Nucleobase assemblies supported by uranyl cation coordination and other non-covalent interactions

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Abstract. We describe synthesis and solid state structural description of uranyl complexes of carboxylate functionalized adenine and uracil derivatives. The metal coordination through carboxylate pendant leads to the formation of dimeric assemblies, whereas the directional nature of hydrogen bonding interaction supported by nucleobases and aqua ligands, result in the generation of complex 3-D architectures containing embedded nucleobase ribbons.

Keywords. Adenine ribbon; uracil tetrad; uranyl complex; hydrogen bonding.

1. Introduction

Metal ion coordination and the use of non-covalent interactions, such as hydrogen bonding and $\pi-\pi$ stacking, are commonly employed to design inorganic–organic hybrid materials using smaller building blocks, which can be tuned for directionality of interaction and provide a scope of maximizing non-covalent interactions.[1–24] The supramolecular architectures generated from such ligands, at times decorated with suitable functionalities that further support metal-coordination and hydrogen bonding interactions, simultaneously, is of great relevance in achieving structural complexity. Thus, it is realized that the possibility of invoking more than one stabilizing interaction in a premeditated fashion ensures significant advantages over pure coordination polymers and affords versatile entry into interesting topologies.[25–37]

Heterocyclic nucleobases blend the possibility of stable metal ion coordination, while offering biologically relevant hydrogen bonding sites that could be eventually used for interactions with other biological macromolecules.[38,39] Thus, the use of nucleobases has indeed emerged as a much pursued area of research in bioinorganic chemistry.[40,41] We have a long-standing interest to explore metal coordination and hydrogen bonding capability of adenine nucleobases, for generating novel complex structures with interesting photophysical properties, for direct patterning of crystal structures on designed surfaces for AFM measurements and for achieving catalysis of certain chemical and biochemical reactions.[42–47] Recently, we have chemically attached nucleobases, such as adenine or uracil, to modify single-walled carbon nanotubes with coordinating ligands that can further interact with metal ions to reveal a new class of metalized nanotubes, with possible catalytic applications.[48–50]

In continuing our efforts to combine metal coordination and hydrogen bonding strategies, we studied crystallographic signatures of two nucleobase derivatives bearing carboxyl pendant: namely, 3-(N9-adeninyl) propanoic acid (**HL1**) and 3-(N1-uracilyl) propanoic acid (**HL2**) with uranyl cations $(UO_2)^{2+}$. Uranyl(VI) cations are known as hard Lewis acid centers and demonstrate selectivity for O-donors,[51–54] as suggested by numerous reports concerning uranyl-carboxylate or polycarboxylate frameworks.[55–64] Moreover, hybrid materials based on U(VI) metal center offer interest in terms of their unique properties and potential application in the areas associated with optics, magnetism, ion exchange and catalysis.[65] There are some instances where uranyl complexes have been used for catalysis of certain reactions.[66–71] In this context, we have demonstrated sunlight-mediated photolytic cleavage of nucleic acids by coordinated uranyl cations.[72] Another aspect of the study deals with the bio-coordination chemistry of U(VI) ions.[73] This paper aims to discuss the structural consequences observed for uranyl complexes of two nucleobase derivatives as shown in scheme 1.

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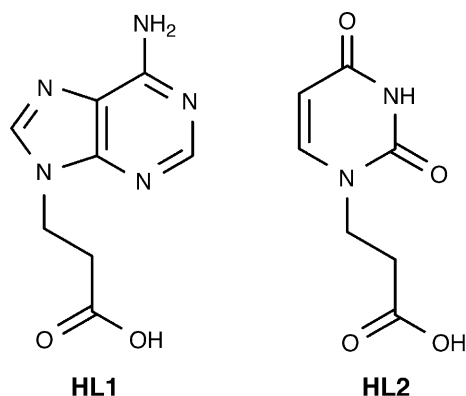
Scheme 1. Molecular structure of **HL1** and **HL2** ligands bearing carboxyl pendant.

2. Experimental

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

2.1 *Synthesis of 3-(N9-adeninyl) propanoic acid (HL1) and 3-(N1-uracilyl) propanoic acid (HL2)*

The synthesis and characterization of the ligands **HL1**[47] and **HL2**[48] used in the present study has already been discussed in our previous publications.

2.2 *Synthesis of complex 1 [$C_{16}H_{24}N_{10}O_{10}U$]*

HL1 (100 mg, 1.0 eq.), $UO_2(NO_3)_2 \cdot 6H_2O$ (121 mg, 0.5 eq.) and demineralized water (5 mL) were placed in a 10 mL Teflon liner stainless steel bomb and heated at 120°C for 5 days under autogenous pressure which afforded light yellow crystals of complex **1**. The product was recovered after filtration and washed with water (80 mg, 44% yield, based on U(VI) precursor). HRMS (ES+ mode): For complex **1** [2.**L1**+UO_2+H]$^+$ = calculated: 683.1840, found: 683.1843.

2.3 *Synthesis of complex 2 [$C_{14}H_{18}N_4O_{12}U$]*

HL2 (100 mg, 1.0 eq.), $UO_2(NO_3)_2 \cdot 6H_2O$ (136 mg, 0.5 eq.) and demineralized water (5 mL) were placed in a tightly closed 10 mL Teflon liner and heated at 100°C for 48 h under autogenous pressure which resulted in a clear light yellow solution. The solution was filtered and kept for slow evaporation which afforded block shape crystals of complex **2** after two week period

(55 mg, 30% yield, based on U(VI) precursor). For complex **2** [2.**L2**+UO_2+H]$^+$ = calculated: 637.1296, found: 637.1295.

2.4 *Crystal structure determination and refinement*

Crystals were coated with light hydrocarbon oil and mounted in the 100 K dinitrogen stream of a Bruker SMART APEX CCD diffractometer equipped with CRYO Industries low-temperature apparatus and intensity data were collected using graphite-monochromated Mo-Kα radiation. The data integration and reduction were processed with SAINT software.[74] An absorption correction was applied.[75] Structures were solved by the direct method using SHELXS-97 and refined on F^2 by a full-matrix least-squares technique using the SHELXL-97 program package.[76] Non-hydrogen atoms were refined anisotropically. In the refinement, hydrogens were treated as riding atoms using the SHELXL default parameters, however for the water molecules in both the crystal structures, the hydrogen atoms were located on Fourier map and refined freely though DFIX constrain were applied to fix the O–H distance.

3. Results and discussion

Block shape yellow coloured crystals of complex **1** [$C_{16}H_{24}N_{10}O_{10}U$] and **2** [$C_{14}H_{18}N_4O_{12}U$] were obtained *via* hydrothermal reaction by dissolving stoichiometric amounts of uranyl nitrate hexahydrate and **HL1** or **HL2** as described in the experimental section. X-ray crystallographic analysis revealed that complex **1** crystallized in a monoclinic space group $C\,2/c$, whereas complex **2** crystallized in a triclinic space group '$P-1$'. The asymmetric unit in both the cases consisted of a UO_2^{+2} ion of half-occupancy neutralized by either **L1** or **L2** anion, along with two and one water molecule, respectively (figure 1). The crystal structure refinement parameters for both the complexes are given in table 1.

Both of these complexes are zero-dimensional and exhibit formation of coordination complexes with a 1:2 M:L stoichiometry as shown in figure 1, where U(VI) center is connected to eight oxygen atoms and leading to a distorted hexagonal bipyramid geometry for U(VI) center. The axial sites of this hexagonal bipyramid are occupied by doubly bonded oxo ligands (namely O3 and O4 in case of **1**; O5 and its symmetry equivalent in case of **2**) with a shorter bond length and a linear O=U=O bond angle. The remaining four oxygen atoms are contributed by a pair of carboxylate group coordinated in bidentate chelate mode (O1, O2 and their symmetry equivalents in case of **1**; O3, O4 and their

(a)

(b)
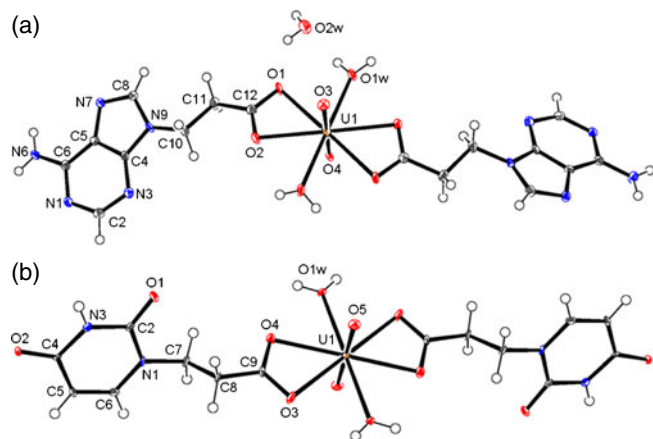
Figure 1. Molecular structure of complexes at 50% probability level with labelling of unique atoms: **(a)** for complex **1**, and **(b)** for complex **2**. Bond distances (in Å) for **1**: U–O1=2.494(3), U–O2=2.490(3), U–O3=1.785(4), U–O4=1.741(4), U–O1W=2.438(3) and for **2**: U–O3=2.473(6), U–O4=2.479(6), U–O5=1.771(6), U–O1W=2.470(6).

symmetry equivalents in case of **2**). Two C–O bond lengths of carboxylate groups are nearly equivalent being consistent with its binding mode (η–O,O′). The remaining two oxygen atoms are attributed to aqua ligands (O1W and its symmetry equivalents). Together, these six atoms make a hexagonal equatorial plane of the polyhedra around U(VI) center (see figure 1 caption for detailed bond geometries; selected bond lengths and bond angles for both the complexes are summarized in table 2). Interestingly, in complex **1,** an extra water molecule (O2W) is found trapped in the lattice as solvent of crystallization. The U(VI) atom in complex **1** lies on two-fold rotational axis along O=U=O bond, whereas in case of **2** it lies on the center of inversion.

Although, crystal lattice of both complexes consist only of L–M–L species, it is important to investigate the interaction of these basic units in the crystal lattice. The extended network of highly ordered H-bond connections, due to the presence of potential complementary hydrogen bonding sites like nucleobase moiety and H_2O molecules, give rise to complex 3-D frameworks that are worthy of detailed discussion. The important

Table 1. Crystal structure refinement parameters for the complexes **1** and **2**.

Identification code	Complex **1**	Complex **2**
Empirical formula	$C_{16}H_{24}N_{10}O_{10}U$	$C_{14}H_{18}N_4O_{12}U$
Mr	754.48	672.35
Crystal system	Monoclinic	Triclinic
Space group	$C\ 2/c$	$P\ -1$
a/Å	26.7030(4)	7.122(3)
b/Å	7.0740(2)	8.426(4)
c/Å	13.7080(4)	8.469(4)
α/°	90	79.253(4)
β/°	119.405(2)	79.751(5)
γ/°	90	70.624(3)
Volume/Å^3	2255.81(10)	467.3(4)
Z	4	1
Dx/Mg m^{-3}	2.222	2.389
$F(000)$	1448	318
μ/mm^{-1}	7.274	8.761
θ range for data collection/°	4.22 to 25.03	2.59 to 25.34
Limiting indices	$-26 \rightarrow h \rightarrow 31$, $-8 \rightarrow k \rightarrow 6$, $-16 \rightarrow l \rightarrow 15$	$-8 \rightarrow h \rightarrow 4$, $-10 \rightarrow k \rightarrow 9$, $-10 \rightarrow l \rightarrow 9$
Reflections collected	5482	2429
Unique reflections	1994	1662
R(int)	0.0387	0.0212
Completeness to θ	= 25.03, 99.4	= 25.34, 97.3%
Data/restraints/parameters	1994/4/181	1662/2/138
Goodness-of-fit on F^2	1.097	1.339
R1 and R2 [$I>2\sigma(I)$]	0.0248, 0.0569	0.0324, 0.0976
R1 and R2 (all data)	0.0284, 0.0586	0.0343, 0.1065
Largest diff. peak and hole/e.Å^{-3}	1.563 and -1.182	1.853 and -2.913

Table 2. Selected U–O bond lengths and O–U–O bond angles for complex **1** and **2**.[#]

Bond lengths (Å)		Bond angles (°)			
Complex 1					
U1–O1	2.494(3)	O1–U1–O1[i]	176.27(15)	O2–U1–O3	89.34(7)
U1–O1[i]	2.494(3)	O1–U1–O2[i]	128.35(10)	O2–U1–O4	90.66(7)
U1–O2	2.490(3)	O1–U1–O2	51.70(10)	O2–U1– O1W	115.73(11)
U1–O2[i]	2.490(3)	O1–U1–O3	91.86(7)	O2–U1–O1W[i]	64.28(11)
U1–O3	1.785(4)	O1–U1–O4	88.14(7)	O3–U1–O4	180.000(2)
U1–O4	1.741(4)	O1–U1–O1W	64.08(11)	O3–U1–O1W	90.29(8)
U1–O1W	2.438(3)	O1–U1–O1W[i]	115.90(11)	O4–U1–O1W	89.71(8)
U1–O1W[i]	2.438(3)	O2–U1–O2[i]	178.68(14)	O1W–U1–O1W[i]	179.42(16)
Complex 2					
U1–O3	2.473(6)	O3–U1–O3[ii]	180.0(3)	O4–U1–O5	87.8(2)
U1–O3[ii]	2.473(6)	O3–U1–O4	52.4(2)	O4–U1–O5[ii]	92.2(2)
U1–O4	2.477(6)	O3–U1–O4[ii]	127.6(2)	O4–U1–O1W	63.84(18)
U1–O4[ii]	2.477(6)	O3–U1–O5	90.1(2)	O4–U1–O1W[ii]	116.16(18)
U1–O5	1.771(6)	O3–U1–O5[ii]	89.9(2)	O5–U1–O5[ii]	180.000(1)
U1–O5[ii]	1.771(6)	O3–U1–O1W	116.26(19)	O5–U1–O1W	88.3(2)
U1–O1W	2.470(6)	O3–U1–O1W[ii]	63.74(19)	O5–U1–O1W[ii]	91.7(2)
U1–O1W[ii]	2.470(6)	O4–U1–O4[ii]	180.0(2)	O1W–U1–O1W[ii]	180.000(1)

[#] Symmetry transformation (i) −x, y, 1.5−z; (ii) 2−x, 2−y, −z

parameters of these H-bonds for both the complexes are summarized in table 3.

3.1 *Crystal structure analysis of 1*

The part of the crystal lattice of **1** built around uranyl polyhedron is shown in figure 2 and crystal structure analysis shows the crucial role played by hydrogen bonding interactions, involving adenine and coordinated/non-coordinated water molecule, on overall crystal packing.

The monoanionic ligand **L1** adopts *anti*-conformation with respect to C10–C11, with a torsion angle of 174.8° between adenine and carboxylate moiety. Thus, adenine residues are protruded in an

Table 3. Hydrogen bonding table for complexes **1** and **2**.[#]

D–H···A	Symmetry of A	d_{D-H}	$d_{H···A}$	$d_{D···A}$	∠D–H···A
Complex 1					
N6–H6A···O2W	1/2−x, 1/2−y, −z	0.86	2.19	3.032(6)	166
N6–H6B···N3	x, 1−y, −1/2+z	0.86	2.20	2.911(5)	140
O1W–H1W1···O2W	−x, 1−y, −z	0.79(3)	1.99(3)	2.771(5)	168(5)
O1W–H2W1···N1	−1/2+x, 1/2+y, z	0.80(5)	1.95(5)	2.741(6)	170(5)
O2W–H1W2···O1	−x, 1−y, −z	0.80(4)	2.08(6)	2.774(6)	145(5)
O2W–H2W2···N7	x, 1−y, 1/2+z	0.81(4)	2.01(4)	2.796(5)	165(8)
C8–H8···O3	−x, 2−y, −z	0.93	2.53	3.429(6)	162
C11–H11A···O3	−x, 2−y, −z	0.97	2.55	3.497(5)	164
Complex 2					
N3–H3···O2	1−x, −y, 1−z	0.86	1.96	2.793(9)	162
O1W–H1W···O2	1−x, 1−y, 1−z	0.82(8)	2.09(8)	2.822(9)	148(9)
O1W–H2W···O2	1+x, 1+y, z	0.82(14)	2.04(13)	2.821(9)	160(14)
C5–H5···O1	−1+x, y, z	0.93	2.35	3.196(11)	151
C6–H6···O1W	−1+x, y, z	0.93	2.58	3.409(10)	148
C6–H6···O4	−1+x, y, z	0.93	2.53	3.343(11)	146
C8–H8B···O5	−1+x, y, z	0.97	2.48	3.294(12)	141

[#] Where 'D' is donor and 'A' is acceptor; the bond lengths are in (Å) and angles are in (°)
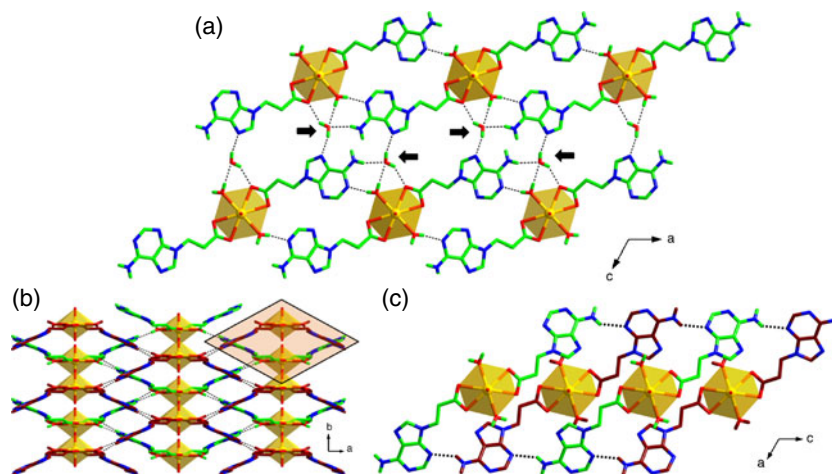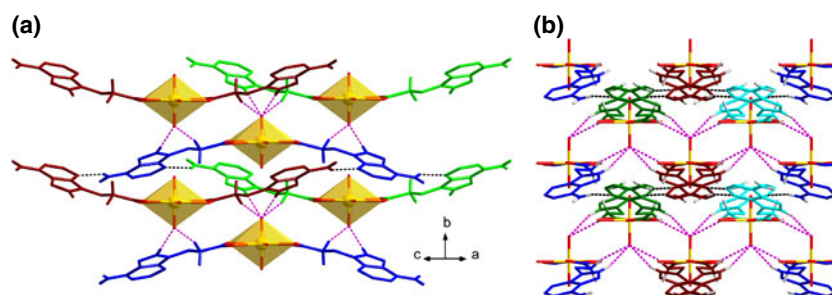
Figure 2. **(a)** Part of the crystal lattice of complex **1** showing hydrogen bonding network (solvent water molecule involved in quadruple H-bond has been highlighted with arrow); **(b)** view of H-bonded 3-D crystal lattice showing orientation of different adenine residues, with respect to U(VI) polyhedron, highlighted with different colour; **(c)** view of highlighted portion in 'b' showing embedded adenine ribbon running along *c*-axis (colour code: green or brown-C or H, blue-N, red-O and yellow-U).

outward direction, however they are not oriented in an anti-parallel fashion as they lie on the same side of the uranium polyhedra as can be seen from figure 2b. For the better understanding of various H-bonding schemes, the lattice has been discriminated on the basis of orientation of adenine residues, with respect to the uranyl polyhedral, as represented with two different colour codes. This orientation of adenine residues allows hydrogen bonding interaction between N3 nitrogen and one of the exocyclic amino hydrogen i.e., N6–H6B$\cdots$N3 ($d_{H\cdots N}$ = 2.20 Å) to take place. As a consequence, it results in an array of adenine ribbon-like arrangement, propagating along *c*-axis as shown in figure 2c. Adenine ribbons through Watson–Crick and Hoogsteen type base pairing have been reported,[77–79] but in the present example the involvement of Watson–Crick or Hoogsteen face is not invoked for the generation of adenine ribbons. Instead, interplay of metal-coordination and hydrogen bonding interaction between exocyclic amino group and ring nitrogen is solely responsible for such architecture.

Significant interaction rendered by water molecules was also observed in the lattice. The coordinated aqua ligand O1W forms a pair of O1W–H2W1$\cdots$N1 ($d_{H\cdots N}$ = 1.95(5) Å) and O1W–H1W1$\cdots$O2W ($d_{H\cdot O}$ = 1.99(3) Å) hydrogen bonds with adenine residues and with non-coordinated lattice water molecules (O2W), respectively. This results in an increase in the dimensionality of the crystal structure. It is interesting to note the role played by lattice water molecule O2W in complex **1**,

which is involved in multiple hydrogen bonding interactions (double donor and acceptor), as shown with a black arrow in figure 2a. The O2W molecule acts as a donor for O1 oxygen of coordinated carboxylate group (O2W–H1W2$\cdots$O1; $d_{H\cdots O}$ = 2.08(6) Å) and adenine N7 nitrogen (O2W–H2W2$\cdots$N7; $d_{H\cdots N}$ = 2.01(4) Å), whereas it acts as an acceptor for coordinated aqua ligand O1W and remaining exocyclic amino hydrogen (N6–H6A$\cdots$O2W; $d_{H\cdots O}$ = 2.19 Å). All these H-bond interactions eventually generate a complex 3-D assembly while providing added strength to the lattice. Recently, the complexation behaviour of **L1** ligand along with other modified adenine ligands towards Co(II) center was reported by us.[80]

It is indeed noteworthy to mention that both oxo-atoms occupying the axial site of uranyl polyhedra, i.e., O3 and O4, are crystallographically non-equivalent and one of them (O3) displays weak C–H$\cdots$O interaction with C8–H of adenine and C11–H present in the linker. Probably, because of the electron affinity of the carboxylate group adjacent to this carbon atom (C11), its H-atoms are relatively acidic and prone to be involved in sp^3–C-H$\cdots$O-M interactions.[81] In complex **1**, we observed that O3 atoms also acts as H-bond acceptor for two C–H sites [C8–H ($d_{H\cdots O}$ = 2.53 Å) and C11–H ($d_{H\cdots O}$ = 2.55 Å)] as shown in figure 3. The distances for these C–H$\cdots$O interactions are within the sum of their van der Waals radii of 1.72 Å. Such weak C–H$\cdots$O interaction are significant for the stabilization of complex structures and they have been successfully

Figure 3. (a) Part of the crystal lattice of complex **1** showing C–H···O interactions connecting one of the axial oxygen atom of the uranyl polyhedra with C8–H and C11–H atoms as shown with pink fragmented bonds; (b) view of the crystal lattice close to *a*-axis showing 2-D network along (011) plane.

exploited in crystal engineering and material science.[82–85] Together with N–H···N interactions, this C–H···O interaction allows connectivity between different L–M–L units consequently resulting in a 2-D network along the (011) plane (figure 3b). The other crystal stabilizing interaction comes from π–π stacking between adenine residues with a centroid separation of 3.37 Å.

### 3.2 *Crystal structure analysis of 2*

Part of the crystal lattice of **2** is shown in figure 4 where uracil moieties and coordinated aqua ligands
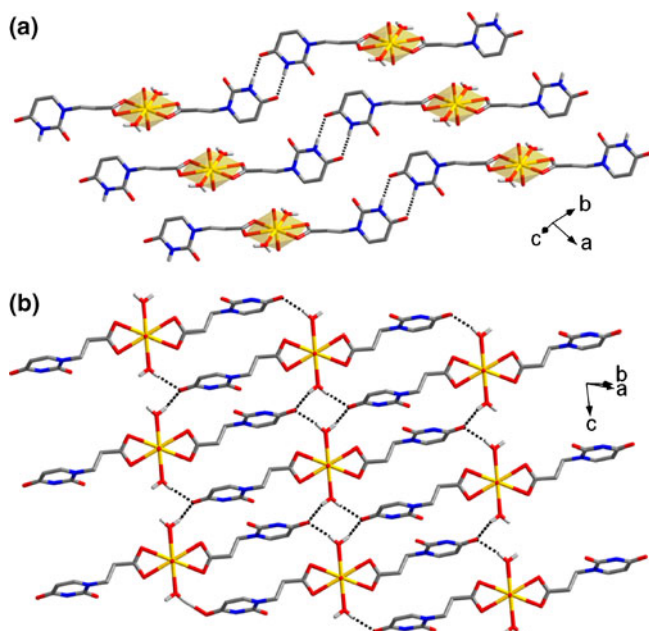
Figure 4. (a) Self-association of uracil moiety *via* H-bonding in case of **2**; (b) Interaction between uracil moiety and coordinated aqua ligands along *c*-axis (H-bonds are shown with fragmented black bonds) (colour code: gray-C; light gray-H, blue-N, red-O and yellow-U).

decipher intricate H-bonding schemes to influence overall supramolecular assembly. The monoanionic ligand **L2** adopts *anti*-conformation along C7–C8 bond with a torsion angle of 171.9°, between uracil and carboxylate moiety, similar to **1**. Careful analysis of the crystal lattice shows that uracil moieties of different L–M–L species self-associate *via* strong N3–H3···O2 ($d_{H···O}$ = 1.96 Å) interaction through the Watson–Crick face, in a phenomenon known for the uracil moiety,[86,87] which eventually results in the formation of 1D polymeric species as depicted in figure 4a. Interestingly, the coordinated aqua ligand interacts with O2 oxygen atoms of different uracil moieties along *c*-axis as shown in figure 4b. The donor-acceptor distances for both the hydrogen atoms present on the aqua ligand, O1W–H1W···O2^i (i=1−x, 1−y, 1−z) and O1W–H2W···O2^{ii} (ii=1+x, 1+y, z), are almost similar with $d_{O···O}$ = 2.82 Å indicating comparable interactions from both the sides. Thus, O2 oxygen simultaneously acts as an H-bond acceptor for three different centers, where two are aqua ligands and the third one is uracil NH hydrogen. The N3-H···O2 and O1W-H···O2 interactions are almost perpendicular to each other as visualized by comparing figure 4a and figure 4b.

Further stabilization of the crystal lattice in **2** comes from various C–H···O interactions similar to **1**. Notably, the remaining carbonyl oxygen (O1) of uracil moiety interacts with C5–H ($d_{C5–H5···O1}$ = 2.35 Å), which results in the formation of neatly packed uracil ribbon structure running along *a*-axis, as shown in figure 5. An interesting aspect of the lattice structure concerns formation of a homouracil tetrad structure where four uracil moieties interact with each other by utilizing N3–H and C5–H as hydrogen bond donors, while pyrimidine carbonyl oxygens O1 and O2 act as hydrogen bond acceptors (figure 5).[88,89] The L–M–L species constituting the tetrad structures are further reinforced
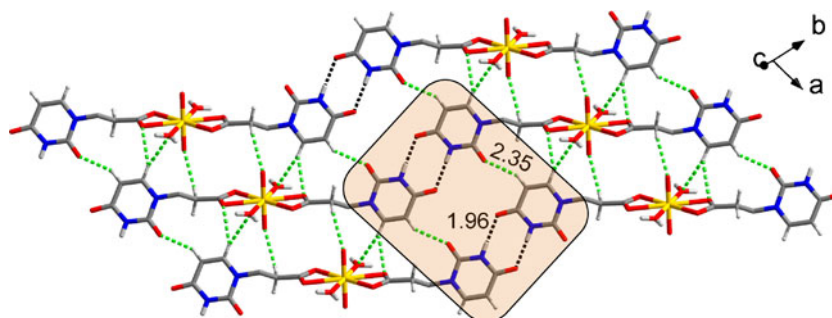
Figure 5. Crystal lattice of **2** showing neatly packed uracil ribbons running along *a*-axis, with an embedded homouracil tetrad structure (boxed); C–H···O interactions are shown with green fragmented bonds (bond lengths are in Å).

through a variety of C-H···O interactions as shown in figure 5 (also see table 3). Thus, uracil–uracil interaction to generate uracil ribbon extends the lattice in two-dimensions close to the (110) plane, whereas the participation of aqua ligands in H-bonding further increases the dimensionality to generate a 3-D network.

4. Conclusion

In conclusion, we have synthesized and investigated uranyl complexes of carboxylic acid functionalized adenine and uracil analogues. This exercise expands the coordination space provided by unmodified adenine and uracil moieties and relies on stable interactions achieved with U(VI) and carboxylate functionality. It was observed that H-bonding schemes offered by nucleobase analogs, in addition to the presence of carboxylate groups supporting metal coordination, results in complex 3D-crystal lattice structures. An interesting interplay of variety of H-bonding interactions also generates embedded nucleobase ribbons as a part of larger three-dimensional framework supported by weak interactions.

Supporting information

X-ray crystallographic data in CIF format are given. CCDC contains the supplementary crystallographic data for this paper with a deposition number of CCDC **827791** (complex **1**) and **827792** (complex **2**). Copies of this information can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK. [Fax: +44–1223/336–033; e-mail: deposit@ccdc.cam.ac.uk].

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