



## Combination of covalent and hydrogen bonding in the formation of 3D uranyl-carboxylate networks

Sudipta Dalai<sup>a,\*</sup>, Madhusudan Bera<sup>a</sup>, Abhinandan Rana<sup>a</sup>, Durga Sankar Chowdhuri<sup>a</sup>, Ennio Zangrando<sup>b</sup>

<sup>a</sup> Department of Chemistry and Chemical Technology, Vidyasagar University, Midnapore 721 102, WB, India

<sup>b</sup> Dipartimento di Scienze Chimiche, University of Trieste, 34127 Trieste, Italy

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### ABSTRACT

Four compounds containing uranyl cation  $[\text{UO}_2]^{2+}$  have been synthesized hydrothermally by reacting uranyl acetate and uranyl nitrate with various N/O donor ligands. The structure of all compounds was elucidated by single crystal X-ray diffraction study. Compound  $[(\text{UO}_2)(6\text{-methylnicotinato})_3](\text{H}_3\text{O})\cdot 4\text{H}_2\text{O}$  (**1**) is a discrete complex (0D), that gives rise in the crystal to hydrophilic channels, while  $[(\text{UO}_2)(\text{OH})(\mu_2\text{-3-pyridylpropionato})]_n$  (**2**) and  $[(\text{UO}_2)(\text{H}_2\text{O})(\mu_3\text{-4,4'-oxybis(benzoato)})]_n$  (**3**) show the formation of 1D coordination polymers. Moreover, oxalate anions, formed in situ by using 5-methylisophthalic or 2,3-pyrazinedicarboxylic acid as reactant ligands, gave rise to a 2D coordinating network  $[(\text{UO}_2)_2(\mu_2\text{-oxalate})(\mu_2\text{-OH})_2(\text{H}_2\text{O})_2]_n\cdot n\text{H}_2\text{O}$  (**4**). All the complexes expanded their dimensionality to 3D through hydrogen bonds.

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### 1. Introduction

The study of metal–organic solids continues to be a great interest due to the variety in solid structures which can be applied to shape selective catalysis [1–7], ion exchange [8], molecular sieving [9], gas separation [10], gas storage [11–18], and host guest chemistry [19–21]. Although the design and synthesis of such materials are influenced by many factors like the coordination trend of metal centers, the nature of ligands used, the metal–ligand ratio, the reaction conditions etc., the judicious selection of multifunctional organic ligand is still an effective approach [22–27]. Literature survey revealed that transition metals, lanthanides and actinides are competent of presenting fascinating networks [28–31].

Uranium offers interesting architectures due to its higher coordination number in comparison to main group/transition elements and the structural diversity depends on the reaction condition as well as choice of organic ligands [28]. It is perceptible; however, that the tricky application of hydrogen bonding and other non-covalent interactions during the synthesis of such materials are becoming an area of interest and the possibility of generating unpredicted dimensionality is opening up in connection to novel topologies [32].

Although a large number of 1D and 2D MOFs of uranium are reported in the literature [33–36], examples of the 3D networks are few in number [37]. In most of the cases the 3D topologies are pro-

duced either by the mixed metal uranium(IV) fluorides with different  $\text{Ni}(\text{H}_2\text{O})_{6-x}\text{F}_x$  octahedra [38] and by uranyl–lanthanide heterometallic complexes [39]. Borkowshi and Cahill reported a 3D structure of uranium obtained by cross linking of adipic acid [40]. However, the construction of 3D building networks of uranium species through hydrogen bond are scarce.

With the aim to derive new network topologies, in this work we have synthesized four uranyl complexes by using two heterocyclic monocarboxylates (6-methylnicotinic acid, trans-3-(3-pyridyl)acrylic acid) and three aromatic dicarboxylates (4,4'-oxo-bis benzoic acid, 5-methylisophthalic acid and 2,3-pyrazinedicarboxylic acid) as organic linkers for their capability of participating in hydrogen bonding and/or in metal coordination. Although some complexes with 6-methylnicotinic acid [41], trans-3-(3-pyridyl)acrylic acid [42–46], and 4,4'-oxo-bis benzoic acid [47] with different transition metals have been reported, the construction of uranium coordination polymers using these ligands has never been tried. Single crystal X-ray analysis shows that all the synthesized complexes present a 3D network through hydrogen bonding.

### 2. Experimental

#### 2.1. General consideration

Caution! Because uranium is a radioactive and chemically toxic element, standard precautions for handling such materials should

\* Corresponding author. Fax: +91 3222 275 329.

E-mail address: [icsd2@yahoo.com](mailto:icsd2@yahoo.com) (S. Dalai).

be followed.  $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were purchased from Fluka, 6-methylnicotinic acid, trans-3-(3-pyridyl)acrylic acid 4,4'-oxo-bis benzoic acid, 5-methylisophthalic acid and 2,3-pyrazinedicarboxylic acid from Sigma–Aldrich Inc. All were used without further purification. Elemental analyses (C, H, N) were performed using a Perkin–Elmer 240C elemental analyzer.

## 2.2. Preparation of $[(\text{UO}_2)(6\text{-methylnicotinato})_3](\text{H}_3\text{O}) \cdot 4\text{H}_2\text{O}$ (**1**)

A mixture of  $\text{UO}_2(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$  (0.106 g, 0.25 mmol), 5-methylnicotinic acid (0.1028 g, 0.75 mmol), Triethylamine (0.1 ml,

0.75 mmol) and demineralized water (10 ml) was taken in a sealed 25 ml Teflon-lined stainless steel vessel. Yellow crystals of complex **1** appeared within 3 days upon heating at 150 °C under autogenous pressure. Yield: 50%. Elemental Anal. Calc. for  $\text{C}_{21}\text{H}_{29}\text{N}_3\text{O}_{13}\text{U}$  (**1**): C, 42.14; N, 5.46; H, 3.79. Found: C, 42.19; N, 5.32; H, 3.74%.

## 2.3. Preparation of $[(\text{UO}_2)(\text{OH})(\mu_2\text{-3-pyridylpropionato})]_n$ (**2**)

A mixture of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.251 g, 0.5 mmol), trans-3-(3-pyridyl)acrylic acid (0.1491 g, 1 mmol), NaOH (0.04 g, 1 mmol) and  $\text{H}_2\text{O}$  (15 ml) was stirred at room temperature, then put into a sealed 25 ml Teflon-lined stainless steel vessel, heated at 160 °C for 7 days, cooled to room temperature and then filtered. Glossy yellow crystals were obtained from the filtrate after 7 days. Yield: 60%. Elemental Anal. Calc. for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_{10}\text{U}_2$  (**2**): C, 22.08; N, 3.21; H, 1.62. Found: C, 21.98; N, 3.15; H, 1.71%.

## 2.4. Preparation of $[(\text{UO}_2)(\text{H}_2\text{O})(\mu_3\text{-4,4'-oxybis(benzoato)})]_n$ (**3**)

Compound **3** was synthesized by the similar procedure as described for complex **2**. The ligand 4,4'-oxo-bis benzoic acid (0.1291 g, 0.5 mmol) is used instead of trans-3-(3-pyridyl)acrylic acid. Needle shaped yellow crystals of **3** were obtained from solution after 15 days. Yield: 60%. Elemental Anal. Calc. for  $\text{C}_{14}\text{H}_{10}\text{O}_8\text{U}$  (**3**): C, 30.89; H, 1.85. Found: C, 30.86; H, 1.87%.

## 2.5. Preparation of $[(\text{UO}_2)_2(\mu_2\text{-oxalate})(\mu_2\text{-OH})_2(\text{H}_2\text{O})_2]_n \cdot n\text{H}_2\text{O}$ (**4**)

A mixture of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.251 g, 0.5 mmol), 5-methylisophthalic acid (0.09 g, 0.5 mmol), NaOH (0.04 g, 1 mmol) and demineralized water (10 ml) was sealed in a 25 ml Teflon-lined stainless steel vessel. Yellow crystals of complex **4** appeared within

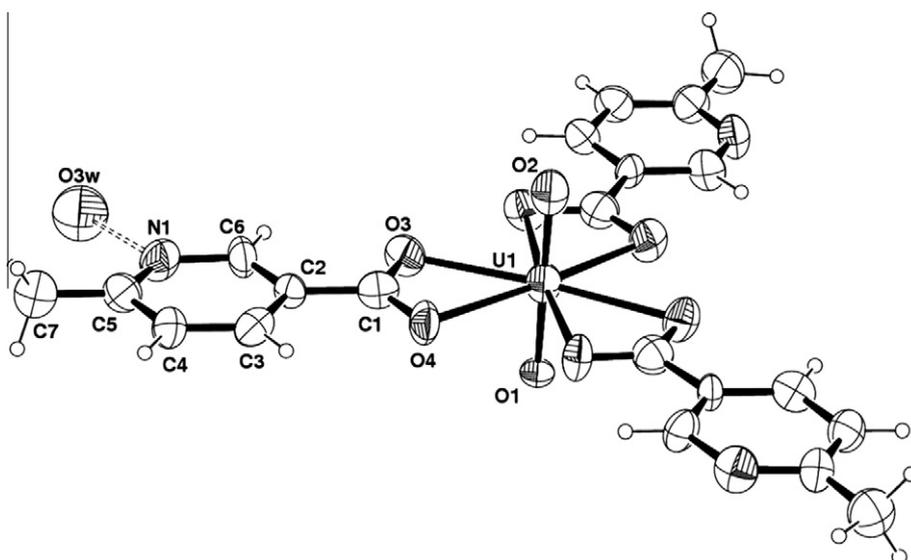
**Table 1**  
Crystallographic data and details of structure refinements for complexes **1–3**.

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	$\text{C}_{21}\text{H}_{29}\text{N}_3\text{O}_{13}\text{U}$	$\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_{10}\text{U}_2$	$\text{C}_{14}\text{H}_{10}\text{O}_8\text{U}$
Formula weight	769.50	870.35	544.25
Crystal system	trigonal	orthorhombic	monoclinic
Space group	$P\bar{3}1c$	$Pbca$	$P2_1/c$
<i>a</i> (Å)	16.271(3)	23.933(4)	16.018(3)
<i>b</i> (Å)		18.704(3)	8.884(2)
<i>c</i> (Å)	6.822(2)	8.494(1)	10.200(2)
$\beta$ (°)			95.71(2)
<i>V</i> (Å <sup>3</sup> )	1564.1(6)	3802.3(10)	1444.3(5)
<i>Z</i>	2	8	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.634	3.041	2.503
$\mu$ (mm <sup>-1</sup> )	5.248	17.075	11.279
<i>F</i> (0 0 0)	744	3104	1000
$\theta_{\text{max}}$ (°)	24.15	26.42	29.65
Reflections collected	17 378	54 496	16 791
Unique reflections	1318	3869	4045
Independent reflections ( <i>R</i> <sub>int</sub> )	0.0640	0.0790	0.0600
Observed <i>I</i> > 2σ ( <i>I</i> )	681	2247	2917
Parameters	114	271	214
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	0.774	0.906	0.935
<i>R</i> 1/ <i>wR</i> 2 <sup>a</sup> ( <i>I</i> > 2σ ( <i>I</i> ))	0.0447/ 0.0904	0.0562/0.1316	0.0436/ 0.1037
<i>R</i> 1/ <i>wR</i> 2 <sup>a</sup> (all data)	0.0957/ 0.0976	0.0934/0.1466	0.0619/ 0.1097
$\Delta\rho$ (e/Å <sup>3</sup> )	0.849, -0.460	2.625, -1.921	1.068, -1.897

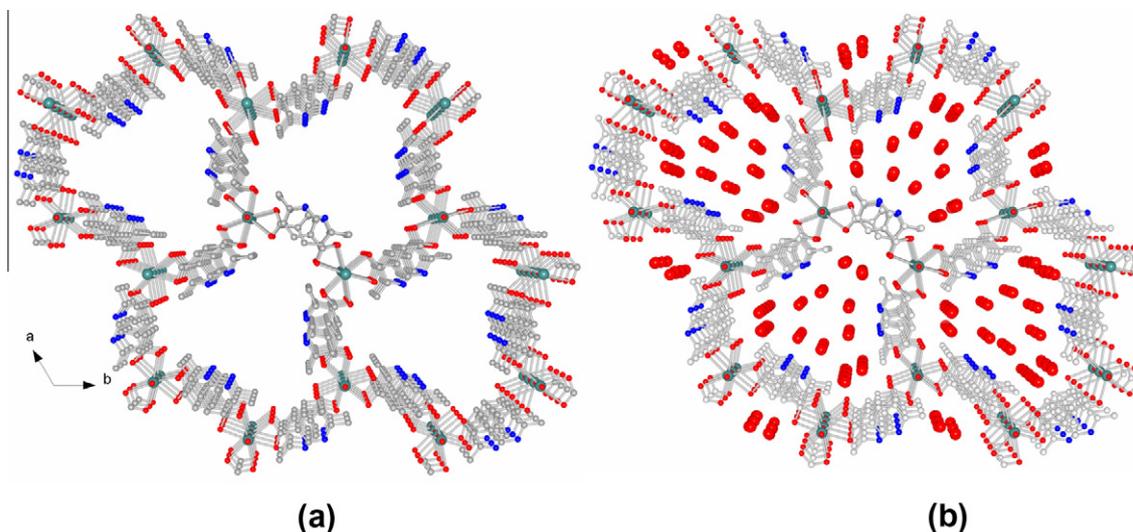
$$^a R1 = \sum \|F_o\| - |F_c| / \sum \|F_o\|, wR2 = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

**Table 2**  
Selected bond lengths (Å) and angles (°) of **1**.

U(1)–O(1)	1.76(2)	U(1)–O(3)	2.457(12)
U(1)–O(2)	1.74(3)	U(1)–O(4)	2.507(16)
O(2)–U(1)–O(3)	90.5(3)	O(1)–U(1)–O(4)	89.7(6)
O(1)–U(1)–O(3)	89.5(3)	O(3)–U(1)–O(4)	54.2(4)
O(2)–U(1)–O(4)	90.3(6)		



**Fig. 1.** The  $[\text{UO}_2(6\text{-methylnicotinato})_3]^-$  complex anion of **1** with labelling scheme of the independent atoms. The H-bond between the methylnicotinato nitrogen and a  $\text{H}_3\text{O}^+$ / $\text{H}_2\text{O}$  oxygen is indicated.



**Fig. 2.** (a) View of the crystal packing of **1** showing the channels built by  $[(\text{UO}_2)(6\text{-methylnicotinato})_3]$  fragments and (b) disordered  $\text{H}_2\text{O}/\text{H}_3\text{O}^+$  species (big spheres) bound to the framework through H-bonds.

6 days upon heating at  $160^\circ\text{C}$  under autogenous pressure. Yield: 65%. Elemental Anal. Calc. for  $\text{C}_2\text{H}_8\text{O}_{13}\text{U}_2$  (4): C, 3.35; H, 1.12. Found: C, 3.41; H, 1.19%.

The same compound is formed by a different reaction when a mixture of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.251 g, 0.5 mmol), 2,3-pyrazinedicarboxylic acid (0.084 g, 0.5 mmol), KOH (0.056 g, 1 mmol) and demineralized water (10 ml) was sealed in a 25 ml Teflon-lined stainless steel vessel. Yellow crystals of complex **4** appeared within 3 days upon heating at  $160^\circ\text{C}$  under autogenous pressure. Yield: 50%. Elemental Anal. Calc. for  $\text{C}_2\text{H}_8\text{O}_{13}\text{U}_2$  (4): C, 3.35; H, 1.12. Found: C, 3.4; H, 1.17%.

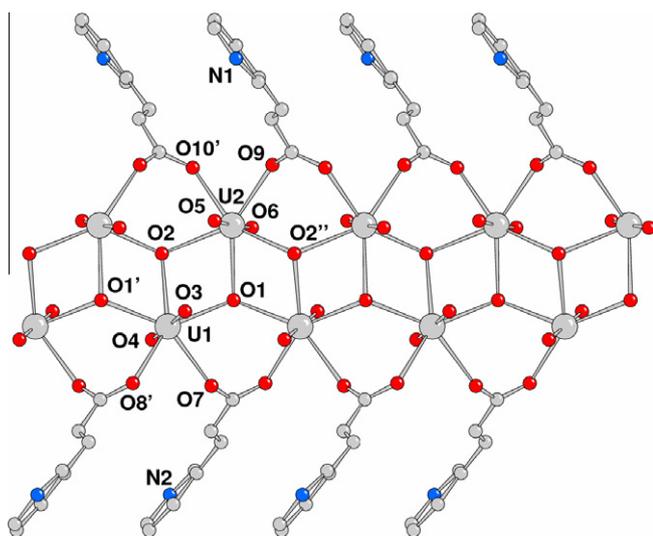
### 3. X-ray crystallography

Crystal data and details of data collections and refinements for the structures reported are summarized in Table 1. Data collections were carried at room temperature on a Nonius DIP-1030H system (Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ , graphite monochromatized). Cell refinement, indexing and scaling of all the data sets were per-

formed using programs DENZO and SCALEPACK [48]. All the structures were solved by direct methods and subsequent Fourier analyses [49] and refined by the full-matrix least-squares method based on  $F^2$  with all observed reflections [49]. In complex **1** the residuals were interpreted as a disorder water molecule (O1w, O2w with occupancies 0.56(8)/0.44(8)) and an oxygen atom (O3w) to which was assigned an occupancy of 0.6666, based on peak height. The short H-bond distance between N1 and O3w ( $2.79(3) \text{ \AA}$ ) could indicate a  $\text{H}_3\text{O}^+$  cation for the latter in order to guarantee the charge neutrality of the  $\text{UO}_2$  complex. However diffraction data did not allow fixing the H atoms of these species, being likely disordered. The hydrogen atoms of compounds **2** and **3** were fixed at geometrical positions or derived from the  $\Delta F$  map (constrained O–H distances at  $0.85 \text{ \AA}$ ) and their contribution was included in the final cycles of refinement. All the calculations were performed using the WINGX System, Ver 1.80.05 [50].

### 4. Results and discussion

Four complexes containing a central uranyl cation  $[\text{UO}_2]^{2+}$  moiety with monocarboxylate anions (6-methylnicotinate and trans-3-(3-pyridyl)acrylate) and with aromatic dicarboxylate (4,4'-oxo-bis-benzoate, 5-methylisophthalate and 2,3-pyrazinedicarboxylate), have been synthesized, namely  $[(\text{UO}_2)(6\text{-methylnicotinato})_3](\text{H}_3\text{O}) \cdot 4\text{H}_2\text{O}$  (**1**),  $[(\text{UO}_2)(\text{OH})(\mu_2\text{-3-pyridylpropionato})]_n$  (**2**),  $[(\text{UO}_2)(\text{H}_2\text{O})(\mu_3\text{-4,4'-oxybis(benzoato)})]_n$  (**3**), and  $[(\text{UO}_2)_2(\mu_2\text{-$



**Fig. 3.** 1D ribbon of compound **2** running along axis  $c$  showing the labelling scheme of oxygen donors.

**Table 3**  
Selected bond ( $\text{\AA}$ ) and angles ( $^\circ$ ) of **2**.

U(1)–O(1)	2.395(8)	U(2)–O(1)	2.442(9)
U(1)–O(1)#1	2.356(8)	U(2)–O(2)	2.447(8)
U(1)–O(2)	2.490(9)	U(2)–O(2)#2	2.415(9)
U(1)–O(3)	1.752(10)	U(2)–O(5)	1.766(11)
U(1)–O(4)	1.729(11)	U(2)–O(6)	1.786(10)
U(1)–O(7)	2.372(11)	U(2)–O(9)	2.349(10)
U(1)–O(8)#1	2.465(10)	U(2)–O(10)#1	2.455(9)
O(4)–U(1)–O(3)	177.8(4)	O(5)–U(2)–O(6)	176.5(4)
O(1)–U(1)–O(2)	68.6(3)	O(1)–U(2)–O(2)	68.5(3)
O(1)#1–U(1)–O(2)	70.4(3)	O(2)–U(2)–O(10)#1	75.6(3)
O(1)#1–U(1)–O(8)#1	75.0(3)	O(9)–U(2)–O(10)#1	72.8(3)
O(7)–U(1)–O(8)#1	72.2(3)	O(9)–U(2)–O(2)#2	78.9(3)
O(7)–U(1)–O(1)	75.4(3)	O(2)#2–U(2)–O(1)	70.3(3)

Symmetry codes: #1  $x, -y + 1/2, z + 1/2$ ; #2  $x, -y + 1/2, z - 1/2$ .

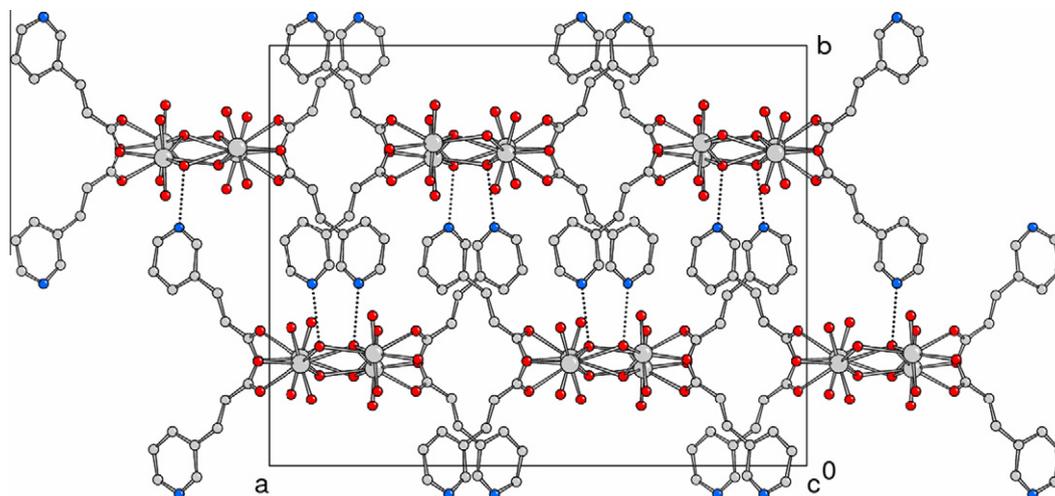


Fig. 4. Crystal packing of **2** viewed down axis *c* showing the H-bond interactions between the aqua ligands and pyridine N atoms.

Table 4  
Hydrogen bonds (Å, °).

D–H	<i>d</i> (D–H)	<i>d</i> (H···A)	<DHA	<i>d</i> (D···A)	A	
<b>Complex 2</b>						
O(1)–H(1)	0.98	1.82	173	2.794(15)	N(1)	$-x + 3/2, y + 1/2, z$
O(2)–H(2A)	0.98	1.82	169	2.793(16)	N(2)	$-x + 2, -y + 1, -z + 2$
<b>Complex 3</b>						
O(1w)–H(1)	0.85(6)	1.98(7)	167(9)	2.808(8)	O(2)	$x, -y + 3/2, z + 1/2$
O(1w)–H(2)	0.86(6)	2.36(8)	141(7)	3.078(8)	O(5)	$-x + 1, y + 1/2, -z + 3/2$

oxalate)( $\mu_2$ -OH) $_2$ (H $_2$ O) $_2$ ] $_n$ ·*n*H $_2$ O (**4**). The oxalate anion of the latter resulted by using the 5-methylisophthalic or 2,3-pyrazinedicarboxylic acid as reactant ligand. All the complexes have been determined by X-ray single crystal analysis, but the crystal structural determination of (**4**), showing a 2D layered network, has been already reported [57] and it will be not described.

#### 4.1. Structure description of [(UO $_2$ )(6-methylnicotinato) $_3$ ](H $_3$ O).4H $_2$ O (**1**)

The structure consists of discrete [(UO $_2$ )(6-methylnicotinato) $_3$ ] $^-$  complex anions located on crystallographic three-fold axes counterbalanced by H $_3$ O $^+$  cations. An ORTEP drawing of the complex is shown in Fig. 1 and a selection of bond lengths and angles is reported in Table 2. The UO $_2^{2+}$  unit is chelated by carboxylate groups of three 6-methylnicotinato ligands with U–O bond lengths of 2.457(12) and 2.507(16) Å, and a chelating angle of 54.2(4)°. These values, although at low accuracy, agree with those reported for analogous derivatives with benzoate [51–53], salicylate [54], *p*-aminosalicylate [55] and 2-aminobenzenecarboxylate [56]. The residuals in the  $\Delta F$  map were interpreted as disordered lattice water oxygens. In order to guarantee the electroneutrality we believe (see Section 2) that the partially occupied species O3w could be a H $_3$ O $^+$  cation, being at a short H-bond distance from the nicotinate nitrogen atom (N1···O3w = 2.79(3) Å). Beside this interaction, the crystal packing shows an H-bonding scheme occurring between the disordered water molecule O1w/O2w with carboxylate O4 (O···O 2.89 Å). Finally the packing evidences the presence of hydrophilic channels having diameter of ca. 9.7 Å and extending parallel to axis *c* filled by the disordered water molecules (Fig. 2). The same framework was also found in the salicylate [54] and *p*-aminosalicylate derivatives [55], where the tubular arrangement is occupied by water molecules and sodium ions, respectively.

#### 4.2. Structure description of [(UO $_2$ )(OH)( $\mu_2$ -3-pyridylpropionato)] $_n$ (**2**)

The X-ray structural characterization of **2** shows a 1D ladder-like coordination polymer running parallel to axis *c* and formed by (UO $_2$ ) $^{2+}$  units connected by  $\mu_3$ -OH groups (Fig. 3). Thus the pentagonal metal polyhedra are connected each other sharing two edges. The two crystallographic independent uranium atoms U1 and U2 constitute the side rails of the ladder and are alternatively separated by 3.881(1) and 3.934(1) Å, with an intermetallic angle of 65.95(2)°. In addition the ribbon is flanked by the 3-pyridylpropionato ligands bridging adjacent metals (Fig. 3). Both the indepen-

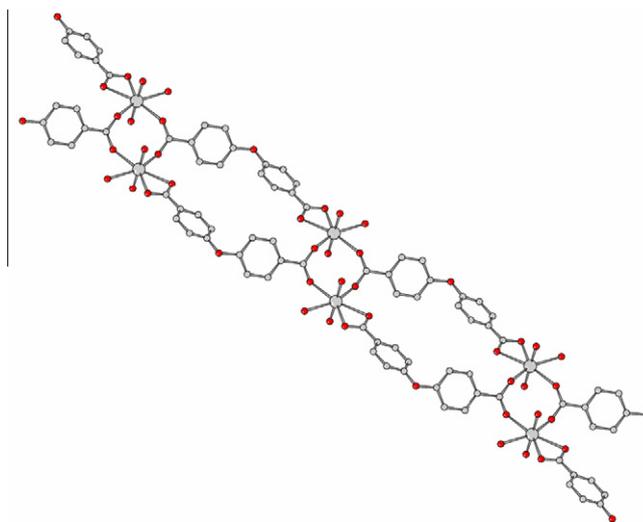


Fig. 5. The 1D coordination polymer of **3**.

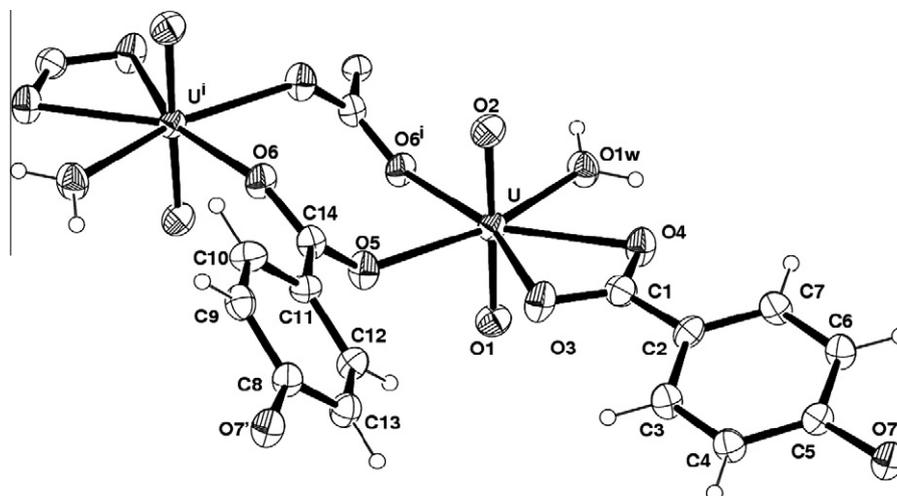


Fig. 6. Detail of the polymeric arrangement **3** showing the centrosymmetric eight-membered ring with labeling scheme of independent atoms.

dent U atoms are in a distorted pentagonal bipyramidal geometry being connected in the equatorial plane by three hydroxyl anions and two oxygens from different carboxylate groups. The U=O bond length values reported in Table 3 show comparable values for the two independent uranium atoms (range from 1.729(11) to 1.786(10) Å), following a trend as observed in all the compounds here presented. The U–O(hydroxo) and U–O(carboxylate) bond distances fall in between 2.356(8) and 2.447(8) Å and 2.349(10)–2.465(10) Å, respectively. Fig. 4 depicts the crystal packing that evidences strong H-bonds occurring between OH groups with py nitrogens of adjacent chains (OH...N of 2.79 Å, Table 4) that give rise to a 3D supramolecular structure.

#### 4.3. Structure description of $[(\text{UO}_2)(\text{H}_2\text{O})(\mu_3\text{-}4,4'\text{-oxybis(benzoato)})_n]$ (**3**)

The crystal structure comprises of 1D coordination polymers built by  $[\text{UO}_2(\text{H}_2\text{O})^{2+}]_2$  units connected by a pair of 4,4'-oxybis(benzoate) anions in a head-to-tail arrangement as shown in Fig. 5. In each organic moiety one carboxylate group acts as bridging, the other as chelating ligand towards the metals. This lead to 8- and 28-membered rings that alternate along the chain: in the former arrangement the metals are separated by 5.274 Å while the intermetallic distance spanned by the oxybis(benzoate) anion is 16.018(3) Å. The uranyl units are equatorially coordinated by five oxygen atoms, resulting in a pentagonal bipyramidal environment (Fig. 6). The almost linear  $\text{UO}_2^{2+}$  unit presents U=O distances of 1.758(5) and 1.770(5) Å (Table 5). The U–O bond distances of bridging carboxylate group are shorter (U–O5 = 2.322(5), U–O6 = 2.332(5) Å) in comparison with those of the chelating carbox-

ylate (U–O3 and U–O4 of 2.401(5) and 2.435(5) Å, respectively), and the U–O1w is even slightly longer (2.468(5) Å). The angle at oxygen of the oxybis(benzoate) connector presents an angle of 120.8(5)° and the phenyl rings form an a dihedral angle of 59.5(3)°. The aqua ligands act as H donors towards symmetry related oxygen atoms O2 and O5 of adjacent chains leading to a 3D structure, but the packing does not show  $\pi$ – $\pi$  interactions between phenyls.

## 5. Conclusion

In this paper we describe the crystal structure of three uranium organic frameworks (UOFs) having uranyl cation  $[\text{UO}_2]^{2+}$  as central species. The use of 6-methylnicotinato, 3-pyridylpropionato, and 4,4'-oxybis(benzoato) lead to a discrete complex and to two 1D uranium polymers, which expand their dimensionality to 3D supramolecular network through an extensive hydrogen bonding scheme.

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## Appendix A. Supplementary material

CCDC 758155–758157 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2010.06.043](https://doi.org/10.1016/j.ica.2010.06.043).

Table 5

Selected bond lengths (Å) and angles (°) of **3**.

U–O(1)	1.758(5)	U–O(3)	2.401(5)
U–O(2)	1.770(5)	U–O(4)	2.435(5)
U–O(5)	2.322(5)	U–O(1w)	2.468(5)
U–O(6)#1	2.332(5)		
O(5)–U–O(3)	77.20(18)	O(5)–U–O(3)	77.20(18)
O(1)–U–O(2)	178.7(3)	C(1)–O(3)–U	93.8(4)
O(3)–U–O(4)	54.21(17)	C(1)–O(4)–U	92.7(4)
O(4)–U–O(1w)	71.59(18)	C(14)–O(5)–U	136.8(5)
O(6)#1–U–O(1w)	74.53(19)	C(14)–O(6)–U#1	142.8(5)
O(5)–U–O(6)#1	82.58(19)		

Symmetry code: #1  $-x+1, -y+1, -z+1$ .

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