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# Contrasting Structure-Directing Effects in the Uranyl–Phthalate/Isophthalate Isomer Systems

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**ABSTRACT:** Reaction of uranyl cations with phthalic (H<sub>2</sub>pht) or isophthalic (H<sub>2</sub>ipht) acids under solvo-hydrothermal conditions was performed in the presence of 3d-block metal cations associated with chelating nitrogen donors gave nine zero-, mono- or diperiodic complexes. [UO<sub>2</sub>(pht)<sub>2</sub>Zn(phen)<sub>2</sub>]<sub>2</sub>·4H<sub>2</sub>O (**1**), where phen is 1,10-phenanthroline, is a heterometallic, tetranuclear complex, while counterion separation in [Ni(bipy)<sub>3</sub>][UO<sub>2</sub>(pht)(NO<sub>3</sub>)<sub>2</sub>] (**2**), where bipy is 2,2'-bipyridine, yields a monopерiodic, helical uranyl ion complex crystallized in pure enantiomeric form. The dipерiodic network in [Ni(phen)<sub>3</sub>][(UO<sub>2</sub>)<sub>3</sub>(O)(pht)<sub>3</sub>]·6H<sub>2</sub>O (**3**) displays pseudo-trigonal, cup-like cavities containing part of the bulky counterions. [(UO<sub>2</sub>)<sub>2</sub>(O)(pht)<sub>2</sub>Ni(cyclam)(H<sub>2</sub>O)]<sub>2</sub>·H<sub>2</sub>O (**4**), where cyclam is 1,4,8,11-tetraazacyclotetradecane, is a discrete, bis(μ<sub>3</sub>-oxo)-bridged tetranuclear uranyl complex of common geometry, to which two Ni(cyclam)<sup>2+</sup> moieties are attached through oxo bonding to uranyl. Separation of the 3d-block metal ion complex in [Ni(cyclam)]<sub>2</sub>[(UO<sub>2</sub>)<sub>7</sub>(pht)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>] (**5**) and [Cu(*R,S*-Me<sub>6</sub>cyclam)][(UO<sub>2</sub>)<sub>5</sub>(O)<sub>2</sub>(pht)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]·4H<sub>2</sub>O (**6**), where *R,S*-Me<sub>6</sub>cyclam is 7(*R*),14(*S*)-5,5,7,12,12,14-hexamethylcyclam, results in the formation of quasi-planar dipерiodic networks hydrogen bonded to the counterions. The three isophthalate complexes [(UO<sub>2</sub>)<sub>2</sub>(ipht)<sub>3</sub>Cu(bipy)<sub>2</sub>]·H<sub>2</sub>O (**7**), [(UO<sub>2</sub>)<sub>2</sub>(ipht)<sub>2</sub>(HCOO)<sub>2</sub>Ni(cyclam)] (**8**) and [(UO<sub>2</sub>)<sub>2</sub>(ipht)<sub>2</sub>(HCOO)<sub>2</sub>Cu(*R,S*-Me<sub>6</sub>cyclam)] (**9**) crystallize as heterometallic dipерiodic species with Cu(bipy)<sub>2</sub><sup>2+</sup> being decorating only in **7**, while Ni<sup>2+</sup> and Cu<sup>2+</sup> in **8** and **9** bridge uranyl-containing chains into a network with V<sub>2</sub>O<sub>5</sub> topology.

## INTRODUCTION

The study of metal ion complexes involving different isomeric forms, either positional or conformational, of multidentate ligands provides a unique opportunity to investigate the effect of small or moderate geometric variations on the structure of the species formed. This approach has proved quite rewarding in the particular domain of uranyl-containing coordination polymers or frameworks,<sup>1-5</sup> in which several groups of isomeric polycarboxylate ligands have been extensively used. Ligands derived from the cyclohexane skeleton, such as cyclohexanedicarboxylates, are particularly noteworthy in this respect since they enable exploitation of both constitutional (positional) isomerism (1,2, 1,3 or 1,4 positions of the carboxylate groups on the ring, each isomer being *cis* or *trans* and some of them being chiral) and conformational isomerism (axial or equatorial carboxylate groups and chair or boat forms of the ring), which have been exploited to generate a series of very diverse uranyl ion complexes.<sup>6</sup> Several families of heterofunctional ligands displaying positional isomerism only (ignoring rotamers about the C-CO<sub>2</sub><sup>-</sup> bond) and a mixture of hard and soft coordination sites such as pyridinedicarboxylates,<sup>7-9</sup> 2,2'-bipyridinedicarboxylates,<sup>10-12</sup> or methyl-substituted pyrazoledicarboxylates<sup>13</sup> are well known. The most obvious source of positional isomers of simple polycarboxylates however is the large family based on the benzene ring, such as benzenetricarboxylates,<sup>14-20</sup> phenylenediacetates,<sup>21,22</sup> and of course the simplest group of all, 1,2-, 1,3- and 1,4-benzenedicarboxylates (phthalate, isophthalate and terephthalate, respectively). Phthalate has been shown to be involved in the construction of several uranyl-containing coordination polymers,<sup>23-31</sup> among which a remarkable nanotubular assembly<sup>23</sup> which exists also with neptunyl.<sup>32</sup> Overall, phthalate often acts as a convergent ligand and chelates the uranyl ion with formation of a 7-membered ring. Isophthalate is also found in several uranyl-based species which show a departure from the convergent character of

phthalate,<sup>25,27,33–41</sup> a tendency even more marked with terephthalate which often gives honeycomb networks with large hexagonal rings<sup>42–44</sup> and triperiodic frameworks,<sup>45,46</sup> sometimes displaying entanglement.<sup>47,48</sup> We have recently explored the effect of bulky counterions and structure-directing agents on the periodicity and structure of anionic uranyl ion complexes with polycarboxylates,<sup>6,9,20–22,49–51</sup> a study which we have now extended to phthalic and isophthalic acids (denoted H<sub>2</sub>pht and H<sub>2</sub>ipht, respectively). Nine zero-, mono- and diperic complexes, all with additional 3d-block metal cations associated either with the *N,N'*-chelating species 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen), or with the azamacrocycles cyclam (1,4,8,11-tetraazacyclotetradecane) or *R,S*-Me<sub>6</sub>cyclam (meso isomer, 7(*R*),14(*S*)-5,5,7,12,12,14-hexamethylcyclam), have been synthesized and characterized by their crystal structures.

## EXPERIMENTAL SECTION

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

[UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 4H<sub>2</sub>O (RP Normapur, 99%) was purchased from Prolabo. Phthalic and isophthalic acids were from Aldrich. [Ni(cyclam)(NO<sub>3</sub>)<sub>2</sub>] and [Cu(*R,S*-Me<sub>6</sub>cyclam)(NO<sub>3</sub>)<sub>2</sub>] were synthesized as previously described.<sup>52,53</sup> Elemental analyses were performed by MEDAC Ltd. For all syntheses, the mixtures of demineralized water and organic cosolvent were placed in 10 mL tightly closed glass vessels and heated at 140 °C in a sand bath, under autogenous pressure.

[UO<sub>2</sub>(pht)<sub>2</sub>Zn(phen)<sub>2</sub>] $\cdot$ 4H<sub>2</sub>O (**1**). H<sub>2</sub>pht (17 mg, 0.10 mmol), [UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 4H<sub>2</sub>O (35 mg, 0.07 mmol), Zn(NO<sub>3</sub>)<sub>2</sub> $\cdot$ 6H<sub>2</sub>O (30 mg, 0.10 mmol), and 1,10-phenanthroline (36 mg,

0.20 mmol) were dissolved in a mixture of water (0.9 mL) and *N,N*-dimethylformamide (DMF) (0.2 mL). Yellow crystals of complex **1** were obtained within two days (34 mg, 64% yield based on the acid). Anal. Calcd for C<sub>80</sub>H<sub>56</sub>N<sub>8</sub>O<sub>24</sub>U<sub>2</sub>Zn<sub>2</sub>: C, 45.32; H, 2.66; N, 5.29. Found: C, 45.01; H, 2.56; N, 5.12%.

*[Ni(bipy)<sub>3</sub>][UO<sub>2</sub>(pht)(NO<sub>3</sub>)<sub>2</sub>]* (**2**). H<sub>2</sub>pht (17 mg, 0.10 mmol), [UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 4H<sub>2</sub>O (35 mg, 0.07 mmol), Ni(NO<sub>3</sub>)<sub>2</sub> $\cdot$ 6H<sub>2</sub>O (15 mg, 0.05 mmol), and 2,2'-bipyridine (24 mg, 0.15 mmol) were dissolved in a mixture of water (0.7 mL) and acetonitrile (0.2 mL). Orange crystals of complex **2** were obtained within one week (24 mg, 45% yield based on U). Anal. Calcd for C<sub>46</sub>H<sub>32</sub>N<sub>8</sub>NiO<sub>18</sub>U<sub>2</sub>: C, 36.36; H, 2.12; N, 7.37. Found: C, 36.34; H, 2.12; N, 7.01%.

*[Ni(phen)<sub>3</sub>][UO<sub>2</sub>(O)(pht)<sub>3</sub>]* $\cdot$ 6H<sub>2</sub>O (**3**). H<sub>2</sub>pht (17 mg, 0.10 mmol), [UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 4H<sub>2</sub>O (35 mg, 0.07 mmol), Ni(NO<sub>3</sub>)<sub>2</sub> $\cdot$ 6H<sub>2</sub>O (15 mg, 0.05 mmol), and 1,10-phenanthroline (27 mg, 0.15 mmol) were dissolved in a mixture of water (0.7 mL) and DMF (0.2 mL). Orange crystals of complex **3** were obtained within one week (18 mg, 38% yield based on U). Anal. Calcd for C<sub>60</sub>H<sub>48</sub>N<sub>6</sub>NiO<sub>25</sub>U<sub>3</sub>: C, 35.57; H, 2.39; N, 4.15. Found: C, 35.62; H, 2.26; N, 4.25%.

*[UO<sub>2</sub>(O)(pht)<sub>2</sub>Ni(cyclam)(H<sub>2</sub>O)]<sub>2</sub>* $\cdot$ H<sub>2</sub>O (**4**). H<sub>2</sub>pht (17 mg, 0.10 mmol), [UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 4H<sub>2</sub>O (35 mg, 0.07 mmol), and [Ni(cyclam)(NO<sub>3</sub>)<sub>2</sub>] (20 mg, 0.05 mmol) were dissolved in a mixture of water (0.7 mL) and DMF (0.2 mL). Orange crystals of complex **4** were obtained overnight (17 mg, 42% yield based on U). Anal. Calcd for C<sub>52</sub>H<sub>70</sub>N<sub>8</sub>Ni<sub>2</sub>O<sub>29</sub>U<sub>4</sub>: C, 26.68; H, 3.01; N, 4.79. Found: C, 27.14; H, 2.93; N, 4.64%.

*[Ni(cyclam)]<sub>2</sub>[UO<sub>2</sub>]<sub>7</sub>(pht)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>* (**5**). H<sub>2</sub>pht (17 mg, 0.10 mmol), [UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 4H<sub>2</sub>O (35 mg, 0.07 mmol), and [Ni(cyclam)(NO<sub>3</sub>)<sub>2</sub>] (20 mg, 0.05 mmol) were dissolved in a mixture of water (0.7 mL) and acetonitrile (0.2 mL). Orange crystals of complex **5** were obtained overnight (7 mg, 18% yield based on U). Anal. Calcd for C<sub>84</sub>H<sub>80</sub>N<sub>10</sub>Ni<sub>2</sub>O<sub>52</sub>U<sub>7</sub>: C, 26.24; H, 2.10; N, 3.64. Found: C, 26.43; H, 2.14; N, 3.43%.

$[\text{Cu}(\text{R},\text{S}\text{-Me}_6\text{cyclam})][(\text{UO}_2)_5(\text{O})_2(\text{pht})_4(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$  (**6**).  $\text{H}_2\text{pht}$  (17 mg, 0.10 mmol),  $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$  (35 mg, 0.07 mmol), and  $[\text{Cu}(\text{R},\text{S}\text{-Me}_6\text{cyclam})(\text{NO}_3)_2]$  (24 mg, 0.05 mmol) were dissolved in a mixture of water (0.7 mL) and acetonitrile (0.2 mL). A few orange crystals of complex **6** were obtained overnight.

$[(\text{UO}_2)_2(\text{ipht})_3\text{Cu}(\text{bipy})_2] \cdot \text{H}_2\text{O}$  (**7**).  $\text{H}_2\text{ipht}$  (17 mg, 0.10 mmol),  $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$  (35 mg, 0.07 mmol),  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (23 mg, 0.10 mmol), and 2,2'-bipyridine (32 mg, 0.20 mmol) were dissolved in a mixture of water (0.7 mL) and tetrahydrofuran (THF) (0.2 mL). Green crystals of complex **7** were obtained within one week, mixed with similarly colored, but larger crystals of the previously described complex  $[\text{UO}_2\text{Cu}(\text{C}_2\text{O}_4)_2(\text{bipy})]$ .<sup>54</sup>

$[(\text{UO}_2)_2(\text{ipht})_2(\text{HCOO})_2\text{Ni}(\text{cyclam})]$  (**8**).  $\text{H}_2\text{ipht}$  (17 mg, 0.10 mmol),  $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$  (35 mg, 0.07 mmol), and  $[\text{Ni}(\text{cyclam})(\text{NO}_3)_2]$  (20 mg, 0.05 mmol) were dissolved in a mixture of water (0.7 mL) and DMF (0.2 mL). A few yellow crystals of complex **8** were obtained within one week.

$[(\text{UO}_2)_2(\text{ipht})_2(\text{HCOO})_2\text{Cu}(\text{R},\text{S}\text{-Me}_6\text{cyclam})]$  (**9**).  $\text{H}_2\text{ipht}$  (17 mg, 0.10 mmol),  $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$  (35 mg, 0.07 mmol), and  $[\text{Cu}(\text{R},\text{S}\text{-Me}_6\text{cyclam})(\text{NO}_3)_2]$  (24 mg, 0.05 mmol) were dissolved in a mixture of water (0.7 mL) and DMF (0.2 mL). Purple crystals of complex **9** were obtained within one week (29 mg, 63% yield based on U). Anal. Calcd for  $\text{C}_{34}\text{H}_{46}\text{CuN}_4\text{O}_{16}\text{U}_2$ : C, 31.26; H, 3.55; N, 4.29. Found: C, 31.09; H, 3.44; N, 3.98%.

**Crystallography.** The data were collected at the temperature of 100(2) K using a Bruker D8 Quest diffractometer (Incoatec Microfocus Source ( $\text{I}\mu\text{S}$  3.0 Mo); PHOTON III area detector) operated through APEX3.<sup>55</sup> The data were processed with SAINT,<sup>56</sup> and absorption effects were corrected empirically with SADABS.<sup>57,58</sup> All structures were solved by intrinsic phasing with SHELXT,<sup>59</sup> expanded by subsequent difference Fourier synthesis and refined by full-matrix least-squares on  $F^2$  with SHELXL,<sup>60</sup> using the ShelXle interface.<sup>61</sup> Carbon-bound

hydrogen atoms were introduced at calculated positions and treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH<sub>3</sub>). The hydrogen atoms bound to nitrogen atoms in complexes **4**, **6**, **8** and **9** were found on difference electron density maps and those in **5** were introduced at calculated positions; their isotropic displacement parameter was either refined or fixed to 1.2 times that of the corresponding nitrogen atom and restraints on bond lengths were applied. The hydrogen atoms of the water molecules (some of them with partial occupancy) were not found in **1** and partially or completely found in **3**, **4**, **6** and **7**, and they were refined with restraints. The Flack parameter in complex **2** was 0.012(5). Crystal data and structure refinement parameters are given in Table 1. Drawings were made with ORTEP-3<sup>62</sup> or VESTA,<sup>63</sup> and topological analyses with ToposPro.<sup>64</sup>

## RESULTS AND DISCUSSION

**Synthesis.** Crystals of all complexes **1–9** were grown at 140 °C (solvo-hydrothermal conditions), and not during cooling. The different combinations of 3d metal cation-containing species and organic solvents were systematically tested, the compounds reported being the outcome of the only experiments giving crystalline materials. The organic cosolvent was either DMF (complexes **1**, **3**, **4**, **8** and **9**), acetonitrile (**2**, **5** and **6**), or THF (**7**), but it only affected directly the nature of the complex formed in the cases of **8** and **9** which incorporate formate anions generated from DMF hydrolysis, as often observed.<sup>65,66</sup> Complex **7** was obtained together with the previously reported [UO<sub>2</sub>Cu(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(bipy)]<sup>54</sup> (see Experimental Section); oxalate formation under such conditions is a frequently observed,<sup>67,68</sup> but only in some cases has the mechanism been elucidated.<sup>69,70</sup> Oxo-bridged uranyl oligomers are found in the three complexes **3**, **4** and **6**, as very frequently observed in uranyl chemistry,<sup>3</sup> the formation of oxo

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

	1	2	3	4	5
chemical formula	C <sub>80</sub> H <sub>56</sub> N <sub>8</sub> O <sub>24</sub> U <sub>2</sub> Zn <sub>2</sub>	C <sub>46</sub> H <sub>32</sub> N <sub>8</sub> NiO <sub>18</sub> U <sub>2</sub>	C <sub>60</sub> H <sub>48</sub> N <sub>6</sub> NiO <sub>25</sub> U <sub>3</sub>	C <sub>52</sub> H <sub>70</sub> N <sub>8</sub> Ni <sub>2</sub> O <sub>29</sub> U <sub>4</sub>	C <sub>84</sub> H <sub>80</sub> N <sub>10</sub> Ni <sub>2</sub> O <sub>52</sub> U <sub>7</sub>
<i>M</i> (g mol <sup>-1</sup> )	2120.12	1519.56	2025.84	2340.70	3845.21
cryst syst	monoclinic	tetragonal	triclinic	triclinic	triclinic
space group	<i>C</i> 2/ <i>c</i>	<i>P</i> 4 <sub>1</sub> 2 <sub>1</sub> 2	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	23.1532(7)	9.5470(2)	13.4424(5)	9.0930(3)	9.7965(3)
<i>b</i> (Å)	11.5507(4)	9.5470(2)	16.6043(5)	11.7062(5)	12.9433(4)
<i>c</i> (Å)	29.7563(10)	51.5757(17)	16.6449(6)	16.1843(6)	21.0165(6)
$\alpha$ (deg)	90	90	118.7976(13)	75.3754(18)	91.9867(13)
$\beta$ (deg)	111.8213(13)	90	90.3785(17)	85.4880(17)	95.7230(13)
$\gamma$ (deg)	90	90	91.7473(16)	71.4634(17)	110.3668(14)
<i>V</i> (Å <sup>3</sup> )	7387.7(4)	4700.9(3)	3253.2(2)	1580.43(11)	2478.94(13)
<i>Z</i>	4	4	2	1	1
reflns colled	308848	114067	257309	124206	197696
indep reflns	6999	6050	12366	6003	9393
obsd reflns [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	6695	5935	11511	5699	8936
<i>R</i> <sub>int</sub>	0.037	0.053	0.066	0.055	0.041
params refined	542	340	874	451	700
<i>R</i> <sub>1</sub>	0.017	0.017	0.022	0.024	0.029
<i>wR</i> <sub>2</sub>	0.043	0.040	0.055	0.056	0.074
<i>S</i>	1.053	1.216	1.078	1.203	1.040
$\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	-0.42	-0.83	-1.13	-1.24	-4.58
$\Delta\rho_{\max}$ (e Å <sup>-3</sup> )	1.58	0.65	1.83	3.28	3.25

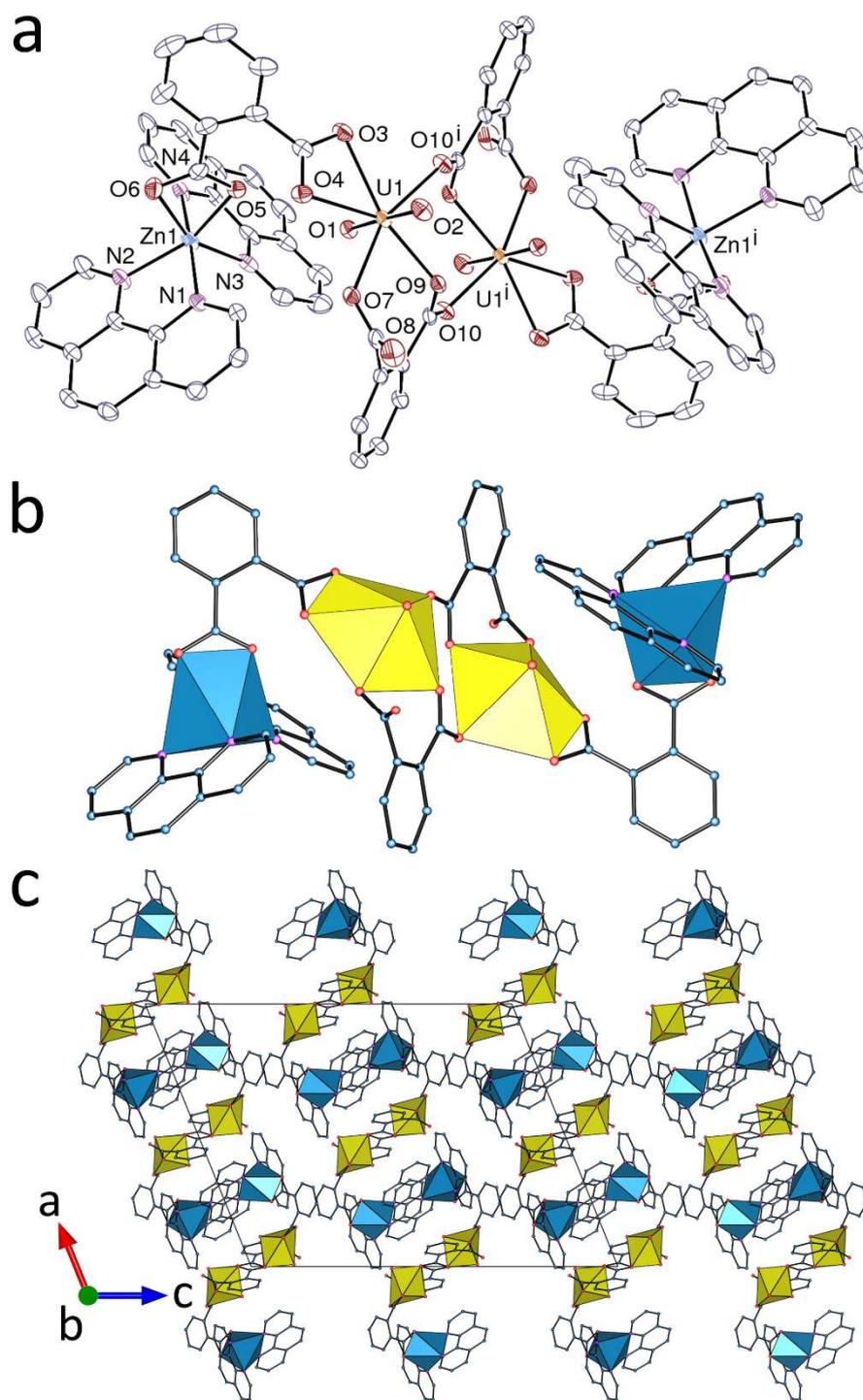
  

	6	7	8	9
chemical formula	C <sub>48</sub> H <sub>64</sub> CuN <sub>4</sub> O <sub>34</sub> U <sub>5</sub>	C <sub>44</sub> H <sub>30</sub> CuN <sub>4</sub> O <sub>17</sub> U <sub>2</sub>	C <sub>28</sub> H <sub>34</sub> N <sub>4</sub> NiO <sub>16</sub> U <sub>2</sub>	C <sub>34</sub> H <sub>46</sub> CuN <sub>4</sub> O <sub>16</sub> U <sub>2</sub>
<i>M</i> (g mol <sup>-1</sup> )	2494.72	1426.32	1217.36	1306.35
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.5132(16)	11.0914(4)	9.0866(4)	10.0151(4)
<i>b</i> (Å)	11.9772(17)	15.9423(6)	9.1159(4)	10.9165(5)
<i>c</i> (Å)	14.4864(18)	24.7133(9)	11.4867(5)	11.0561(5)
$\alpha$ (deg)	90.875(7)	90	68.2652(19)	113.7246(16)
$\beta$ (deg)	109.273(6)	98.5949(14)	82.814(2)	103.0722(17)
$\gamma$ (deg)	112.998(5)	90	74.032(2)	104.3674(17)
<i>V</i> (Å <sup>3</sup> )	1563.0(4)	4320.8(3)	849.44(7)	996.94(8)
<i>Z</i>	1	4	1	1
reflns colled	114293	205550	61127	65545
indep reflns	5912	13193	3205	3795
obsd reflns [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	5487	12195	3174	3587
<i>R</i> <sub>int</sub>	0.056	0.043	0.036	0.049
params refined	443	619	239	270
<i>R</i> <sub>1</sub>	0.017	0.019	0.024	0.016
<i>wR</i> <sub>2</sub>	0.040	0.039	0.069	0.035
<i>S</i>	1.053	1.078	1.307	1.160
$\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	-1.42	-0.86	-2.20	-1.00
$\Delta\rho_{\max}$ (e Å <sup>-3</sup> )	1.61	0.80	2.56	0.74

anions being possibly due to the presence of nitrogen bases (phen in **3**, and tetramine macrocycles after partial dissociation from the metal cations in **4** and **6**), although the ratio base:M<sup>II</sup> in the reaction mixtures is retained in all the products, indicating that little of the base must be consumed by protonation and that hydrolysis of the organic cosolvents (DMF and CH<sub>3</sub>CN) may also play a role in determining the solution acidity/basicity. Implicit in the rather

frequent isolation of “unanticipated” products from solvothermal syntheses is that the full chemistry involved is not simply that of metal ion to ligand coordination. The ratio of uranium to dicarboxylic acid was 7:10 for all syntheses, in order to promote anionic species formation, but the expected ratio of 2:3 is only found in complex **7**, the stoichiometry being 1:1 or close to it (7:8 or 5:4) in most cases (**2–6**, **8** and **9**), and 1:2 in **1**, as a result of the presence in all cases of additional cations and/or anions, some of the latter being unexpected.

**Crystal Structures.** On the basis of known structures (see Introduction), phthalate can be considered distinct from its isomers in its tendency to form oligomeric clusters as well as polymers. In general with uranyl ion complexes of polycarboxylates, as we have discussed recently,<sup>71</sup> fragmentation of polymer structures can be achieved by both competitive metal ion coordination and strong hydrogen bonding, both separately and together, and a recent study<sup>31</sup> of uranyl phthalates has demonstrated the importance of hydrogen bonding effects. Here, in complex **1**,  $[\text{UO}_2(\text{pht})_2\text{Zn}(\text{phen})_2]_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Zn}^{\text{II}}$  competition for carboxylate coordination produces the smallest known uranyl phthalate oligomer. The complex is a centrosymmetric, heterometallic tetranuclear species (Figure 1). The uranyl cation is chelated by two  $\text{pht}^{2-}$  ligands, one through a single carboxylate group ( $\kappa^2\text{O},\text{O}'$  mode) and the other through two carboxylate groups forming a 7-membered chelate ring, plus an additional oxygen donor from

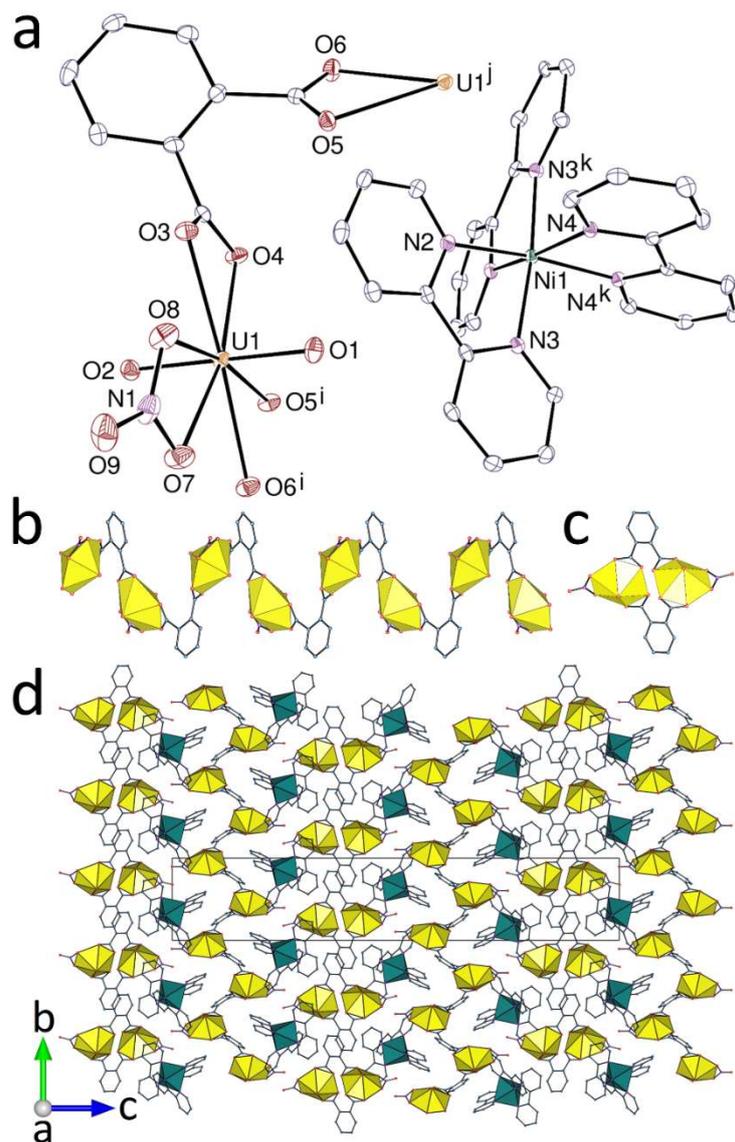


**Figure 1.** (a) View of compound **1** with 50% probability displacement ellipsoids. Symmetry code:  $i = -x, 1 - y, 1 - z$ . (b) View of the tetranuclear assembly with uranium coordination polyhedra yellow and those of zinc blue. (c) View of the packing. The solvent molecules and hydrogen atoms are omitted in all views.

a third ligand, the uranium atom environment being pentagonal bipyramidal [U–O(oxo), 1.7757(17) and 1.7761(18) Å; U–O(carboxylato), 2.4882(18) and 2.4298(18) Å for the

chelating group O3/O4, and 2.3169(17)–2.3775(17) Å for the others]. The chelating and bridging ligand (O7–O10) ensures dimerization through one carboxylate group connecting two uranyl cations in *syn/anti*  $\mu_2$ - $\kappa^1 O:\kappa^1 O'$  mode. The other ligand connects uranyl and Zn<sup>II</sup> cations through double  $\kappa^2 O,O'$ -chelation. The terminal zinc atom is additionally chelated by two phen molecules, its environment being a very distorted octahedron [Zn–O, 2.1256(17) and 2.250(2) Å; Zn–N, 2.109(2)–2.153(2) Å]. The centrosymmetric nature of the molecule means that the Zn<sup>II</sup> centres must be of opposite chirality. Overall, the tetranuclear complex has an S shape, with all aromatic rings directed outward. Analysis of short contacts with PLATON<sup>72</sup> indicates that phen and pht<sup>2-</sup> ligands may form intermolecular parallel-displaced  $\pi$ -stacking interactions [centroid...centroid distances, 3.5207(19)–4.6789(17) Å; dihedral angles, 0–19.73(12)°]. Analysis of the Hirshfeld surface (HSs)<sup>73</sup> with CrystalExplorer (ver. 3.1)<sup>74</sup> indicates that these interactions are complemented by CH... $\pi$  contacts and CH...O hydrogen bonds.<sup>75,76</sup>

Replacement of Zn<sup>II</sup> by Ni<sup>II</sup> and of phen by bipy, now in a threefold molar ratio to the metal ion, allows isolation of the complex [Ni(bipy)<sub>3</sub>][UO<sub>2</sub>(pht)(NO<sub>3</sub>)<sub>2</sub>] (**2**), shown in Figure 2. The uranyl cation is  $\kappa^2 O,O'$ -chelated by two carboxylate groups and one nitrate anion, the uranium atom coordination environment being thus hexagonal bipyramidal [U–O(oxo), 1.765(3) and 1.775(3) Å; U–O(carboxylato), 2.436(3)–2.486(3) Å; U–O(nitrato), 2.506(3) and 2.520(3) Å]. The Ni<sup>II</sup> cation, located on a twofold rotation axis, is tris-chelated by the bipy molecules, giving the usual octahedral environment [Ni–N, 2.086(3)–2.096(3) Å]. The coordination polymer formed is monophasic and running along the [100] or [010] axes of the tetragonal cell, and it has a helical shape with a pitch length equal to the *a* parameter. The value

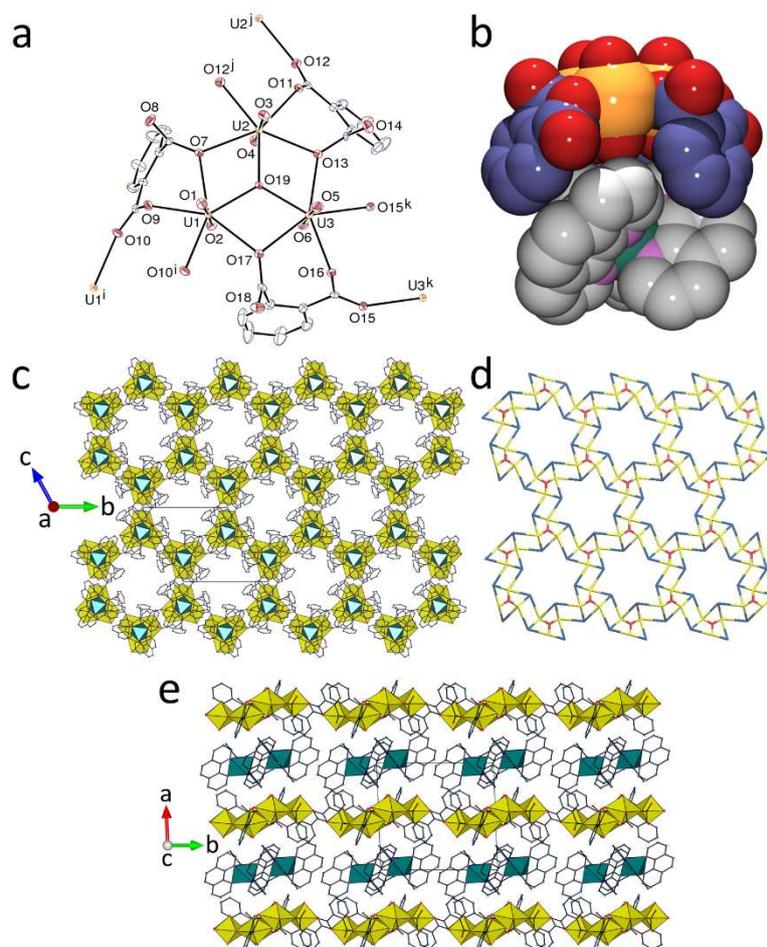


**Figure 2.** (a) View of compound **2** with 50% probability displacement ellipsoids. Symmetry codes:  $i = x - 1/2, 1/2 - y, 3/4 - z$ ;  $j = x + 1/2, 1/2 - y, 3/4 - z$ ;  $k = y, x, 1 - z$ . (b) View of the helical assembly. (c) The same viewed down the helical axis. (d) Packing with uranium coordination polyhedra yellow and those of nickel green. Hydrogen atoms are omitted in all views.

of the Flack parameter [0.012(5)] indicates that the structure, unlike that of complex **1**, corresponds to a pure enantiomer (with left-handed helices and  $\Lambda$ -[Ni(bipy)<sub>3</sub>]<sup>2+</sup> cations in the particular crystal investigated). The polymer chains are arranged in sheets parallel to (001), with the chains directed alternately along the [100] or [010] axes in successive sheets, and the counterions are located in between. Only one parallel-displaced  $\pi$ -stacking interaction may be

present, between the  $\text{pht}^{2-}$  ligand and the bipy ring containing N3 [centroid...centroid distance, 3.920(2) Å; dihedral angle, 21.48(19)°]. Several  $\text{CH}\cdots\pi$  interactions [ $\text{H}\cdots$ centroid distances, 2.71–3.00 Å;  $\text{C}-\text{H}\cdots$ centroid angles, 142–167°] and  $\text{CH}\cdots\text{O}$  hydrogen bonds [ $\text{C}\cdots\text{O}$  distances, 3.106(5)–3.360(5) Å;  $\text{C}-\text{H}\cdots\text{O}$  angles, 121–174°] are visible as well, resulting in a compact packing, the Kitaigorodski packing index (KPI, calculated with PLATON<sup>72</sup>) being 0.71.

Replacement on  $\text{Ni}^{\text{II}}$  of bipy by phen and, perhaps more importantly due to its effect on the acidity of the solution, of acetonitrile by DMF results in formation of the complex  $[\text{Ni}(\text{phen})_3][(\text{UO}_2)_3(\text{O})(\text{pht})_3]\cdot 6\text{H}_2\text{O}$  (**3**). The three crystallographically independent uranyl cations are assembled into a trinuclear secondary building unit (SBU) through a  $\mu_3$ -bridging oxo atom (O19), each of them being also chelated by the two carboxylate groups in one ligand (7-membered ring), and also bound to two carboxylate oxygen donors from two different ligands [ $\text{U}-\text{O}(\text{oxo})$ , 1.771(3)–1.790(3) Å;  $\text{U}-\text{O}(\mu_3\text{-oxo})$ , 2.221(3)–2.236(3) Å;  $\text{U}-\text{O}(\text{carboxylato})$ , 2.360(3)–2.477(3) Å] (Figure 3). The bond lengths with the  $\mu_3$ -oxo anion are well within the range found for such trinuclear arrangements reported in the Cambridge Structural Database (CSD, Version 5.41),<sup>77,78</sup> with an average value of 2.26(6) Å, and the environment around O19 is close to planar as expected, with  $\text{U}-\text{O}-\text{U}$  angles of 119.10(11)–120.28(11)° (sum of the three angles, 358.9°). The  $\text{Ni}^{\text{II}}$  environment is octahedral as usual [ $\text{Ni}-\text{N}$ , 2.072(4)–2.107(3) Å]. The three  $\text{pht}^{2-}$  ligands are similarly connected to three uranium atoms each, with one carboxylate group being *syn/anti*  $\mu_2\text{-}\kappa^1\text{O}:\kappa^1\text{O}'$ -bridging and the other  $\mu_2\text{-}\kappa^1\text{O}:\kappa^1\text{O}$ -bridging, with one oxygen left uncoordinated. The three aromatic rings being located on the same side of the plane defined by the three uranium atoms, this oligomeric SBU is distinctly cup-shaped and the  $[\text{Ni}(\text{phen})_3]^{2+}$  cation is nestled in it (Figure 3b). There is however no parallel-displaced  $\pi$ -stacking interaction present between the  $\text{pht}^{2-}$  ligands and phen units, the only possible such interactions being between phen molecules of neighbouring cations

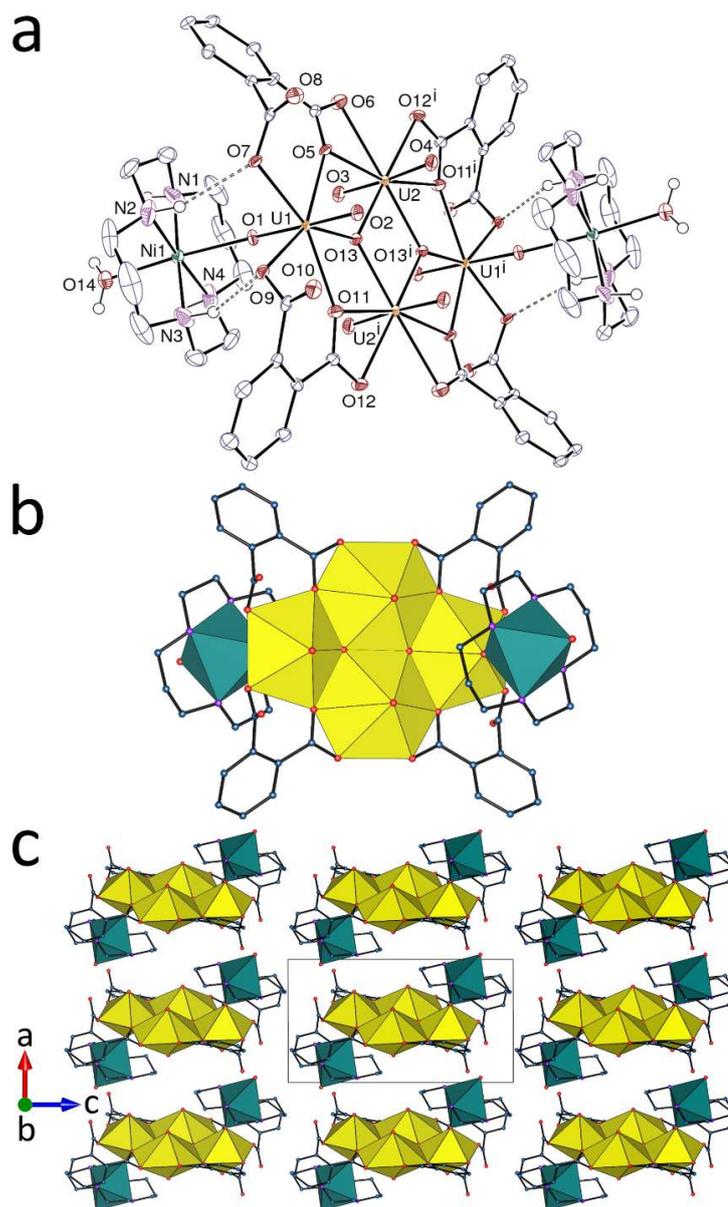


**Figure 3.** (a) View of compound **3** with 50% probability displacement ellipsoids. Counterions, solvent molecules and hydrogen atoms are omitted. Symmetry codes:  $i = 1 - x, 2 - y, 1 - z$ ;  $j = 1 - x, 2 - y, 2 - z$ ;  $k = 1 - x, 1 - y, 1 - z$ . (b) Space-filling view of the cation nestling within the trinuclear cup-like subunit (uranium, yellow; nickel, green; oxygen, red; nitrogen, purple; carbon, blue for the carboxylate ligand, light grey for phen). (c) View of the diperic assembly with uranium coordination polyhedra colored yellow and those of nickel green. (d) Nodal representation of the diperic assembly (uranium, yellow; oxygen, red; carboxylate ligand, blue). (e) Packing with layers viewed edge-on.

[centroid...centroid distances, 3.698(3)–4.044(3) Å; dihedral angles, 0–2.7(2)°]. The only contacts stronger than dispersion here are between each of the three uranyl oxo groups directed inward and two carbon atoms of each phen molecule, with C...O contacts in the range of 2.889(5)–3.382(5) Å. The part of the cation not included in the cup faces three uranyl oxo groups directed outward from another SBU, and forms three CH...O hydrogen bonds with them

[C...O distances, 3.194(6)–3.278(5) Å; C–H...O angles, 140–153°]. Each trinuclear subunit is doubly bridged to three others, resulting in the formation of a diperiodic network parallel to (100). If the trinuclear SBUs are considered as nodes, their arrangement appears to be of the honeycomb type, albeit with double links between the nodes (Figure 3d). Overall, the cations are arranged into layers located in between the diperiodic nets. Each pseudo-threefold-symmetric, planar U<sub>3</sub>O unit confronts above and below the trigonal faces of [Ni(phen)<sub>3</sub>]<sup>2+</sup> cations of the same chirality, such that homochiral columns of ...O(oxo)...[Ni(phen)<sub>3</sub>]<sup>2+</sup>...O(oxo)...[Ni(phen)<sub>3</sub>]<sup>2+</sup>... run parallel to [100], with the opposed trigonal faces of any one cation being involved in either three C...O or three CH...O interactions with the layers. The cations, however lie in hexagonal sheets in which the chirality alternates around the hexagons, so that the overall structure is not chiral. The packing displays pseudo-hexagonal channels directed along [100], which have a width of ~7 Å and contain the partially disordered water molecules (KPI, 0.67).

The complex formed in the presence of [Ni(cyclam)]<sup>2+</sup> cations, [(UO<sub>2</sub>)<sub>2</sub>(O)(pht)<sub>2</sub>Ni(cyclam)(H<sub>2</sub>O)]<sub>2</sub>·H<sub>2</sub>O (**4**), is a discrete, hexanuclear species containing a bis(μ<sub>3</sub>-oxo)-bridged tetra-uranyl core which has previously been found with pht<sup>2-</sup> ligands,<sup>23,24,31,79</sup> and is quite a common motif in uranyl chemistry (Figure 4). The two crystallographically independent uranyl cations are in different environments, one (U1) being bound to one μ<sub>3</sub>-oxo anion and twice chelated by the two carboxylate groups of each of two pht<sup>2-</sup> ligands (7-membered chelate rings), and the other (U2) being bound to two inversion-related μ<sub>3</sub>-oxo anions and κ<sup>2</sup>O,O'-chelated (4-membered ring) by two pht<sup>2-</sup> ligands, the uranium atom environment being pentagonal- and hexagonal-bipyramidal, respectively [U–O(oxo), 1.774(4)–1.814(4) Å; U–O(μ<sub>3</sub>-oxo), 2.151(4)–2.305(4) Å; U–O(carboxylato), 2.578(4)–2.620(4) Å for κ<sup>2</sup>O,O'-chelating groups, and 2.342(4)–2.439(4) Å for the others]. The four

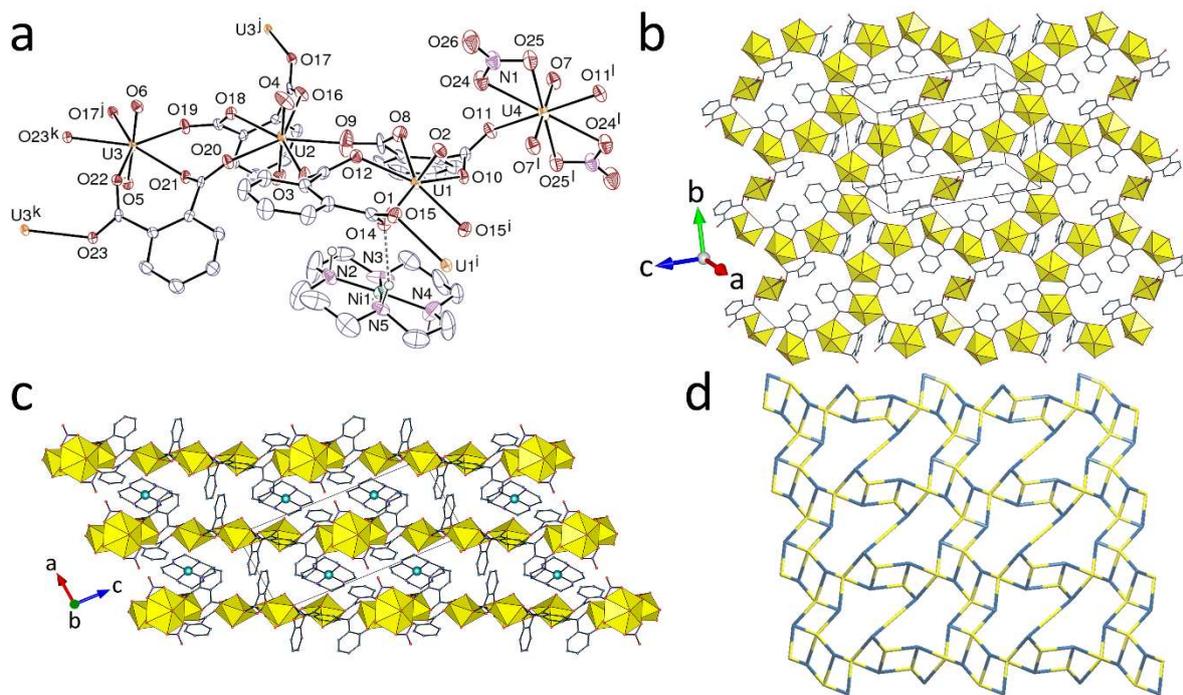


**Figure 4.** (a) View of compound **4** with 50% probability displacement ellipsoids. The solvent molecule and carbon-bound hydrogen atoms are omitted, and the hydrogen bonds are shown as dashed lines. Symmetry code:  $i = 1 - x, 2 - y, 1 - z$ . (b) View of the hexanuclear assembly with uranium coordination polyhedra colored yellow and those of nickel green. (c) View of the packing.

ligands of the cluster all adopt the same coordination mode, with one group chelating and bridging ( $\mu_2\text{-}\kappa^2\text{O},\text{O}';\kappa^1\text{O}$ ) and the other monodentate. What makes this structure unusual is the bonding of the uranyl oxo group O1 to  $\text{Ni}^{\text{II}}$ , the latter being also coordinated to all nitrogen atoms of cyclam and one water molecule, its environment being octahedral and slightly axially

elongated [Ni–N, 2.031(6)–2.075(6) Å; Ni–O(oxo) 2.189(4) Å; Ni–O(aqua) 2.166(4) Å]. It is notable that the oxo-bonding of Ni<sup>II</sup> to uranyl induces a significant lengthening of the U1=O1 bond [1.814(4) Å] with respect to U1=O2 [1.787(4) Å] and the two U2=O bonds [1.774(4) and 1.777(4) Å]. The CSD contains 31 examples of uranyl oxo-bonding to d-block metal cations, but, apart from one case involving U<sup>V</sup> instead of U<sup>VI</sup>,<sup>80</sup> there is only one recently reported complex with Ni<sup>II</sup>, also in its cyclam-complexed form, in which the Ni–O bond is much longer [2.516(4) Å], although the U=O–Ni angle is similar [157.5(2)° compared to 158.3(2)° in **4**].<sup>20</sup> As in this previous case, cyclam forms two hydrogen bonds with two carboxylate groups of the attached uranyl complex [N...O distances, 3.312(7) and 3.167(7) Å; N–H...O, angles 158(6) and 156(6)°], giving a ring with the graph set descriptor<sup>81,82</sup>  $R_2^2(8)$ , and the other two NH groups form bonds with oxo and carboxylate groups of a neighbouring unit. Bonding of two Ni<sup>II</sup> cations results in the complex being overall an heterometallic, neutral hexanuclear species with a planar U<sub>4</sub> core and one [Ni(cyclam)]<sup>2+</sup> moiety protruding sideways on each face, these bulky groups possibly preventing further polymerization.

Replacement of the DMF organic cosolvent used in the synthesis of **4** by acetonitrile, all other things being equal, yields the complex [Ni(cyclam)]<sub>2</sub>[(UO<sub>2</sub>)<sub>7</sub>(pht)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>] (**5**), which does not contain oxo or hydroxo bridges resulting from hydrolysis. The poor anion solvating ability of CH<sub>3</sub>CN may partly explain the presence of coordinated nitrate here as in complex **2**, although the structure of complex **6** (see ahead) shows that it cannot be a dominant factor. The structure contains four crystallographically independent uranium atoms, one of them (U4) located on an inversion centre (Figure 5). The two carboxylate groups of two pht<sup>2-</sup> ligands chelate U1 (7-membered chelate rings), which is also coordinated to one more carboxylate oxygen atom, U2 and U3 are chelated only once and coordinated to three additional carboxylate donors from three different ligands, while U4 connects to two carboxylate donors and two

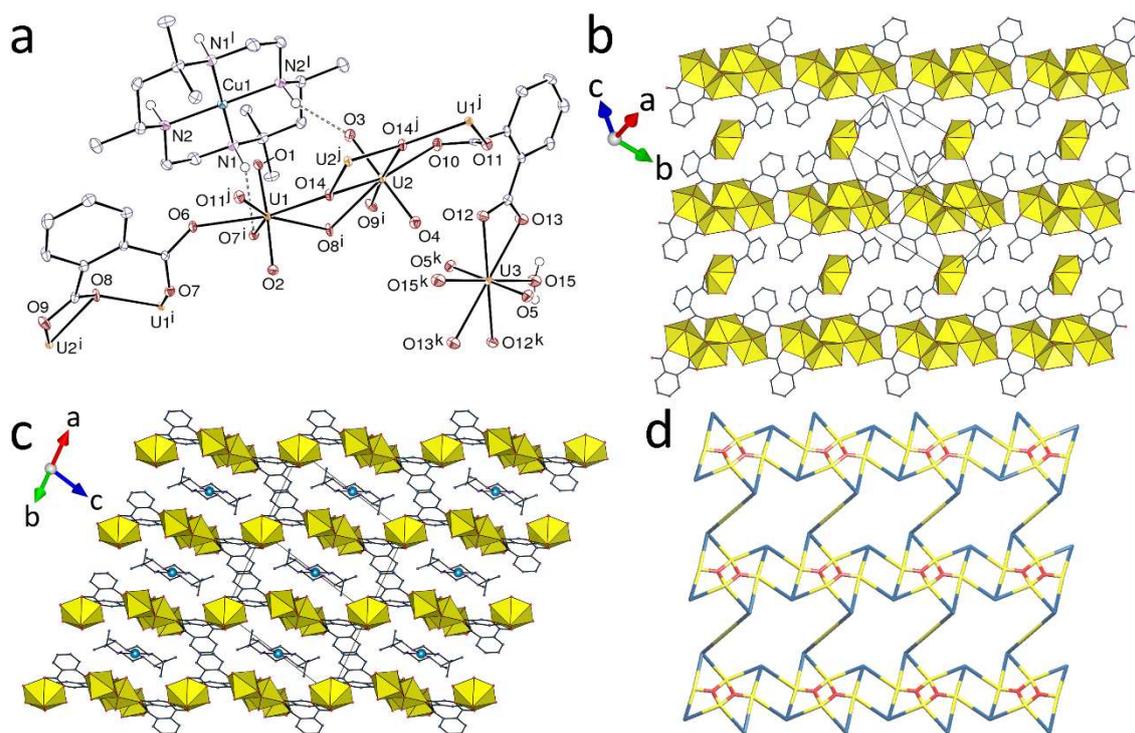


**Figure 5.** (a) View of compound **5** with 50% probability displacement ellipsoids. Carbon-bound hydrogen atoms are omitted and the hydrogen bond is shown as a dashed line. Symmetry codes:  $i = 1 - x, 1 - y, 1 - z$ ;  $j = 2 - x, 1 - y, -z$ ;  $k = 2 - x, 2 - y, -z$ ;  $l = 1 - x, -y, 1 - z$ . (b) View of the dimeric assembly with uranium coordination polyhedra colored yellow. (c) Packing with layers viewed edge-on and nickel atoms shown as green spheres. (d) Nodal representation of the dimeric assembly (uranium, yellow; carboxylate ligand, blue).

chelating nitrate anions, the uranium atom environment being thus pentagonal-bipyramidal for U1–U3 and hexagonal-bipyramidal for U4 [U–O(oxo), 1.758(5)–1.778(4) Å; U–O(carboxylato), 2.352(4)–2.438(5) Å; U–O(nitrato), 2.493(6) and 2.502(6) Å]. The four inequivalent  $\text{pht}^{2-}$  ligands have their two carboxylate groups bound in the  $\mu_2\text{-}\kappa^1\text{O}:\kappa^1\text{O}'$  coordination mode, with one common uranium centre. U1 is a 3-coordinated (3-c) node, U2 and U3 are 4-c nodes, U4 is a simple link, and the four  $\text{pht}^{2-}$  ligands are 3-c nodes in the 7-nodal dimeric coordination polymer parallel to (101), which has the vertex symbol  $\{4.9^2\}\{4^2.6\}_4\{4^2.9^2.11^2\}\{4^3.6^2.8\}$ . In this case, the  $[\text{Ni}(\text{cyclam})]^{2+}$  counterion appears to exert its influence more as a hydrogen bond donor than through axial coordination and is bound to the layers through hydrogen bonding to uranyl oxo and carboxylato groups [N $\cdots$ O distances,

3.025(8)–3.288(8) Å; N–H...O angles, 124–178°], and the packing has a KPI of 0.71. Although uranyl oxo groups are situated appropriately for axial coordination, the corresponding Ni–O distances of 2.800(5) and 2.864(5) Å are much longer than those in complex **4** and thus indicative of a much weaker interaction. Different structure-supporting roles for [Ni(cyclam)]<sup>2+</sup> have been seen in various other uranyl ion complexes<sup>52</sup> and the examples of complexes **4** and **5** confirm that their energies must differ little.

The complex [Cu(*R,S*-Me<sub>6</sub>cyclam)][(UO<sub>2</sub>)<sub>5</sub>(O)<sub>2</sub>(pht)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 4H<sub>2</sub>O (**6**) is once more a bis( $\mu_3$ -oxo)-bridged species, as complex **4**, but it involves a different connectivity of the pht<sup>2-</sup> ligands (Figure 6) resulting from the fact that here all four carboxylate oxygen donors of both the two inequivalent ligands are involved in coordination to uranyl ions. There are three

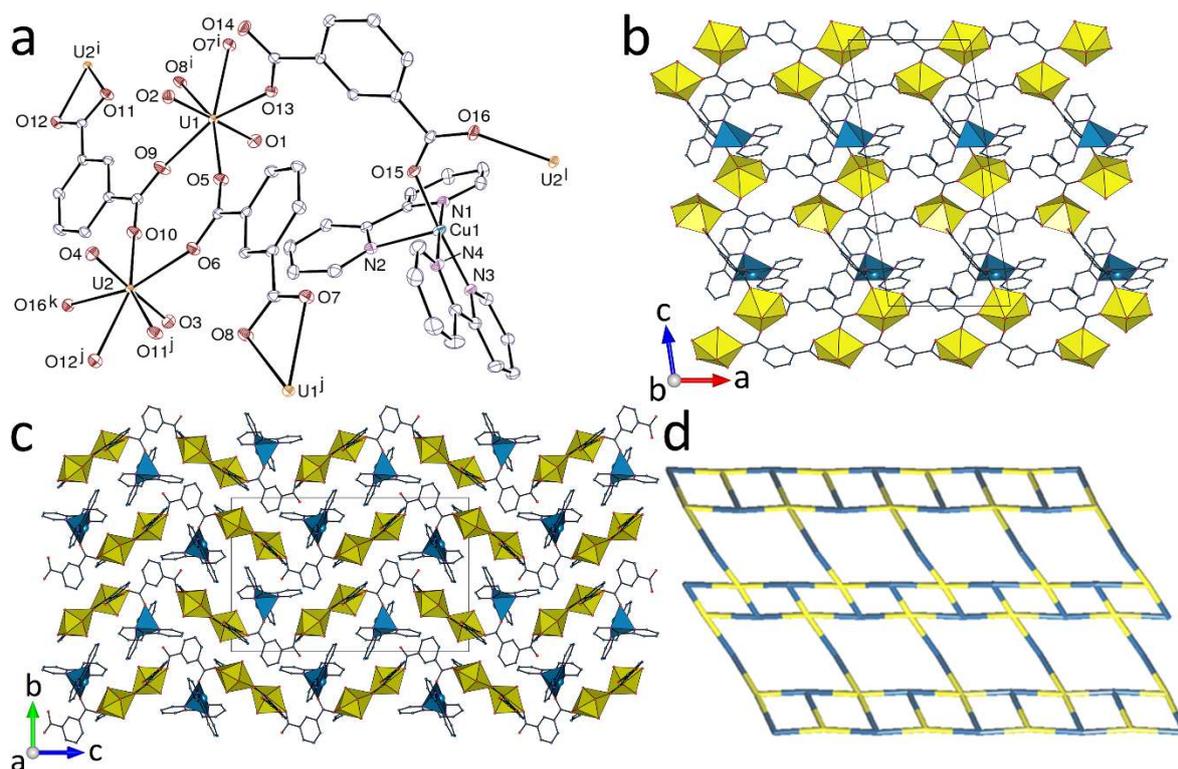


**Figure 6.** (a) View of compound **6** with 50% probability displacement ellipsoids. Solvent molecules and carbon-bound hydrogen atoms are omitted, and hydrogen bonds are shown as dashed lines. Symmetry codes:  $i = 2 - x, 1 - y, 1 - z$ ;  $j = 1 - x, -y, 1 - z$ ;  $k = 2 - x, -y, 2 - z$ ;  $l = 1 - x, 1 - y, 1 - z$ . (b) View of the dimeric assembly with uranium coordination polyhedra colored yellow. (c) Packing with layers viewed edge-on and copper atoms shown as blue spheres. (d) Nodal representation of the dimeric assembly (uranium, yellow; oxygen, red; carboxylate ligand, blue).

inequivalent uranium atoms, one of them (U3) located on an inversion centre. U1 is bound to one  $\mu_3$ -oxo anion, one seven-membered-chelating  $\text{pht}^{2-}$  ligand and two more carboxylate donors, while U2 is bound to two  $\mu_3$ -oxo anions, one  $\kappa^2O,O'$ -chelating carboxylate group and one more carboxylate donor, both being in pentagonal-bipyramidal environments; U3 is  $\kappa^2O,O'$ -chelated by two carboxylate groups and coordinated to two additional donors, its environment being hexagonal-bipyramidal [U–O(oxo), 1.774(3)–1.803(3) Å; U–O( $\mu_3$ -oxo), 2.229(2)–2.310(2) Å; U–O(carboxylato), 2.447(3)–2.528(2) Å for  $\kappa^2O,O'$ -chelating groups, and 2.374(3)–2.470(3) Å for the others]. While the bis( $\mu_3$ -oxo)-bridged tetranuclear unit in **4** contains two uranium atoms in each of the pentagonal- and hexagonal-bipyramidal environments, resulting in each uranium coordination polyhedron sharing two or three edges with its neighbours, the pentagonal-bipyramidal environment of both U1 and U2 here limit the contacts to one or two edges, these being two well-known arrangements in tetranuclear uranyl SBUs.<sup>3</sup> The Cu1...O1 distance involving one uranyl oxo group, 2.716(3) Å, is considerably longer than the Ni–O(oxo) bond length in complex **4**, and somewhat longer than observed when the axial donor is a carboxylate oxygen atom,<sup>9,20,51</sup> though slightly shorter than when the sulfonate ligand is involved.<sup>83</sup> It is also shorter than the Ni...O(oxo) separations observed in complex **5**, showing again that both Ni<sup>II</sup> and Cu<sup>II</sup> complexes of tetraazamacrocycles influence the forms of uranyl carboxylate complexes through a remarkably variable combination of coordinative and hydrogen bonding interactions. The two independent  $\text{pht}^{2-}$  ligands are both 3-c, but differently connected, one of them having one carboxylate group chelating and bridging ( $\mu_2$ - $\kappa^2O,O':\kappa^1O$ ) and the other bridging (*syn/anti*  $\mu_2$ - $\kappa^1O:\kappa^1O'$ ), with one of the metal centres being common to both, while the other ligand has  $\kappa^2O,O'$ -chelating and  $\mu_2$ - $\kappa^1O:\kappa^1O'$ -bridging carboxylate groups. The tetranuclear SBUs are assembled into chains through carboxylate bridges, and U3 bridges further cross-link these chains to form a diperiodic, 5-nodal network

parallel to  $(1\bar{1}\bar{1})$ , that has the vertex symbol  $\{4.10^2\}\{4^2.6\}\{4^3.6^2.8\}_2\{4^3\}$ . These layers are connected into a framework through hydrogen bonding of the counterions to oxo and carboxylato groups [O...O distances, 3.040(4)–3.341(4) Å; O–H...O angles, 120(3)–158(4)°] and parallel-displaced  $\pi$ -stacking interactions [centroid...centroid distance, 3.875(2) Å; dihedral angle, 0°; slippage, 1.74 Å], resulting in a compact packing (KPI, 0.72).

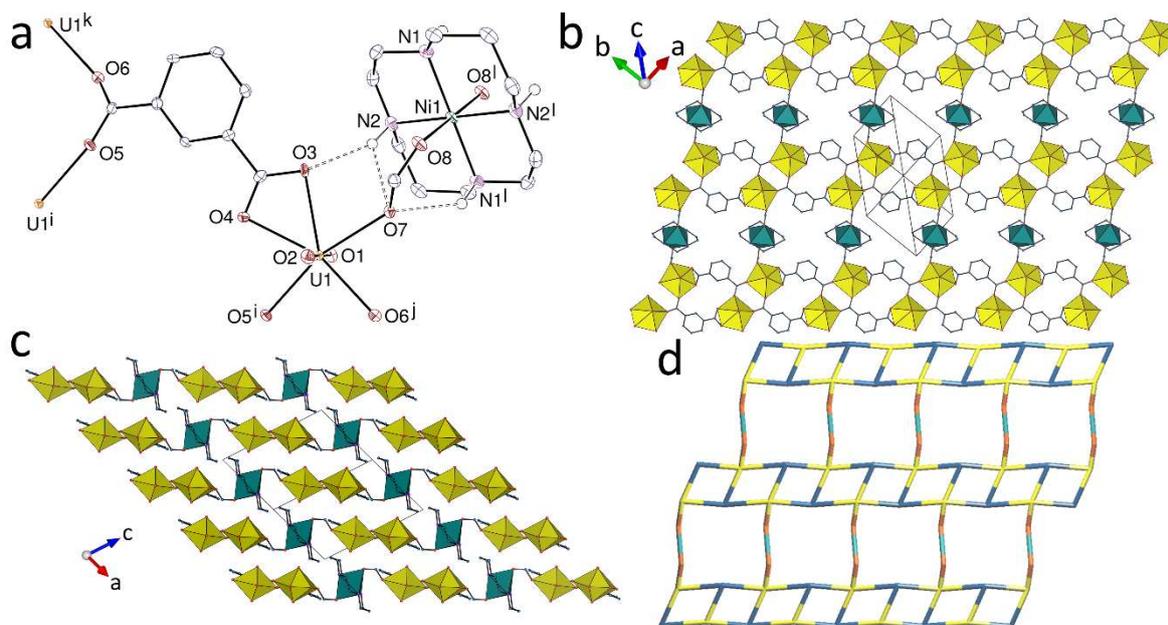
The last three complexes involve the isophthalate ligand, the first discussed,  $[(\text{UO}_2)_2(\text{ipht})_3\text{Cu}(\text{bipy})_2]\cdot\text{H}_2\text{O}$  (**7**), being a heterometallic complex shown in Figure 7. The two inequivalent uranium atoms are  $\kappa^2O,O'$ -chelated by one carboxylate group, three additional donors from three  $\text{ipht}^{2-}$  ligands giving pentagonal-bipyramidal environments [U–O(oxo), 1.7641(17)–1.7884(17) Å; U–O(carboxylato), 2.4299(16)–2.4885(16) Å for  $\kappa^2O,O'$ -chelating groups, and 2.3056(16)–2.3518(16) Å for the others]. The  $\text{Cu}^{\text{II}}$  cation is chelated by two bipy molecules and also coordinated to the carboxylate oxygen atom O15 [Cu–N, 1.995(2)–2.235(2) Å; Cu–O, 1.9688(17) Å], its environment being thus square pyramidal, and it is also involved in a much longer contact with the uranyl oxo atom O4, at 2.5955(17) Å (which, if considered as a coordination bond, would turn the environment into distorted, axially elongated octahedral). Two of the three independent  $\text{ipht}^{2-}$  ligands have  $\kappa^2O,O'$ -chelating and  $\mu_2$ - $\kappa^1O:\kappa^1O'$ -bridging carboxylate groups, the latter forming together an eight-membered ring, and the third ligand has one group bridging and the other monodentate. In its known anionic uranyl ion complex where  $[\text{Ni}(\text{bipy})_3]^{2+}$  is the counterion,  $\text{ipht}^{2-}$  acts as a bis( $\kappa^2O,O'$ )-chelating ligand, a binding mode involving all four carboxylate oxygen donors that is typical of its coordination chemistry.<sup>40</sup> The coordination mode found here is, however, more common, and it may be ascribed to the fact that  $[\text{Cu}(\text{bipy})_2]^{2+}$ , unlike  $[\text{Ni}(\text{bipy})_3]^{2+}$ , can accept other donor atoms. The  $[\text{Cu}(\text{bipy})_2]^{2+}$  units, while perturbing the uranyl–isophthalate interaction, simply act as decorative additions to the diperiodic coordination polymer formed, parallel to (010) and



**Figure 7.** (a) View of compound **7** with 50% probability displacement ellipsoids. The solvent molecule and hydrogen atoms are omitted. Symmetry codes:  $i = x + 1; y, z$ ;  $j = x - 1, y, z$ ;  $k = x, 3/2 - y, z - 1/2$ ;  $l = x, 3/2 - y, z + 1/2$ . (b) View of the diperiodic assembly with uranium coordination polyhedra colored yellow and those of copper blue. (c) Packing with layers viewed edge-on. (d) Nodal representation of the diperiodic assembly (uranium, yellow; carboxylate ligand, blue).

displaying a sawtooth profile when viewed down  $[100]$ , the  $[\text{Cu}(\text{bipy})_2]^{2+}$  units being located within the grooves. The binodal, 3,4-c network has the vertex symbol  $\{4^2.6^3.8\}\{4^2.6\}$  and the topological type  $\text{V}_2\text{O}_5$ , which is frequently found in uranyl-based networks.<sup>9,20,53</sup>  $\pi$ -Stacking interactions are found between the aromatic rings of both  $\text{ipht}^{2-}$  and  $\text{bipy}$  ligands of different layers [centroid $\cdots$ centroid distances, 3.8631(13)–4.3222(14) Å; dihedral angles, 0–20.43(11)°], associated with the usual  $\text{CH}\cdots\pi$  and  $\text{CH}\cdots\text{O}$  interactions, leading to a compact packing (KPI, 0.70).

The complex  $[(\text{UO}_2)_2(\text{ipht})_2(\text{HCOO})_2\text{Ni}(\text{cyclam})]$  (**8**), shown in Figure 8, includes a formate ligand presumed to have been generated by hydrolysis of the DMF cosolvent. The

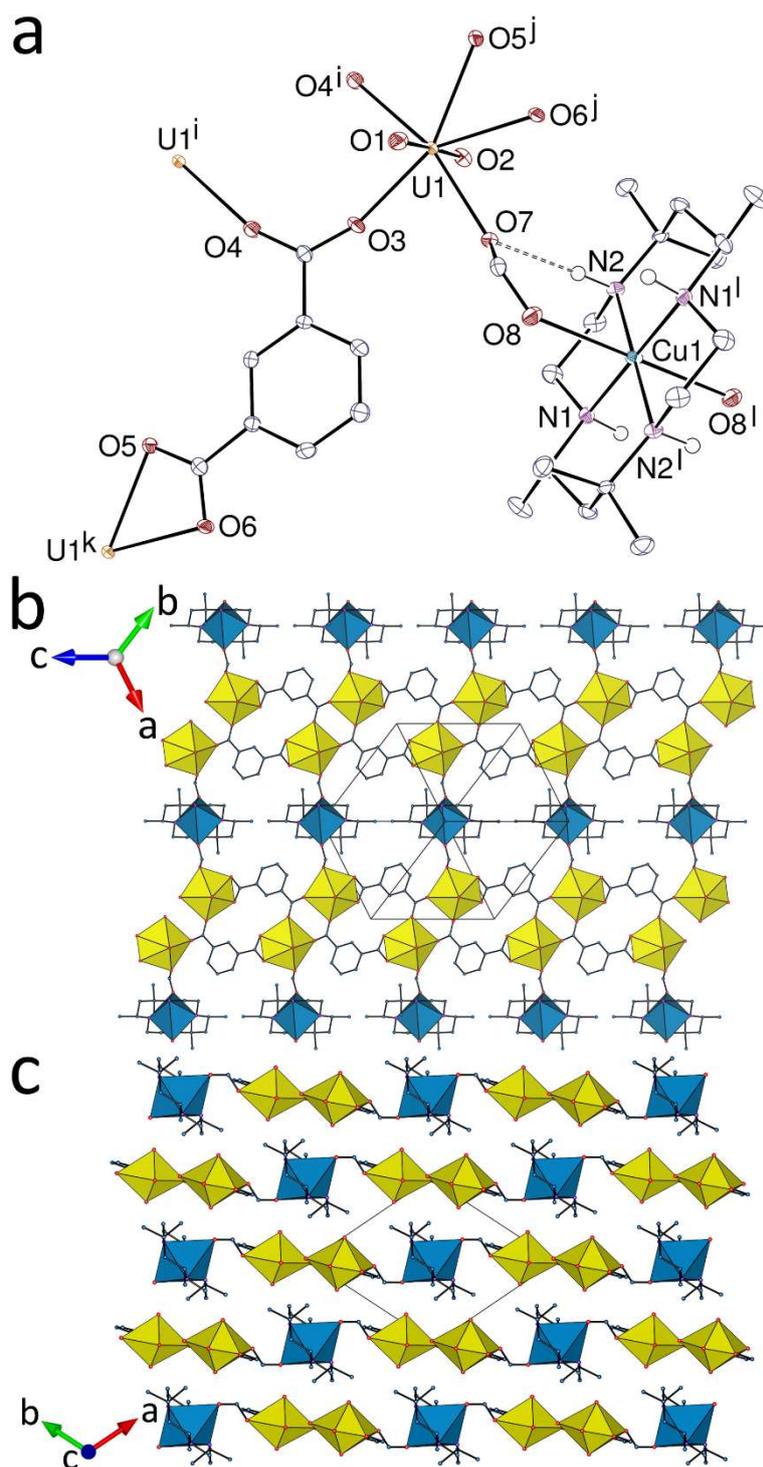


**Figure 8.** View of compound **8** with 50% probability displacement ellipsoids. Carbon-bound hydrogen atoms are omitted and the hydrogen bonds are shown as dashed lines. Symmetry codes:  $i = 1 - x, 1 - y, 1 - z$ ;  $j = x - 1, y + 1, z$ ;  $k = x + 1, y - 1, z$ ;  $l = 1 - x, 2 - y, 2 - z$ . (b) View of the diperiodic assembly with uranium coordination polyhedra colored yellow and those of nickel green. (c) Packing with layers viewed edge-on. (d) Nodal representation of the diperiodic assembly (uranium nodes, yellow; nickel links, green; carboxylate ligand nodes, blue; formate links, orange).

unique  $\text{UO}_2^{2+}$  cation is  $\kappa^2O, O'$ -chelated by one carboxylate and coordinated to two more oxygen atoms from two  $\text{ipht}^{2-}$  ligands and one from formate, the uranium environment being pentagonal-bipyramidal [U–O(oxo), 1.765(5) and 1.780(5) Å; U–O(carboxylato), 2.441(4) and 2.473(5) Å for the  $\kappa^2O, O'$ -chelating group, and 2.316(4)–2.372(4) Å for the others]. In addition to the four nitrogen donors of cyclam,  $\text{Ni}^{\text{II}}$ , located on an inversion centre, is axially bound to two formate anions [Ni–N 2.081(6) and 2.082(6) Å; Ni–O, 2.111(5) Å]. Formate coordination to  $\text{Ni}^{\text{II}}$  is accompanied here by relatively weak  $\text{NH}\cdots\text{O}$  hydrogen bonds [N $\cdots$ O distances, 3.052(7)–3.276(7) Å; N–H $\cdots$ O angles, 133(6)–158(7)°], with formation of  $R_1^2(4)$  and  $R_2^1(6)$  rings. With one carboxylate group  $\kappa^2O, O'$ -chelating and the other  $\mu_2\text{-}\kappa^1O:\kappa^1O'$ -bridging, the  $\text{ipht}^{2-}$  ligand adopts one of the most common bridging modes for isophthalate. As in complex

**7**, a monoperoiodic uranyl-based polymer is present, further formate-bridging of  $[\text{Ni}(\text{cyclam})]^{2+}$  cations resulting in formation of a diperoiodic, 3,4-c binodal network parallel to  $(11\bar{1})$ , which has the same vertex symbol and topology as that in **7**. The layers here are however nearly planar since the decorating groups nestling in the grooves in **7** are absent, and they are possibly linked to one another by parallel-displaced  $\pi$ -stacking interactions between  $\text{ipht}^{2-}$  ligands [centroid...centroid distance, 3.984(4) Å; dihedral angle,  $0^\circ$ ; slippage 1.95 Å], the close arrangement of layers giving a KPI of 0.71.

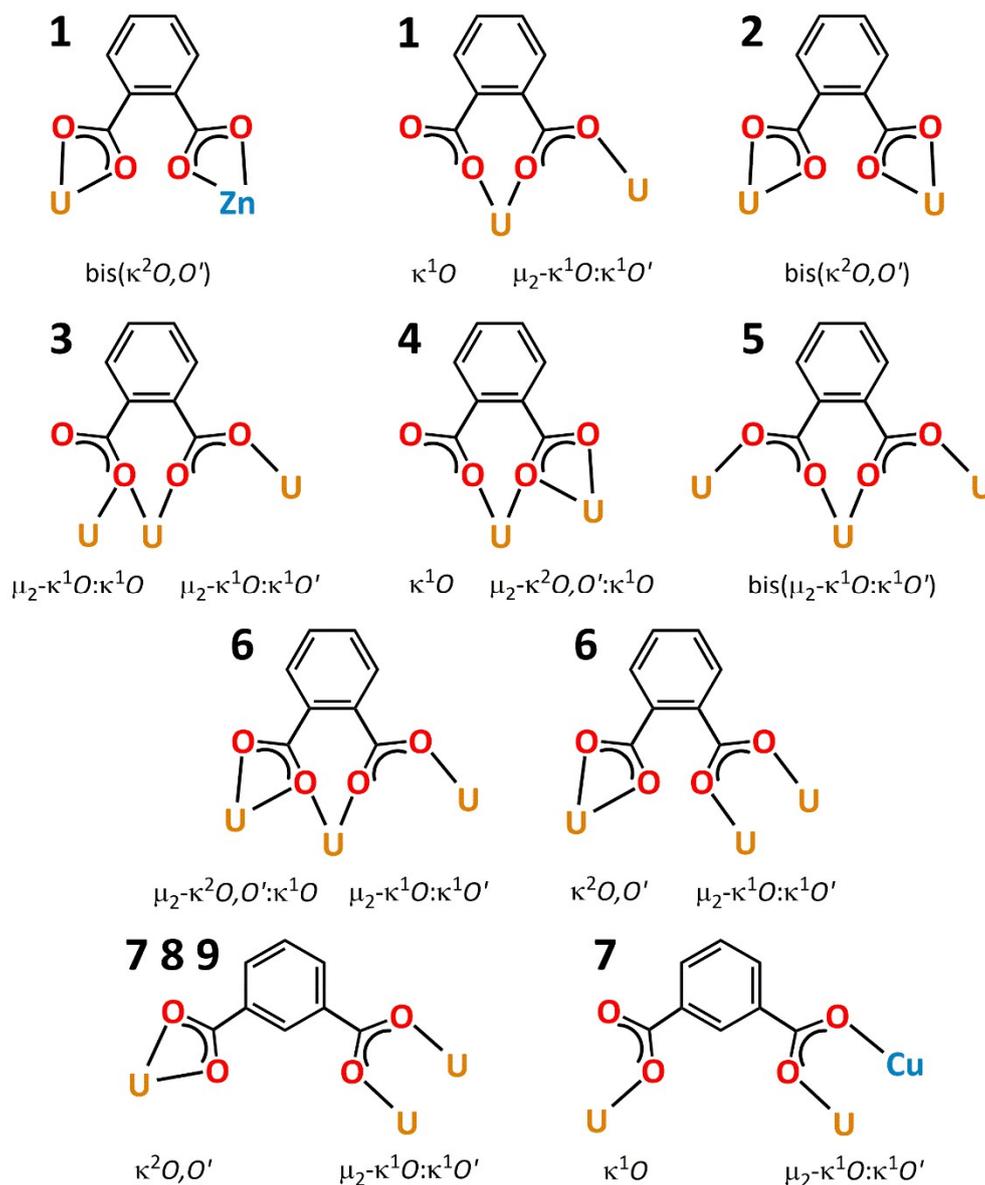
The structure of complex **9**,  $[(\text{UO}_2)_2(\text{ipht})_2(\text{HCOO})_2\text{Cu}(\text{R,S-Me}_6\text{cyclam})]$ , is essentially identical to that of complex **8** with the substitution of  $[\text{Cu}(\text{R,S-Me}_6\text{cyclam})]^{2+}$  for  $[\text{Ni}(\text{cyclam})]^{2+}$  (Figure 9). The uranium environment is analogous to that in **8** [U–O(oxo), 1.764(2) and 1.775(2) Å; U–O(carboxylato), 2.435(2) and 2.481(2) Å for the  $\kappa^2\text{O,O'}$ -chelating group, and 2.327(2)–2.344(2) Å for the others]. Here also, the  $\text{Cu}^{\text{II}}$  cation is located on an inversion centre and it is coordinated to all four nitrogen atoms of the macrocycle [Cu–N, 2.029(3) and 2.048(3) Å], but the Cu–O bond lengths of 2.519(2) Å are again long by comparison with those to  $\text{Ni}^{\text{II}}$  in **7**. However, while the differences in bonding interactions involving  $\text{Ni}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  are quite significant, their influence upon the overall structure is quite subtle, among them a slightly different hydrogen bonding pattern, which is here both intra- and interlayer [N...O distances, 3.040(3) and 3.087(3) Å; N–H...O angles, 156(3) and 176(3) $^\circ$ ;  $R_1^1(6)$  as smallest ring]. The diperoiodic network formed, parallel to  $(110)$  is topologically identical to that in **7**, and here also a  $\pi$ -stacking interaction involving  $\text{ipht}^{2-}$  is possible [centroid...centroid distance, 3.410(2) Å; dihedral angle,  $0^\circ$ ; slippage 2.67 Å], the KPI being 0.70.



**Figure 9.** View of compound **9** with 50% probability displacement ellipsoids. Carbon-bound hydrogen atoms are omitted and the hydrogen bond is shown as a dashed line. Symmetry codes:  $i = -x, 2 - y, 1 - z$ ;  $j = x, y, z + 1$ ,  $k = x, y, z - 1$ ;  $l = 1 - x, 1 - y, 1 - z$ . (b) View of the dimeric assembly with uranium coordination polyhedra colored yellow and those of copper blue. (c) Packing with layers viewed edge-on.

The coordination modes of the  $\text{pht}^{2-}/\text{ipht}^{2-}$  ligands found in the present series of complexes are represented in Scheme 1. Except for that in complex **3**, in which one of the carboxylate groups is  $\mu_2\text{-}\kappa^1\text{O}:\kappa^1\text{O}$ -bridging, these coordination modes are usual ones for these

**Scheme 1. Coordination Modes of  $\text{pht}^{2-}/\text{ipht}^{2-}$  in Complexes 1–9<sup>a</sup>**



<sup>a</sup> The coordination mode symbols are given for each individual carboxylate group.

ligands. Table 2 gives the values of the dihedral angles between each  $\text{-COO}$  group and the aromatic ring ( $\alpha_1$  and  $\alpha_2$ ), and between the two  $\text{-COO}$  groups ( $\beta$ ). Obviously,  $\text{ipht}^{2-}$  is closer

to being planar than  $\text{pht}^{2-}$ , and although some variation exists, no dihedral angle in this case is larger than about  $30^\circ$ . The values for the two ligands in complex **1** show that the angle  $\beta$  for  $\text{pht}^{2-}$  may retain similar values whether a 7-membered ring is formed or not, although the two  $-\text{COO}$  groups are close to being orthogonal to one another in **3** and **4**, and in one ligand in **5**. Overall, the angles in  $\text{pht}^{2-}$  vary widely, in the range of  $\sim 3\text{--}90^\circ$ , an indication that the geometry of the complexes can be subjected to fine-tuning through modification of the additional metal cation-containing species present.

**Table 2. Dihedral Angles (deg) in  $\text{pht}^{2-}/\text{ipht}^{2-}$  in Complexes 1–9**

Ligand	Complex	$\alpha_1$	$\alpha_2$	$\beta$
<b><math>\text{pht}^{2-}</math></b>	<b>1</b>	61.54(15)	22.2(3)	62.5(2)
		55.68(14)	8.6(3)	61.7(2)
	<b>2</b>	59.1(2)	37.2(3)	65.6(4)
		<b>3</b>	7.5(4)	79.3(2)
	7.2(6)		72.7(3)	78.8(3)
	16.3(7)		83.3(2)	89.6(4)
	<b>4</b>	20.2(4)	80.2(4)	80.2(5)
		21.8(3)	71.2(4)	80.6(6)
	<b>5</b>	4.9(12)	59.8(2)	62.8(6)
		32.3(6)	41.5(3)	44.8(7)
		35.7(4)	72.0(5)	84.5(6)
		27.0(7)	32.2(7)	45.4(8)
	<b>6</b>	24.0(3)	30.1(3)	39.8(3)
		2.6(3)	72.8(2)	73.1(4)
	<b><math>\text{ipht}^{2-}</math></b>	<b>7</b>	4.5(3)	8.82(15)
6.7(4)			8.55(18)	7.6(4)
6.5(4)			13.0(3)	13.6(5)
<b>8</b>		19.4(5)	29.2(8)	31.1(10)
<b>9</b>		8.1(5)	15.1(5)	19.5(6)

In the construction of heterometallic uranyl ion coordination polymers and frameworks, the addition of a strongly coordinating but non-bridging ligand along with the heterometal ion provides a useful means of controlling the exact role that the heterometal ion may play. Tetra-aza macrocycles such as cyclam or its hexamethyl homologue *R,S*-Me<sub>6</sub>cyclam, in their preferred coordination mode where the MN<sub>4</sub> unit is essentially planar, can both limit any residual coordination sites on the metal to those in *trans* positions and provide strong hydrogen bonding sites at the bound NH units. Simpler chelate ligands such as 2,2'-bipyridine or 1,10-phenanthroline can be used, depending on the M:chelate stoichiometry, to either completely block direct heterometal ion coordination to the ligand involved in the polymer or oligomer formation with uranyl ion or to leave sites, in a chiral unit in the case of ML<sub>2</sub> species, where additional coordination can occur with a *cis* geometry, both these procedures having been exploited in the present work. The pht<sup>2-</sup> ligand could be expected to coordinate to uranyl ion simply by the formation of 7-membered chelate rings but in its known, structurally characterized complexes with this metal ion it is apparent that although such chelation occurs, it does not prohibit further interactions of the carboxylate units which lead to oligomer and polymer formation. Only in complex **2** and in one ligand only in both **1** and **6** does it show the exclusively bridging function, without 7-membered chelate ring formation, the bridging-only mode being also known in one instance for its aliphatic analogue maleate.<sup>84</sup> In the other complexes with pht<sup>2-</sup>, **3**, **4** and **5**, bridging is always associated with 7-membered chelate ring formation, while ipht<sup>2-</sup> (as well as terephthalate) is necessarily restricted to the bridging mode due to its inability to chelate other than through the formation of 4-membered κ<sup>2</sup>O,O' rings. The formation of discrete, polynuclear species is rather frequent with pht<sup>2-</sup>, and complexes **1** and **4**, both including terminal 3d-block metal complexes, pertain to this category, **4** being one more example containing the common bis(μ<sub>3</sub>-oxo)-bridged tetranuclear uranyl phthalate moiety.<sup>23,24,31,79</sup> Complete separation of the counterion leads to a helical chain in **2** with

bridging-only, bis-chelating  $\text{pht}^{2-}$  ligands, and diperiodic networks in **3**, **5** and **6**, that in **3** displaying  $\mu_3$ -oxo-centered, cup-like cavities accommodating the  $[\text{Ni}(\text{phen})_3]^{2+}$  counterions. Weak interactions (hydrogen bonding,  $\pi$ -stacking) involving the counterions, as well as their varying shape and bulkiness, most probably play a role in determining the geometry of the uranyl-based coordination polymer. It is notable that triperiodic species are utterly absent here. The three complexes with  $\text{ipht}^{2-}$  crystallize as diperiodic networks, either with a terminal, decorating  $\text{Cu}(\text{bipy})_2^{2+}$  moiety in **7**, or with bridging  $\text{Ni}(\text{cyclam})^{2+}$  or  $\text{Cu}(\text{R,S-Me}_6\text{cyclam})^{2+}$  complexes in **8** and **9**.

## CONCLUSIONS

We have reported here the syntheses and crystal structures of five uranyl ion complexes with phthalate and three with isophthalate, all including 3d-block metal cations associated with chelating nitrogen-donor species (bipy, phen, cyclam, *R,S*-Me<sub>6</sub>cyclam) as counterions or structure-directing agents, this combination having proven from our previous work and that of other groups<sup>85-87</sup> to provide a useful way to generate uranyl-containing species with original structures. Apart from two discrete heterometallic complexes (**1** and **4**) and one monopерiodic helical polymer (**2**) obtained with phthalate, all the other compounds are diperiodic, always homometallic with phthalate, and heterometallic with isophthalate, their geometry and topology being dependent upon the presence in some cases of bridging oxo anions, and on the size and shape of the structure-directing agents and the weak interactions they form. The structure-directing effect of the 3d-block metal ion complexes when not part of the coordination polymer are well illustrated by the diperiodic phthalate complex **3** in which they are partly included into pseudo-trigonal, cup-shaped cavities. While both phthalate and isophthalate provide a convergent array of carboxylate groups, even if one not suited to simple chelation in the latter

case, small, oligomeric clusters are readily obtained with phthalate but seem to be unavailable with isophthalate under the conditions used here (although dinuclear species are known<sup>27,88</sup>). For neither ligand isomer is there an indication that closed uranyl-based oligomeric structures, such as rings or cages, with possible application in heterogeneous photocatalysis might be readily obtained (notwithstanding the nanotubular phthalate complex previously reported<sup>23,32</sup>).

## ASSOCIATED CONTENT

### Accession Codes

CCDC 2057792–2057800 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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## Notes

The authors declare no competing financial interest.

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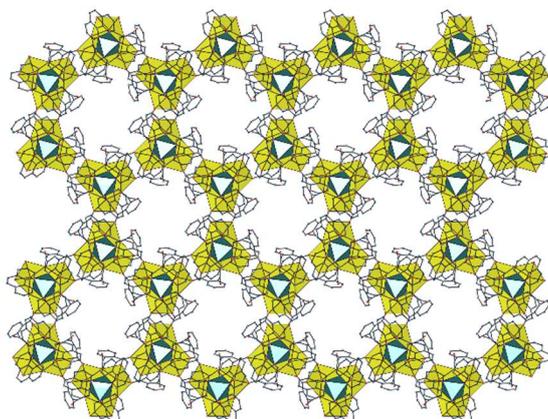
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## **Contrasting Structure-Directing Effects in the Uranyl–Phthalate/Isophthalate Isomer Systems**

Pierre Thuéry and Jack Harrowfield



The use of 3d-block metal cations associated with chelating nitrogen donors as structure-directing agents allowed to crystallize a series of homo- or heterometallic uranyl ion complexes with phthalate or isophthalate. Differences in coordination mode and interaction with the transition metal species result in a diverse set of zero-, mono- and diperic assemblies, some of which have unprecedented geometry.