxyl and carboxylate groups. This chelating coordination mode was confirmed by the crystal structure, but instead of being a molecular dimer, the complex investigated is a three-dimensional polymer (in which, however, dinuclear pseudosubunits, different from those predicted, can be distinguished) that evidences the potential of citric acid in the context of uranyl-organic framework (UOF) synthesis.<sup>9</sup> In order to investigate the influence of the experimental conditions and the possible existence of template effects on the structure of the complexes formed, uranyl complexation by citric acid under hydrothermal conditions in the presence of diamines [DABCO (1,4-diazabicyclo[2.2.2]octane), 2,2'- and 4,4'-bipyridine, and [2.2.2]cryptand, noted 222 hereafter] was investigated, and the results are reported herein. For comparison, the structures of the complexes with a related hydroxycarboxylic diacid, D(-)-citramalic acid [D(-)-2-hydroxy-2-methylbutanedioic acid], including DABCO or 4,4'-bipyridine, are also described.

## Experimental Section

**A. Synthesis.**  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was purchased from Prolabo, citric and D(-)-citramalic acids and 2,2'- and 4,4'-bipyridine were from Fluka, DABCO was from Acros, and [2.2.2]cryptand was from Merck. All were used without further purification. Elemental analyses were performed by Analytische Laboratorien GmbH at Lindlar, Germany.

**1.  $[\text{H}_2\text{DABCO}][\text{UO}_2(\text{Hcit}(\text{H}_2\text{O}))_2 \cdot 2\text{H}_2\text{O}$  1.** Citric acid (85 mg, 0.443 mmol),  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (223 mg, 0.444 mmol), DABCO (50 mg, 0.446 mmol), and demineralized water (4 mL) were placed in a 15 mL tightly closed vessel and heated at 140 °C under autogenous pressure. Light-yellow crystals of complex **1** were obtained within 5 h. As in all of the following cases, the product was recovered after filtration and was washed with water (61% yield). Anal. Calcd for  $\text{C}_{18}\text{H}_{32}\text{N}_2\text{O}_{22}\text{U}_2$ : C, 19.57; H, 2.92; N, 2.54. Found: C, 19.43; H, 3.06; N, 2.52.

**2.  $[\text{H}_2\text{DABCO}][\text{UO}_2(\text{citml})]_2 \cdot 2$  D(-)-Citramalic acid** (59 mg, 0.398 mmol),  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (200 mg, 0.398 mmol), DABCO (45 mg, 0.401 mmol), and demineralized water (3 mL) were placed in a 15 mL tightly closed vessel and heated at 140 °C under autogenous pressure. Light-yellow crystals of complex **2** were obtained within 24 h (40% yield). Anal. Calcd for  $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_{14}\text{U}_2$ : C, 20.35; H, 2.56; N, 2.97. Found: C, 20.22; H, 2.58; N, 2.91.

**3.  $[\text{H}_2\text{-4,4'-bipy}][\text{UO}_2(\text{Hcit})]_2 \cdot 3$**  Citric acid (68 mg, 0.354 mmol),  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (356 mg, 0.709 mmol), 4,4'-bipyridine (56 mg, 0.358 mmol), and demineralized water (3.3 mL) were placed in a 15 mL tightly closed vessel and heated at 180 °C under

autogenous pressure. Only after repeated attempts with different stoichiometries, concentrations, and temperatures was it possible to isolate, under the conditions stated above, a few light-yellow crystals of complex **3** within 24 h, together with a yellow powder. Analysis of the powder indicates that it differs from the crystals, but being insoluble in usual solvents, it was not further characterized.

**4.  $[\text{H}_2\text{-4,4'-bipy}][\text{UO}_2(\text{citml})(\text{H}_2\text{O})]_2 \cdot \text{H}_2\text{O}$  4.** D(-)-Citramalic acid (47 mg, 0.317 mmol),  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (159 mg, 0.317 mmol), 4,4'-bipyridine (50 mg, 0.320 mmol), and demineralized water (3 mL) were placed in a 15 mL tightly closed vessel and heated at 140 °C under autogenous pressure. Light-yellow crystals of complex **2** were obtained within 2 days (52% yield). Anal. Calcd for  $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_{17}\text{U}_2$ : C, 23.04; H, 2.51; N, 2.69. Found: C, 23.08; H, 2.66; N, 2.61.

**5.  $[\text{H}_2\text{-2,2'-bipy}]_2[\text{UO}_2(\text{Hcit})]_2 \cdot 5\text{H}_2\text{O}$  5.** Citric acid (68 mg, 0.354 mmol),  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (178 mg, 0.355 mmol), 2,2'-bipyridine (56 mg, 0.359 mmol), and demineralized water (3 mL) were placed in a 15 mL tightly closed vessel and heated at 140 °C under autogenous pressure. Light-yellow crystals of complex **5** were obtained within 3 days (31% yield). Anal. Calcd for  $\text{C}_{32}\text{H}_{38}\text{N}_4\text{O}_{23}\text{U}_2$ : C, 29.06; H, 2.90; N, 4.24. Found: C, 28.61; H, 2.88; N, 4.05.

**6.  $[\text{H}_2\text{-222}(\text{H}_2\text{O})][\text{UO}_2(\text{Hcit})]_2 \cdot 3\text{H}_2\text{O}$  6.** Citric acid (65 mg, 0.339 mmol),  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (170 mg, 0.339 mmol), [2.2.2]cryptand (128 mg, 0.340 mmol), and demineralized water (3 mL) were placed in a 15 mL tightly closed vessel and heated at 140 °C under autogenous pressure. Light-yellow crystals of complex **6** were obtained within 24 h (73% yield). Anal. Calcd for  $\text{C}_{30}\text{H}_{56}\text{N}_2\text{O}_{28}\text{U}_2$ : C, 26.32; H, 4.12; N, 2.05. Found: C, 26.07; H, 3.98; N, 1.91.

**B. Crystallographic Data Collection and Structure Determination.** The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer<sup>10</sup> using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  0.71073 Å). The crystals were introduced in glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from 10 frames and then refined on all data. The data (combinations of  $\varphi$  and  $\omega$  scans giving complete data sets up to  $\theta = 25.7^\circ$  and a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.<sup>11</sup> The structures were solved by Patterson map interpretation (**3**) or by direct methods (all other compounds) with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least squares on  $F^2$  with SHELXL-97.<sup>12</sup> Absorption effects were corrected empirically with the program SCALEPACK.<sup>11</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Except when otherwise specified, hydrogen atoms bound to oxygen and nitrogen atoms were found on Fourier-difference maps, and all of the others were introduced at calculated positions. All were treated as riding atoms with a displacement parameter equal to 1.2 (OH, NH, CH<sub>2</sub>) or 1.5 (CH<sub>3</sub>) times that of the parent atom. Special details are as follows.

**1. Compound 1.** The half  $\text{H}_2\text{DABCO}$  moiety present in the asymmetric unit is disordered over two positions related by a symmetry center, and a complete ion has been refined with a 0.5 occupancy parameter and with restraints on bond lengths and displacement parameters.

**2. Compound 2.** The absolute configuration determined from the value of the Flack parameter,  $-0.001(19)$ ,<sup>13</sup> is as expected.

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**Table 1.** Crystal Data and Structure Refinement Details

	1	2	3	4	5	6
empirical formula	C <sub>18</sub> H <sub>32</sub> N <sub>2</sub> O <sub>22</sub> U <sub>2</sub>	C <sub>16</sub> H <sub>24</sub> N <sub>2</sub> O <sub>14</sub> U <sub>2</sub>	C <sub>22</sub> H <sub>20</sub> N <sub>2</sub> O <sub>18</sub> U <sub>2</sub>	C <sub>20</sub> H <sub>26</sub> N <sub>2</sub> O <sub>17</sub> U <sub>2</sub>	C <sub>32</sub> H <sub>38</sub> N <sub>4</sub> O <sub>23</sub> U <sub>2</sub>	C <sub>30</sub> H <sub>56</sub> N <sub>2</sub> O <sub>28</sub> U <sub>2</sub>
<i>M</i> (g mol <sup>-1</sup> )	1104.52	944.43	1076.46	1042.49	1322.72	1368.83
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	9.3098(4)	8.3086(4)	7.3131(5)	19.2801(13)	17.3514(15)	16.4966(10)
<i>b</i> (Å)	13.8620(6)	10.3366(3)	8.5411(3)	11.0723(8)	17.2886(17)	20.177(3)
<i>c</i> (Å)	11.0229(3)	14.0153(7)	11.2793(7)	14.2972(8)	15.4500(11)	14.2793(15)
$\alpha$ (°)	90	90	97.375(4)	90	90	90
$\beta$ (°)	99.809(2)	100.247(3)	98.767(3)	110.252(4)	118.538(5)	115.634(6)
$\gamma$ (°)	90	90	106.632(4)	90	90	90
<i>V</i> (Å <sup>3</sup> )	1401.74(9)	1184.47(9)	656.07(7)	2863.4(3)	4071.6(6)	4285.1(8)
<i>Z</i>	2	2	1	4	4	4
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	2.617	2.648	2.725	2.418	2.158	2.122
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	11.640	13.726	12.421	11.376	8.038	7.648
<i>F</i> (000)	1028	860	494	1920	2504	2632
reflns collected	41233	39066	32471	73690	65138	57451
indep reflns	2662	4483	2489	5416	3864	4054
obsd reflns [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	2554	4412	2368	4576	2766	2794
<i>R</i> <sub>int</sub>	0.024	0.051	0.022	0.042	0.034	0.042
params refined	235	310	199	390	280	303
<i>R</i> 1	0.021	0.044	0.016	0.073	0.040	0.059
w <i>R</i> 2	0.044	0.116	0.037	0.153	0.101	0.173
<i>S</i>	1.157	1.057	1.052	1.213	1.049	1.021
$\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	-1.00	-1.81	-1.09	-1.89	-1.42	-1.22
$\Delta\rho_{\max}$ (e Å <sup>-3</sup> )	0.72	2.42	1.17	1.88	0.98	1.95

**3. Compound 4.** One of the citramalate ligands has two carbon atoms disordered over two positions, which have been refined with occupancy parameters constrained to sum to unity and with restraints on bond lengths. Restraints on bond lengths and/or displacement parameters were also applied for some badly behaving atoms.

**4. Compound 5.** Restraints on displacement parameters were applied for some badly behaving atoms in the bipyridine and solvent molecules. The water molecule containing O12 was affected with a 0.5 occupancy parameter in order to retain an acceptable displacement parameter and also because it is located too close from its image by symmetry. The hydrogen atoms bound to oxygen atoms were not found, and they are possibly disordered over several positions compatible with hydrogen bonding.

**5. Compound 6.** The half cryptand moiety is very badly resolved and has been refined with restraints on bond lengths and angles. The three solvent water molecules (O14, O15, and O16) were affected with 0.5 occupancy factors, either in order to retain an acceptable displacement parameter (O14) or because they were too close to one another to be both in fully occupied sites (O15 and O16). The hydrogen atoms bound to oxygen and nitrogen atoms were not found nor were they introduced. The short C9–C9' bond length and some short H···H contacts in the cryptand moiety are due to the bad resolution and resulting imperfect geometry of this molecule.

Crystal data and structure refinement parameters are given in Table 1, and selected distances and angles are given in Table 2. The molecular plots were drawn with SHELXTL<sup>14</sup> and Balls & Sticks.<sup>15</sup>

## Results and Discussion

**A. The Uranyl Polycarboxylate Dimers and Dimer-Based Polymers.** The complex [(UO<sub>2</sub>)<sub>3</sub>(Hcit)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]·2H<sub>2</sub>O, **7**, whose structure has previously been reported,<sup>8</sup> was first

obtained from 1:1:2 or 3:2:4 uranyl/citric acid/NaOH aqueous solutions heated at 180 °C, but it was later synthesized at different conditions in the presence of NaOH, KOH, or CsOH and at temperatures between 140 and 180 °C; it was even obtained at 200 °C in the presence of the diamine 1,4,10-trioxo-7,13-diazacyclopentadecan.<sup>16</sup> It, thus, appears to be the most stable compound in a wide range of experimental conditions. In all of these cases, the species employed as a base is absent from the final product, but this is no more true for the diamines used in the present study, which have been chosen for their hydrogen-bonding potential and the consequent formation of extended frameworks that could be expected. More surprisingly, the citrate coordination mode in compounds **1**, **3**, **5**, and **6** is very different from that in compound **7**, which will be briefly reminded first.

The citrate moieties in compound **7** are chelating one uranyl ion through their hydroxyl (not deprotonated) and  $\alpha$ -carboxylate groups, and they are further bound to four more metal atoms through the  $\alpha$ - and  $\beta$ -carboxylate groups, giving an overall  $\mu_5-1\kappa^2O, O':2\kappa O'':3\kappa O''':4\kappa O'''':5\kappa O'''''$  coordination mode, with only one carboxylate oxygen atom left uncoordinated. Three independent uranyl ions are present in the asymmetric unit, two of them chelated by one citrate and bound to three monodentate oxygen atoms from  $\beta$ -carboxylate groups, whereas the third is bound to two monodentate  $\alpha$ -carboxylate groups and three water molecules. The resulting framework is three-dimensional.

In compounds **1–6** (Figures 1–6), the basic unit in the structure consists of two uranyl ions and two citrate (Hcit) or citramalate (citml) ligands arranged in similar fashion, giving a dimer which can possess an inversion center (**1**, **3**, **4**), a binary axis (**5**, **6**), or be devoid of any crystallographic symmetry (**2**). Each uranium atom is chelated twice through the alkoxide and  $\alpha$ -carboxylate groups of one ligand and

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**Table 2.** Environment of the Uranium Atoms in Compounds **1–6**: Selected Distances (Å) and Angles (°)<sup>a</sup>

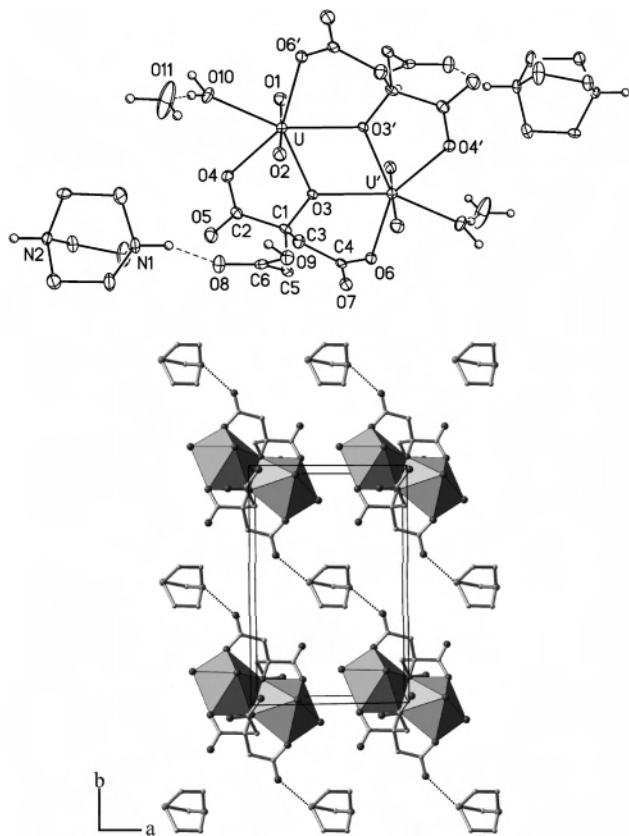
1		2		3	
U–O1	1.777(3)	U1–O1	1.796(7)	U–O1	1.777(3)
U–O2	1.769(3)	U1–O2	1.784(13)	U–O2	1.779(3)
U–O3	2.383(3)	U1–O5	2.361(9)	U–O3	2.377(2)
U–O4	2.389(3)	U1–O6	2.362(9)	U–O4	2.346(2)
U–O3'	2.397(3)	U1–O10	2.375(8)	U–O3'	2.387(2)
U–O6'	2.373(3)	U1–O13	2.355(9)	U–O6'	2.355(2)
U–O10	2.414(3)	U1–O9'	2.447(9)	U–O7''	2.477(2)
U...U'	3.9604(3)	U2–O3	1.823(12)	U...U'	3.9684(3)
		U2–O4	1.743(9)		
		U2–O5	2.406(9)		
		U2–O8	2.343(11)		
		U2–O10	2.376(8)		
		U2–O11	2.360(10)		
		U2–O14''	2.452(9)		
		U1...U2	3.8831(7)		
O1–U–O2	174.52(13)	O1–U1–O2	176.8(5)	O1–U–O2	177.49(10)
O3–U–O4	66.21(9)	O5–U1–O6	66.6(3)	O3–U–O4	66.57(8)
O4–U–O10	74.47(10)	O6–U1–O9'	72.3(3)	O4–U–O7''	72.11(8)
O10–U–O6'	76.50(10)	O9'–U1–O13	76.6(3)	O7''–U–O6'	80.27(8)
O6'–U–O3'	75.34(9)	O13–U1–O10	74.5(3)	O6'–U–O3'	73.98(8)
O3'–U–O3	68.10(11)	O10–U1–O5	70.5(3)	O3'–U–O3	67.20(9)
		O3–U2–O4	176.3(6)		
		O5–U2–O8	71.8(3)		
		O8–U2–O14''	82.2(3)		
		O14''–U2–O11	70.4(3)		
		O11–U2–O10	66.4(3)		
		O10–U2–O5	69.7(3)		
4		5		6	
U1–O1A	1.782(11)	U–O1	1.766(6)	U–O1	1.765(9)
U1–O2A	1.768(12)	U–O2	1.812(7)	U–O2	1.768(10)
U1–O3A	2.351(10)	U–O3	2.368(5)	U–O3	2.354(7)
U1–O4A	2.374(9)	U–O4	2.346(6)	U–O4	2.380(9)
U1–O3A'	2.350(9)	U–O3'	2.400(5)	U–O3'	2.393(8)
U1–O6A'	2.349(10)	U–O6'	2.339(5)	U–O6'	2.356(8)
U1–O8A	2.398(12)	U–O7''	2.400(5)	U–O7''	2.415(8)
U1...U1'	3.8432(12)	U...U'	3.9377(6)	U...U'	3.9176(8)
U2–O1B	1.790(12)				
U2–O2B	1.807(13)				
U2–O3B	2.339(11)				
U2–O4B	2.361(11)				
U2–O3B''	2.373(11)				
U2–O6B''	2.334(10)				
U2–O8B	2.415(11)				
U2...U2''	3.8681(13)				
O1A–U1–O2A	178.1(5)	O1–U–O2	178.1(2)	O1–U–O2	177.9(4)
O3A–U1–O4A	67.6(3)	O3–U–O4	66.87(18)	O3–U–O4	65.9(3)
O4A–U1–O8A	72.0(4)	O4–U–O7''	73.50(19)	O4–U–O7''	75.2(3)
O8A–U1–O6A'	75.4(4)	O7''–U–O6'	77.85(19)	O7''–U–O6'	78.1(3)
O6A'–U1–O3A'	74.8(4)	O6'–U–O3'	73.82(18)	O6'–U–O3'	73.6(3)
O3A'–U1–O3A	70.3(4)	O3'–U–O3	68.5(2)	O3'–U–O3	68.2(3)
O1B–U2–O2B	177.4(6)				
O3B–U2–O4B	71.2(4)				
O4B–U2–O8B	76.0(4)				
O8B–U2–O6B''	72.2(4)				
O6B''–U2–O3B''	71.1(4)				
O3B''–U2–O3B	69.6(3)				

<sup>a</sup> Symmetry codes: **1**, ' = 2 - x, -y, -z; **2**, ' = x - 1, y, z; '' = x + 1, y, z; **3**, ' = 1 - x, 1 - y, 1 - z; '' = x, y + 1, z; **4**, ' = 2 - x, -y, 3 - z; '' = 1 - x, -y, -z; **5**, ' = -x, y, 3/2 - z; '' = x + 1/2, 1/2 - y, z + 1/2; **6**, ' = -x, y, 1/2 - z; '' = x + 1/2, 1/2 - y, z + 1/2.

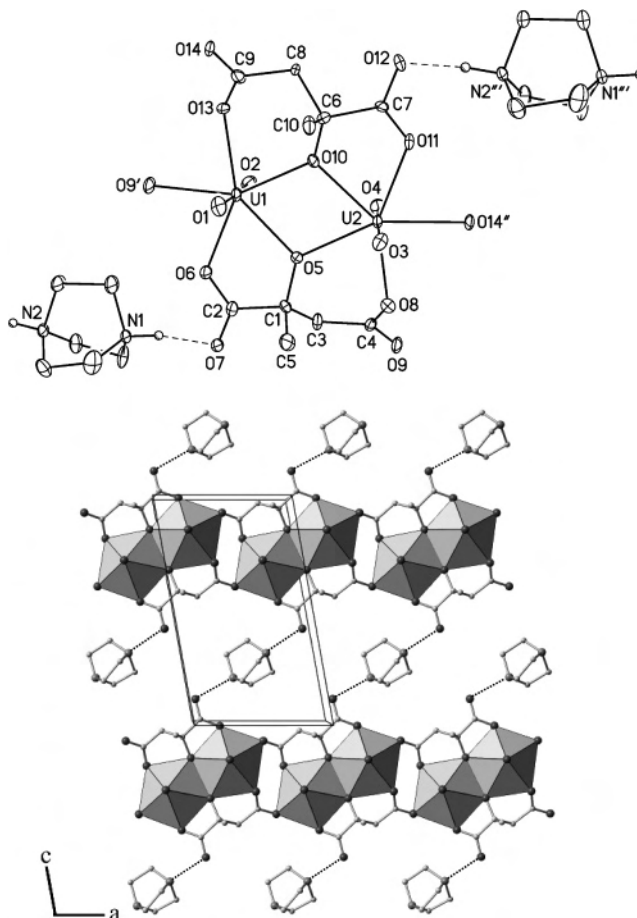
the alkoxide and  $\beta$ -carboxylate groups of the other, the alkoxide group being bridging. Two chelate rings, five- and six-membered, are thus formed around each uranyl ion. The uranium coordination sphere is completed either by a  $\beta$ -carboxylate oxygen atom from a neighboring molecule or by a water molecule, so as to give the usual pentagonal bipyramidal geometry, the coordination polyhedra around neighboring uranium atoms being edge-sharing along the line defined by the two alkoxide oxygen atoms. The average

U–O(alkoxide) bond lengths in the citrate [2.382(15) Å] and the citramalate [2.37(2) Å] compounds are both shorter than the U–O(hydroxyl) bond length in **7** [2.496(10) Å], as expected. In all cases, there is a slight dissymmetry in the alkoxide bridge, the bond length on the same side as the  $\alpha$ -carboxylate group being shorter than the other one by as much as 0.039 Å in compound **6**. The average U–O( $\alpha$ -carboxylate) and U–O( $\beta$ -carboxylate) bond lengths are 2.37-(2) and 2.356(12) Å for citrate and 2.364(6) and 2.345(8) Å





**Figure 1.** Top: View of the complex  $[\text{H}_2\text{DABCO}][\text{UO}_2(\text{Hcit})(\text{H}_2\text{O})]_2 \cdot 2\text{H}_2\text{O}$  **1**. Carbon-bound hydrogen atoms have been omitted for clarity. Hydrogen bonds are shown as dashed lines. Only one position of the rotationally disordered  $\text{H}_2\text{DABCO}$  molecule is represented. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code:  $' = 2 - x, -y, -z$ . Bottom: View of the assemblage in the  $ab$  plane with the solvent molecules omitted. Only the position of the rotationally disordered  $\text{H}_2\text{DABCO}$  molecule connecting the dimers in the plane is represented. The uranium coordination polyhedra are represented, and the other atoms are shown as spheres of arbitrary radii.



**Figure 2.** Top: View of the complex  $[\text{H}_2\text{DABCO}][\text{UO}_2(\text{citml})]_2$  **2**. Carbon-bound hydrogen atoms have been omitted for clarity. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes:  $' = x - 1, y, z$ ;  $'' = x + 1, y, z$ ;  $''' = x + 1, y, z + 1$ . Bottom: View of the two-dimensional assemblage in the  $ac$  plane. The uranium coordination polyhedra are represented, and the other atoms are shown as spheres of arbitrary radii.

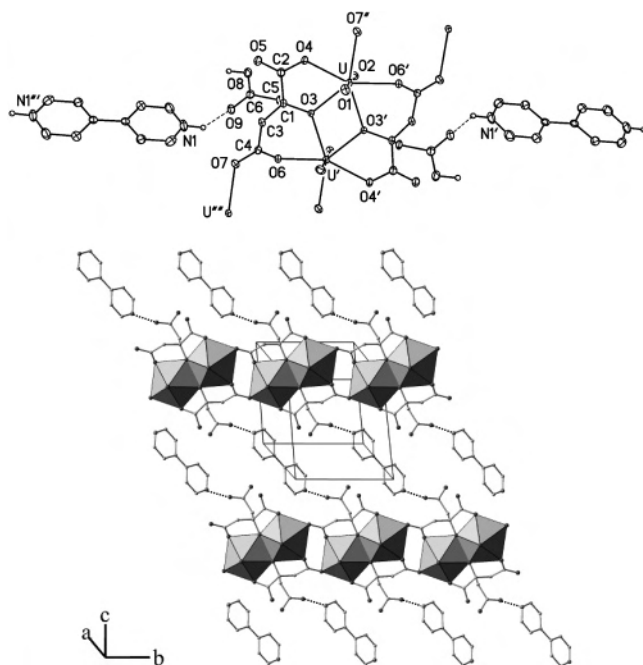
for citramalate, indicating, as in **7**, a very slightly longer bond for  $\alpha$  groups (this order is, however, reversed in **3**). The bond lengths with  $\beta$ -carboxylate donors from neighboring units in compounds **2**, **3**, **5**, and **6** are even longer, with an average value of  $2.44(3)$  Å, which is also larger than the average U–O(alkoxide) bond length. The average U–O(water) bond length in **1** and **4**,  $2.409(8)$  Å, is in agreement with the mean value of  $2.44(4)$  Å from the structures reported in the Cambridge Structural Database (CSD, Version 5.27).<sup>17</sup> The five equatorial donor atoms around uranyl define mean planes with rms deviations in the range of  $0.034$ – $0.126$  Å, and the dihedral angles between the two mean planes in a dimer for the complexes that do not possess an inversion center are  $10.6(2)$ ,  $11.86(4)$ , and  $16.73(9)^\circ$  in **2**, **5**, and **6**, respectively.

The existence of such dimers (with, however, a hydroxyl group in place of the alkoxide) at  $\text{pH} \sim 2$ – $4$  (i.e., comparable to the range in the present syntheses,  $\sim 2$ – $3$ ) has been postulated long ago from potentiometric experiments, together with other species and hydrolysis products at higher pH values,<sup>6b</sup> and it was later confirmed on the basis of various solution experiments,<sup>6c,d,f</sup> with EXAFS measure-

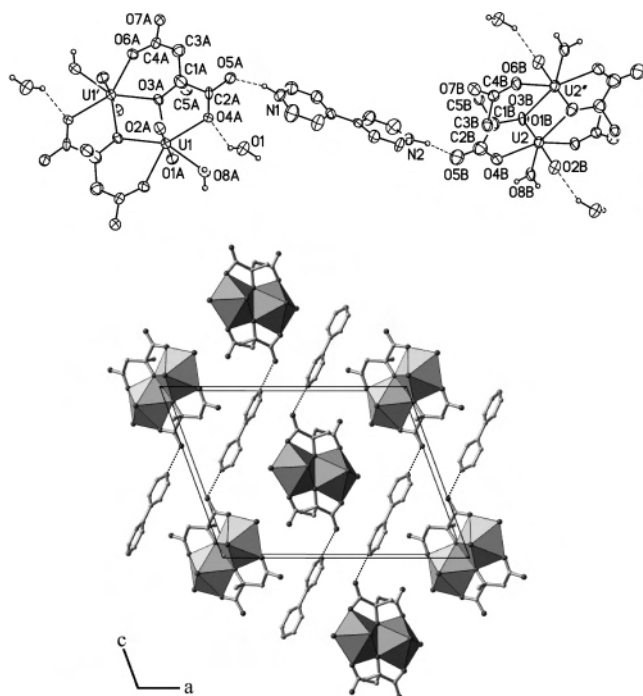
ments, in particular, providing unequivocal evidence.<sup>7a,d</sup> The U...U separation inside the dimers in the present complexes, with an average value of  $3.95(2)$  Å in the citrate and a slightly smaller value of  $3.865(16)$  Å in the citramalate species, nicely matches the values of  $3.89$ – $3.95$  Å determined for citrate from these EXAFS experiments. It is to be noted that a similar dimeric arrangement was observed for uranyl tartrate in solution,<sup>7a</sup> but the crystal structure recently reported for  $[\text{UO}_2(\text{C}_4\text{H}_4\text{O}_6)(\text{H}_2\text{O})]$  grown under hydrothermal conditions does not show the formation of dimers but of a two-dimensional assemblage in which only one of the hydroxyl groups is coordinated,<sup>9k</sup> even at comparable pH values, different species are formed in these very different experimental conditions. The structures of compounds **1**–**6** provide the first solid-state crystallographic characterization of these uranyl dimeric units or subunits with citrate or related ligands. However, several citrate complexes of 3d metal ions are also dimeric, with bridging alkoxide groups, but all three carboxylate groups are generally coordinated,<sup>18</sup> which is prevented by the equatorial bonding requirements of uranyl.

As indicated previously, the fifth atom coordinated to each uranyl ion comes either from a water molecule (compounds **1** and **4**) or from the bridging  $\beta$ -carboxylate group of a

(17) Allen, F. H. *Acta Crystallogr., Sect. B* **2002**, *58*, 380.

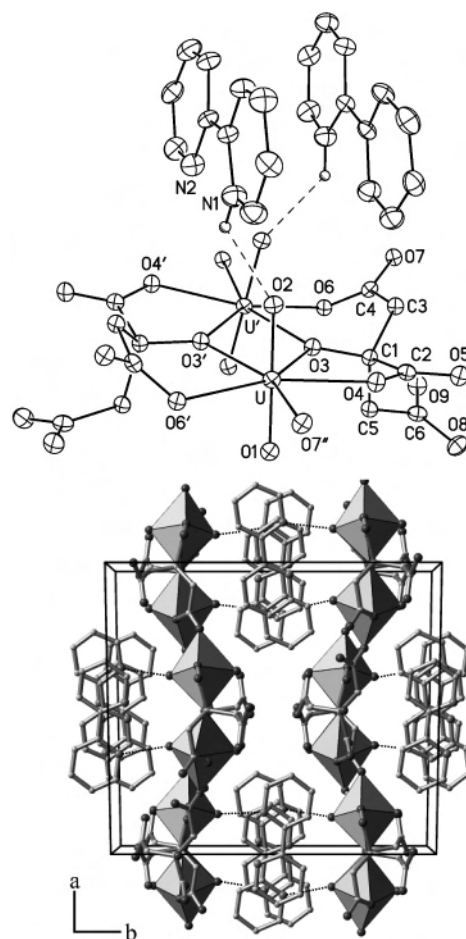


**Figure 3.** Top: View of the complex  $[H_2-4,4'-bipy][UO_2(Hcit)]_2$  **3**. Carbon-bound hydrogen atoms have been omitted for clarity. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: ' =  $1 - x, 1 - y, 1 - z$ ; '' =  $x, y + 1, z$ ; ''' =  $3 - x, -y, 2 - z$ ; '''' =  $x, y - 1, z$ . Bottom: View of the two-dimensional assemblage. The uranium coordination polyhedra are represented, and the other atoms are shown as spheres of arbitrary radii.



**Figure 4.** Top: View of the complex  $[H_2-4,4'-bipy][UO_2(citml)(H_2O)]_2 \cdot H_2O$  **4**. Carbon-bound hydrogen atoms have been omitted for clarity. Hydrogen bonds are shown as dashed lines. Only one position of the disordered part is represented. Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes: ' =  $2 - x, -y, 3 - z$ ; '' =  $1 - x, -y, -z$ . Bottom: View of the assemblage in the  $ac$  plane with the solvent molecules omitted. The uranium coordination polyhedra are represented, and the other atoms are shown as spheres of arbitrary radii.

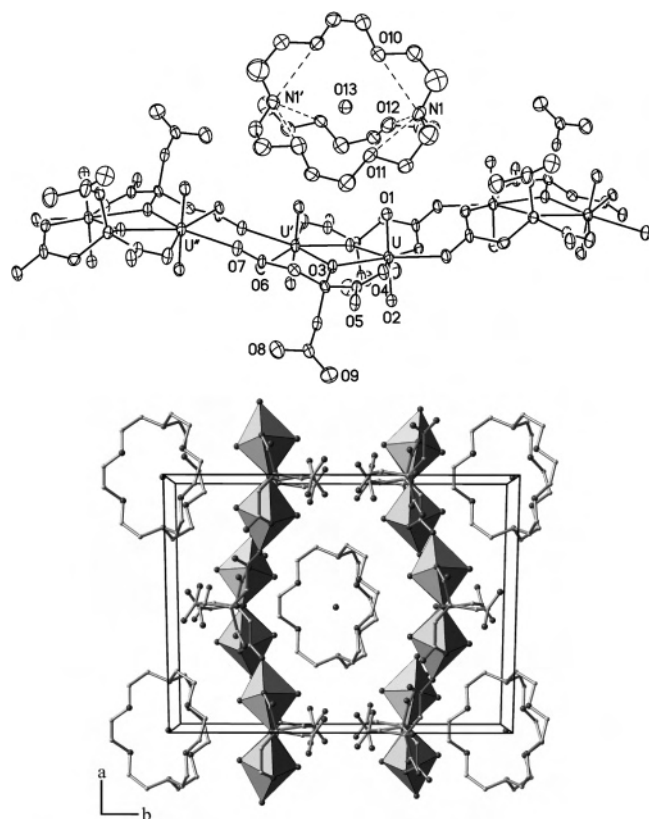
neighboring dimer (**2**, **3**, **5**, and **6**). The first case corresponds to the formation of the isolated dianionic dimers  $[UO_2-$



**Figure 5.** Top: View of the complex  $[H-2,2'-bipy]_2[UO_2(Hcit)]_2 \cdot 5H_2O$  **5**. Carbon-bound hydrogen atoms and solvent molecules have been omitted for clarity. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 10% probability level. Symmetry codes: ' =  $-x, y, 3/2 - z$ ; '' =  $x + 1/2, 1/2 - y, z + 1/2$ . Bottom: View of the assemblage in the  $ab$  plane with the solvent molecules omitted. The uranium coordination polyhedra are represented, and the other atoms are shown as spheres of arbitrary radii.

$(Hcit)(H_2O)]_2^{2-}$  and  $[UO_2(citml)(H_2O)]_2^{2-}$  with a  $\mu_2-1\kappa^2O, O'$ :  $2\kappa^2O, O''$  coordination mode for each polycarboxylate ligand. Such completion of the coordination sphere by a water molecule agrees with the EXAFS findings, in which this oxygen atom was, however, unresolvable from the other equatorial donors.<sup>7a</sup> One-dimensional chains or ribbons are formed in the second case, with the  $\beta$ -carboxylate group bound through its two oxygen atoms in monodentate fashion, thus giving an overall  $\mu_3-1\kappa^2O, O':2\kappa^2O, O'':3\kappa O'''$  coordination mode. The successive dimeric subunits in these chains are related either by translations along one of the cell axes in **2** and **3** or by a glide plane in **5** and **6**. In the first case, the chains are rectilinear, whereas they are undulated in the second (Figures 5 and 6). The factors influencing the

(18) See, for example: (a) Burojevic, S.; Shweky, I.; Bino, A.; Summers, D. A.; Thompson, R. C. *Inorg. Chim. Acta* **1996**, *251*, 75. (b) Shweky, I.; Bino, A.; Goldberg, D. P.; Lippard, S. J. *Inorg. Chem.* **1994**, *33*, 5161. (c) Velayutham, M.; Varghese, B.; Subramanian, S. *Inorg. Chem.* **1998**, *37*, 1336. (d) Tsaramyris, M.; Kaliva, M.; Salifoglou, A.; Raptopoulou, C. P.; Terzis, A.; Tangoulis, V.; Giapintzakis, J. *Inorg. Chem.* **2001**, *40*, 5772. (e) Dakanali, M.; Kefalas, E. T.; Raptopoulou, C. P.; Terzis, A.; Voyiatzis, G.; Kyrikou, I.; Mavromoustakos, T.; Salifoglou, A. *Inorg. Chem.* **2003**, *42*, 4632.



**Figure 6.** Top: View of the complex  $[\text{H}_2\text{-222}(\text{H}_2\text{O})][\text{UO}_2(\text{Hcit})_2]\cdot 3\text{H}_2\text{O}$  **6**. Hydrogen atoms and solvent molecules have been omitted for clarity. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 20% probability level. Symmetry codes: ' =  $-x, y, 1/2 - z$ ; '' =  $x - 1/2, 1/2 - y, z - 1/2$ . Bottom: View of the assemblage in the  $ab$  plane with the solvent molecules omitted. The uranium coordination polyhedra are represented, and the other atoms are shown as spheres of arbitrary radii.

formation of either dimers or chains seem to be impossible to rationalize on the basis of the present experiments since both forms were obtained with each ligand, at identical temperatures (except for compound **3**), and in the cases of the pairs of compounds **1, 2** and **3, 4**, with the same diamines. It may be noted that the arrangement of dimeric units in compounds **1** and **2** is very similar since they are only slightly pushed away from one another along one cell axis in **1**, with respect to their position in **2**, with interdimer  $\text{U}\cdots\text{U}$  separations of 5.9154(4) and 5.1846(7) Å in **1** and **2**, respectively. The difference in arrangement is, however, much more important between **3** and **4**.

### B. Polycarboxylate Conformation and Configuration.

The citrate conformation can be described by the two torsion angles defined by the five-carbon backbone corresponding to the central atom and the two  $\beta$ -carboxylic/ate groups<sup>19</sup> (C1, C3, C4, C5, and C6 in the present structures). The pairs of torsion angles (C4–C3–C1–C5, C6–C5–C1–C3) are 54.5 and 164.2° in **1**, 49.6 and 46.5° in **3**, 57.8 and 34.9° in **5**, and 69.4 and 56.0° in **6**, showing that the citrate is never in extended conformation but always presents some degree of twisting, with four atoms nearly coplanar in compound **1** only. However, the coordinated  $\beta$ -carboxylate group is

always associated with a nearly gauche angle, whereas the other, protonated group has a less constrained geometry. In the centrosymmetric citrate dimers in **1** and **3**, the uncoordinated carboxylic groups are located on each side of the dimer mean plane, and they are involved in hydrogen bonds, both as donors toward carboxylate groups of neighboring molecules and as acceptors from the protonated  $\text{H}_2\text{DABCO}$  or  $\text{H}_2\text{-4,4'-bipy}$  cations (the former being very disordered in **1** and being also involved in hydrogen bonds with coordinated carboxylate groups). In the citrate dimers located on a binary axis (**5** and **6**), both uncoordinated groups are on the same side, and they are involved in hydrogen bonds with the solvent water molecules.

Compound **2** crystallizes in the chiral space group  $P2_1$ , and the absolute configuration determined from the value of the Flack parameter is in agreement with that of the enantiomer used, D-(–)-citramalic acid. As a consequence, the two methyl substituents are located on the same side of the mean plane of the dimer, which admits a pseudosymmetry binary axis (being, thus, close to **5** and **6** in overall geometry). However, compound **4**, obtained from the same ligand under similar conditions (in particular, at the same temperature of 140 °C) with, as the sole difference, a heating time of 48 instead of 24 h, crystallizes in the centrosymmetric space group  $P2_1/c$  with two half dimers in the asymmetric unit. Citramalic acid has, thus, been racemized in this experiment (the possibility that this was also the case in the synthesis of **2**, with subsequent crystallization of the two enantiomers in different crystals, giving a racemic conglomerate by spontaneous resolution,<sup>20</sup> cannot, however, be absolutely excluded). Racemization of amino acids under hydrothermal conditions is known to occur,<sup>21</sup> but enantiomeric ligands such as (1*R*,3*S*)-(+)-camphoric acid<sup>9j</sup> or L-(+)-tartaric acid<sup>9k,22</sup> were not found to racemize at temperatures of 140 or 180 °C, respectively, although the latter was found to undergo oxidative cleavage into oxalic acid upon prolonged heating.<sup>9k</sup> It may be noted that the complexing behavior of citramalic acid is little known since there is only one structure of a citramalate complex reported in the CSD, which is that of the molybdenum carbonyl species  $(\text{NET}_4)_2\text{-}[\text{Mo}(\text{CO})_3(\text{Hcitml})]$  obtained from organic solvents at room temperature and in which the ligand Hcitml, with the hydroxyl group protonated, acts as a tridentate ligand.<sup>23</sup>

**C. Template Effects and Hydrogen-Bonded Assemblies.** The diamines DABCO, 4,4'-bipyridine, and [2.2.2]-cryptand in compounds **1–4** and **6** are doubly protonated, whereas 2,2'-bipyridine in **5** has gained a single proton and adopts the most stable cis, planar geometry.<sup>24</sup> However, only  $\text{H}_2\text{DABCO}$  and  $\text{H}_2\text{-4,4'-bipy}$  display hydrogen atoms suitable to form divergent hydrogen bonds since [2.2.2]cryptand is

(19) Glusker, J. P. *Acc. Chem. Res.* **1980**, *13*, 345.

(20) Flack, H. D.; Bernardinelli, G. *Acta Crystallogr., Sect. A* **1999**, *55*, 908.

(21) (a) Huber, C.; Wächtershäuser, G. *Science* **1998**, *281*, 670. (b) Kawamura, K.; Yukioka, M. *Thermochim. Acta* **2001**, *375*, 9. (c) Nemoto, A.; Horie, M.; Imai, E. I.; Honda, H.; Hatori, K.; Matsuno, K. *Origins Life Evol. Biosphere* **2005**, *35*, 167.

(22) Thushari, S.; Cha, J. A. K.; Sung, H. H. Y.; Chui, S. S. Y.; Leung, A. L. F.; Yen, Y. F.; Williams, I. D. *Chem. Commun.* **2005**, 5515.

(23) Takuma, M.; Ohki, Y.; Tatsumi, K. *Organometallics* **2005**, *24*, 1344.

(24) Howard, S. T. *J. Am. Chem. Soc.* **1996**, *118*, 10269.



protonated in the in–in form, with trifurcated intramolecular N–H···O hydrogen bonds, as inferred from N···O distances, and with an included water molecule likely involved in disordered hydrogen bonding with the ether groups.

As indicated above, the dimeric units are arranged similarly in compounds **1** and **2**, and the H<sub>2</sub>DABCO ions, notwithstanding the disorder present in **1**, are also involved in similar hydrogen-bonding patterns. In complex **1**, the diammonium ions connect adjacent dimers along the diagonal of the *ab* plane through their coordinated  $\beta$ -carboxylate groups, thus giving chains which are further linked through hydrogen bonds between the carboxylic groups (O9) located on either side of the dimers and the atoms O7 of  $\beta$ -carboxylate groups from neighboring units and also between the carboxylic group and the diammonium ions. The water molecules also contribute to the formation of a three-dimensional framework, being hydrogen bonded to one another and to three carboxylate groups. In the citramalate complex **2**, the situation is simpler due to the absence of carboxylic groups and water molecules. The polymeric chains running along the *a* axis are connected by diammonium ions bound to the  $\alpha$ -carboxylate atoms O7 and O12, thus giving a two-dimensional assemblage parallel to the *ac* plane.

In compound **3**, which is also devoid of water molecules, the 4,4'-bipyridinium units also link adjacent polymeric chains, but this time through hydrogen bonds with the citrate uncoordinated  $\beta$ -carboxylic group. The latter is also a hydrogen bond donor toward the  $\alpha$ -carboxylate group of a neighboring unit related to the first by an inversion center, thus expanding the framework in the third dimension. The carboxylic group is absent in the citramalate complex **4**, but the coordinated and solvent water molecules provide additional linkers. The dimers are assembled in chains by 4,4'-bipyridinium units hydrogen bonded to the  $\alpha$ -carboxylate groups. The coordinated water molecules are connected to the  $\beta$ -carboxylate groups of two neighboring molecules through their two hydrogen atoms, whereas the solvent water molecules are bonded to the  $\alpha$ -carboxylate groups and uranyl oxo groups. All of these bonds result in the formation of an intricate three-dimensional network. In both structures, the 4,4'-bipyridinium molecules are planar or nearly planar, with dihedral angles between the two aromatic rings of 0° in **3** and 11(1)° in **4**.

Compounds **5** and **6** comprise similar undulated uranyl citrate chains that define channels parallel to the *c* axis, in which the counterions are located. In compound **5**, the ammonium ions are hydrogen bonded to uranyl oxo groups, whereas they are not involved in intermolecular hydrogen bonds in **6**, so that in neither case do they participate in the linking of different chains. The 2,2'-bipyridinium ions in **5** are nearly planar [dihedral angle between the two aromatic rings 4.7(3)°], and they are stacked along the *c* axis so that parallel-displaced  $\pi$ -stacking interactions may be present [shortest centroid···centroid distance 3.78 Å, dihedral angle 3.1°, centroid offset 1.12 Å]. Solvent water molecules are present in both cases, and although their hydrogen atoms could not be located, numerous hydrogen bonds involving the water molecules, the  $\alpha$ -carboxylate and  $\beta$ -carboxylic

groups, and the uranyl oxo groups can be inferred from the O···O contacts, which result in the formation of three-dimensional networks.

The simplest arrangement in the series is, thus, the two-dimensional one found in compound **2**, in which neither carboxylic groups nor water molecules are present. In this case, the diammonium ions play the role of divergent linkers which was expected. The same is true in compounds **1**, **3**, and **4**, but the presence of carboxylic groups in **1** and **3** and/or water molecules in **1** and **4**, with the various hydrogen-bonding interactions associated, complicates the scheme. In particular, direct links between the carboxylic and carboxylate groups of neighboring complex units are found in **1** and **3**. The assemblages in **5** and **6** depend primarily on the solvent water molecules, with formation of open structures in which the channels are occupied by the counterions.

The obtainment of different uranyl citrate topologies in the absence of amines (three-dimensional framework) or in the presence of amines either able to act as divergent linkers (dimers or linear chains) or not (undulated, channel-defining chains) evidences template or structure-directing effects. The latter have been much investigated in the case of organic-templated uranium-containing inorganic species,<sup>25</sup> but only recently were examples reported in the field of metal–organic frameworks incorporating lanthanide ions,<sup>91,26</sup> whereas, to the best of our knowledge, none has been described up to now among UOFs.

## Conclusion

The present structures provide the first crystallographic evidence of the 2:2 dinuclear model of uranyl citrate proposed much earlier by Rajan and Martell<sup>6b</sup> and later confirmed by EXAFS measurements.<sup>7a,d</sup> However, the structure previously obtained in the absence of amines (i.e., in a hydrothermal medium which is likely closer to those encountered in the natural environment) is different in both stoichiometry and citrate bonding mode, which points to the great versatility of this multidentate and multifunctional ligand. The possibility to obtain different complexes, depending on the presence of additional organic species, is nonetheless important for the assessment of metal mobility in natural repositories. It may be noted that, in all cases, uranium chelation involving all of the hydroxyl or alkoxide groups occurs, which is known to prevent biodegradation of the complexes.<sup>4a</sup> The present results also provide accurate structural data which can be useful for the theoretical modeling of uranyl–carboxylate complexes, such as the DFT

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calculations recently reported,<sup>27</sup> although comparison of solution and solid-state structures may not always be straightforward.

From the viewpoint of UOF synthesis, the uranyl/citrate and uranyl/citramalate systems, in the presence of the diamines investigated herein, consistently give dimers or dimer-based polymers, with additional pendent, uncomplexed carboxylic groups in the case of citrate. Differences in the polymeric chain topologies can be ascribed to template effects. The complex units can be assembled through

divergent hydrogen bond donors to form two- or three-dimensional assemblages, the diammonium ions H<sub>2</sub>DABCO and H<sub>2</sub>-4,4'-bipyridine being particularly well suited as linkers,<sup>28</sup> or they can define channels embedding nonlinking counterions such as H-2,2'-bipyridine and H<sub>2</sub>-222. These results confirm the interest of citric acid and related ligands in UOF synthesis.

**Supporting Information Available:** Tables of crystal data, atomic positions and displacement parameters, anisotropic displacement parameters, and bond lengths and bond angles in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(28) Multiple linker UOFs, including 4,4'-bipyridine and aliphatic dicarboxylates, were recently reported: Borkowski, L. A.; Cahill, C. L. *Cryst. Growth Des.* **2006**, *6*, 2248.