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Article

(6,3)-Honeycomb Structures of Uranium(VI) Benzenedicarboxylate Derivatives: The Use of Noncovalent Interactions to Prevent Interpenetration

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Four two-dimensional coordination polymers containing the uranyl cation (UO_2^{2+}), $(NH_4)UO_2(BDC)_{1.5}\cdot 2.5H_2O$ (**1**), $KUO_2(NDC)_{1.5}\cdot 2H_2O$ (**2**), $[C(NH_2)_3]UO_2(NDC)_{1.5}\cdot 2H_2O$ (**2b**), and $UO_2(HBDC\text{–}Br)_2$ (**3**) (BDC = 1,4-benzenedicarboxylate, NDC = 1,4-naphthalenedicarboxylate, BDC–Br = 2-bromoterephthalate) have been synthesized by hydrothermal reactions. Compounds **1**–**2b** have the same honeycomb (6,3) net but with two-fold interpenetration in **1** and without interpenetration in **2** and **2b**. The use of 2-bromoterephthalate yields compound **3** with a (4,4) net. The structures of **2** and **2b** show that the interpenetration can be prevented by the addition of a bulky substituent to the ligand. Maintaining the desired topology, however, requires a careful choice of the substituent group. Compounds **1**, **2**, and **2b** have a similar structural arrangement to that of benzenetricarboxylic acid (trimesic acid, H_3BTC). In H_3BTC, the six rings are formed by hydrogen bonding and the interpenetration is more complex than that in **1**. Crystal data: **1**, triclinic, space group $P\bar{1}$, $a = 10.453(8)$ Å, $b = 12.316(9)$ Å, $c = 13.441(10)$ Å, $\alpha = 78.49(1)°$, $\beta = 82.17(1)°$, $\gamma = 85.57(1)°$, and $Z = 4$; **2**, monoclinic, space group $C2/c$, $a = 12.7795(9)$ Å, $b = 19.728(1)$ Å, $c = 15.379(1)$ Å, $\beta = 92.247(1)°$, and $Z = 8$; **2b**, monoclinic, space group $C2/c$, $a = 12.7214(8)$ Å, $b = 19.645(1)$ Å, $c = 17.065(1)$ Å, $\beta = 98.896(1)°$, and $Z = 8$; **3**, monoclinic, space group $P2_1/c$, $a = 7.873(5)$ Å, $b = 18.358(14)$ Å, $c = 6.893(5)$ Å, $\beta = 115.96(2)°$, and $Z = 2$.

Introduction

Inorganic–organic hybrid compounds have been studied for their potential applications as new functional materials and because of their structural diversity.[1] One strategy for constructing frameworks is to combine molecular building blocks with a rigid bridging ligand to form extended structures analogous to known simple hydrogen-bonded organic networks.[2] Often, the crystal structures of organic compounds contain honeycomb networks because of the availability of three-coordinated vertices. In transition-metal coordination polymers, trigonal and trigonal-bipyramidal coordination geometries are known but are less common.[3]

At present, we are investigating the synthesis of framework structures formed by reactions of the uranyl cation UO_2^{2+} and both inorganic and organic bridging ligands. Many inorganic frameworks containing UO_2^{2+} have been reported, particularly those with oxygen donor groups, where the uranyl cation adopts square, pentagonal, or hexagonal-bipyramidal coordination geometry.[4] In contrast, relatively few extended uranyl frameworks containing organic ligands are known.[5]

In the construction of hybrid frameworks, aromatic polycarboxylates, for example, 1,4-benzenedicarboxylate (BDC), are commonly used as bridging ligands because they are sterically rigid and chemically robust[6] and can adopt mono-

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dentate or chelating coordination modes.[7] For example, in the square-grid network of $UO_2\cdot$opyca (where opyca is 1-oxo-4-carboxypyridine), two kinds of opyca ligands are present; the carboxylate group is monodentate in one and bidentate in the other.[8]

Here, we show that the combination of BDC in which both carboxylate groups are bidentate, with the hexagonal-bipyramidal $UO_2O_{6/2}$ building unit providing two- and three-coordinated vertices and leading to the formation of a uranium 1,4-benzenedicarboxylate, $NH_4UO_2BDC_{1.5}\cdot 2.5H_2O$ (**1**), with a layer structure based on two-fold interpenetrated (6,3) nets. It is well-known that metal−organic framework structures possessing large voids tend to form with interpenetrated or entangled topologies. Preventing interpenetration is a challenge to obtaining a high surface area and porosity, although recently, several interpenetrating frameworks with highly porous structures have been reported.[9] We have investigated different approaches to preventing the interpenetration of the layers found in $NH_4UO_2BDC_{1.5}\cdot 2.5H_2O$ by modification of the BDC linker with bulky substituents. This strategy is successful using 1,4-naphthalenedicarboxylic acid (NDC), $KUO_2NDC_{1.5}\cdot 2H_2O$ (**2**), and $[C(NH_2)_3]UO_2NDC_{1.5}\cdot H_2O$ (**2b**), but the use of 2-bromoterephthalic acid results in a different structure that is stabilized by the hydrogen bond to the bromine substituent, $UO_2(HBDC{-}Br)_2$ (**3**).

Experimental Section

Materials and Methods. All the reactants were reagent grade and used as purchased without further purification. The infrared spectra were measured on a Galaxy Series FTIR 5000 spectrometer with pressed KBr pellets. Thermal analyses were performed on a TGA V5.1A Dupont 2100 instrument from room temperature to 600 °C with a heating rate of 3 °C/min in air.

Synthesis of $NH_4UO_2(1,4\text{-}BDC)_{1.5}\cdot 2.5H_2O$ (1). A mixture of $UO_2(OAc)_2\cdot 2H_2O$ (0.12 mmol, 50 mg), 1,4-dicyanobenzene (0.24 mmol, 30.7 mg), and H_2O (0.5 mL) was heated in a 23 mL stainless steel reactor with a Teflon liner at 160 °C for 3 days. The yellow block-shaped crystals were filtered and washed with water and acetone. Yield: 79.3% based on uranium. Anal. Calcd for $C_{12}H_{15}NO_{10.5}U$: C, 24.88; H, 2.61; N, 2.42. Found: C, 24.47; H, 2.76; N, 2.44. IR (KBr): 3737.6m (br), 1643.1w, 1533.1s, 1510.0m, 1405.9vs, 1315.2w, 1153.2w, 1106.9w, 1012.5w, 925.7m, 883.2w, 844.7s, 813.8w, 746.3m, 686.5w, 532.3w cm^{-1}.

Synthesis of $KUO_2(1,4\text{-}NDC)_{1.5}\cdot 2H_2O$ (2). A mixture of $UO_2(NO_3)_2\cdot 6H_2O$ (0.21 mmol, 83 mg), 1,4-naphthalenedicarboxylic acid (0.42 mmol, 91 mg), KOH (0.84 mmol, 47.1 mg), and H_2O (1.0 mL) was heated in a 23 mL stainless steel reactor with a Teflon liner at 150 °C for 24 h. The yellow block-shaped crystals were filtered and washed with water and acetone. Yield: 62.0% based on uranium. Anal. Calcd for $C_{18}H_{13}KO_{10}U$: C, 32.72; H, 1.97. Found: C, 32.26; H, 1.71. IR (KBr): 3609.14w, 3436.54w (br), 1636.31w, 1594.85w, 1531.21s, 1459.85s, 1416.46vs, 1363.43s, 1261.22m, 1204.33w, 1163.83w, 1039.45w, 923.74s, 877.45w, 841.78s, 785.85m, 743.24w, 670.14w, 594.93m, 572.75m, 520.68w, 445.47m cm^{-1}.

Synthesis of $[C(NH_2)_3]UO_2(1,4\text{-}NDC)_{1.5}\cdot H_2O$ (2b). A mixture of $UO_2(NO_3)_2\cdot 6H_2O$ (0.21 mmol, 83 mg), 1,4-naphthalenedicarboxylic acid (0.42 mmol, 91 mg), KOH (0.84 mmol, 47.1 mg), $[C(NH_2)_3]NO_3$ (guanidine nitrate, 0.42 mmol, 51 mg), and H_2O (1.0 mL) was heated in a 23 mL stainless steel reactor with a Teflon liner at 150 °C for 12 h. The yellow block-shaped crystals were filtered and washed with water and acetone. Yield : 65.0% based on uranium. Anal. Calcd for $C_{19}H_{17}N_3O_9U$: C, 34.09; H, 2.56; N, 6.28. Found: C, 34.47; H, 2.69; N, 6.25. IR (KBr): 3638.1w, 3367.6m (br), 3187.8s (br), 1680.7s, 1666.2s, 1610.3w, 1593.9w, 1533.1s, 1518.7w, 1460.8m, 1420.3s, 1363.4s, 1263.2m, 1207.2w, 1166.7w, 1156.1w, 10338.5w, 1026.9w, 968.1w, 934.3s, 891.0w, 877.5w, 843.7s, 788.7m, 751.1w, 671.1w, 601.7w, 587.2m, 566.1m, 443.6m, 418.5w cm^{-1}.

Synthesis of $UO_2(HBDC{-}Br)_2$ (3). A mixture of $UO_2(NO_3)_2\cdot 6H_2O$ (0.21 mmol, 83 mg), 2-bromo-1,4-benzenedicarboxylic acid (0.42 mmol, 103 mg), H_2O (1.6 mL), and ethanol (0.16 mL) was heated in a 23 mL stainless steel reactor with a Teflon liner at 150 °C for 24 h. The yellow elongated square-pyramidal crystals were filtered and washed with water and acetone. Yield: 53.7% based on uranium. Anal. Calcd for $C_{16}H_8Br_2O_{10}U$: C, 25.35; H, 1.06. Found: C, 25.68; H, 1.02. IR (KBr): 3066.3m (br), 2898.5w, 2477.3w, 1959.3w, 1841.7w, 1673.9vs, 1570.7s, 1544.7vw, 1529.3m, 1481.1m, 1431.9w, 1403.0s, 1371.1m, 1284.4w, 1261.2vw, 1246.8s, 1157.1w, 1145.5w, 1043.3w, 980.6w, 944.0s, 884.2m, 866.9w, 827.3m, 816.7m, 794.5w, 755.0m, 706.8m, 693.3m, 671.1w, 582.4w, 533.2m, 515.0m cm^{-1}.

Crystallographic Studies. Single crystals of suitable dimensions for **1**−**3** were used for the structure determinations. All measurements were made with a Siemens SMART platform diffractometer equipped with a 1 K CCD area detector. A hemisphere of data (1271 frames at 5 cm detector distance) was collected for each phase using a narrow-frame method with scan widths of 0.3° in ω and an exposure time of 30−45 s/frame. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability, and the maximum correction applied to the intensities was <1%. The data were integrated using the Siemens *SAINT* program,[10] with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. The structures were solved by direct methods and refined on F^2 by full-matrix least squares using *SHELXTL*.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically with geometric constrains. The structure of $(UO_2)(BrC_8H_4O_4)_2$ was refined with a merohedral twin model in space group $P2_1/c$ with the twin mirror plane (1, 0, −2) that is parallel to the structural layers. The volume ratio of the twin components was refined to 0.48(1)/0.52. Since this ratio is close to 0.5, the crystal approaches the space group symmetry *Cmca* with the orthorhombic unit cell $a = 6.893$, $b = 14.157$, and $c = 18.358$ Å. Refinements of a highly disordered structure model in this orthorhombic unit cell led to "nonpositive definite thermal parameters" for most of the atoms. Crystal data for the compounds **1**−**3** are summarized in Table 1.

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Table 1. Crystallographic Data for Compounds **1**−**3**

	1	**2**	**2b**	**3**
chemical formula	$C_{12}H_{15}NUO_{10.5}$	$C_{18}H_{13}KUO_{10}$	$C_{19}H_{17}N_3UO_9$	$C_{16}H_8Br_2UO_{10}$
fw	579.28	666.41	669.39	758.08
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$C2/c$	$P2_1/c$
a, Å	10.453(8)	12.7795(9)	12.7214(8)	7.873(5)
b, Å	12.316(9)	19.728(1)	19.645(1)	18.358(14)
c, Å	13.441(1)	15.379(1)	17.065(1)	6.893(5)
α, deg	78.49(1)			
β, deg	82.17(1)	92.247(1)	98.896(1)	115.96(2)
γ, deg	85.57(1)			
V, Å^3	1678(2)	3874.3(5)	4213.4(5)	895.8(11)
Z	4	8	8	2
T, K	293(2)	293(2)	296(2)	273(2)
ρ_c, g cm^{-3}	2.284	2.192	2.085	2.803
μ(Mo Kα), mm^{-1}	9.730	8.649	7.761	13.577
R1, wR2 [$I > 2\sigma(I)$]^a	0.0275, 0.0610	0.0261, 0.0666	0.0272, 0.0609	0.0482, 0.0881
R1, wR2 (all data)^a	0.0423, 0.0657	0.0330, 0.0689	0.0451, 0.0672	0.0957, 0.0990

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)_2/\Sigma w(F_o^2)^2]^{1/2}$.

Results and Discussion

Synthesis. The hydrolysis of 1,4-dicyanobenzene and reaction with $UO_2(OAc)_2 \cdot 2H_2O$ under hydrothermal conditions gave compound **1**, $NH_4UO_2(BDC)_{1.5} \cdot 2.5H_2O$. The in situ hydrolysis reaction of cyanide to carboxylate provides an excellent synthetic route to this compound as well as to the formation of single crystals with suitable size for X-ray study, as previously reported for other compounds.[12] The chemical analysis of **1** indicates the presence of nitrogen, and consequently, the negative $[UO_2(BDC)_{1.5}]^-$ layer charge balance is assumed to be compensated by NH_4^+ formed by the hydrolysis of dicyanobenzene. We were unable to synthesize **1** by using H_2BDC directly. Reactions at different pH values gave small amounts of amorphous yellow powders and mostly recrystallized H_2BDC. Compound **1** was obtained in crystalline form when Na_2BDC and $UO_2(NO_3)_2 \cdot 6H_2O$ were used as the reactants, but substantial amounts of a yellow microcrystalline impurity phase were also present in the product. The hydrothermal reaction of 1,4-naphthalenedicarboxylic acid (H_2NDC) with $UO_2(NO_3)_2 \cdot 6H_2O$ in the presence of KOH gave compound **2**, $KUO_2(NDC)_{1.5} \cdot 2H_2O$. Guanidine nitrate was added to the synthesis for **2**, as both a charge-balancing component and in an attempt to template an open channel. The synthesis, however, yielded compound **2b**, $[C(NH_2)_3][UO_2(1,4\text{-}NDC)_{1.5}] \cdot H_2O$ with a structure closely related to that of **2**. The hydrothermal reaction of 2-bromoterephthalic acid ($H_2BDC{-}Br$) with $UO_2(NO_3)_2 \cdot 6H_2O$ in a H_2O/EtOH mixture gave compound **3**, $UO_2(HBDC{-}Br)_2$. The use of a small amount of ethanol plays a critical role in the formation of this compound. The same reaction conditions used for **2** and **2b** gave compound **3** with a small amount of unreacted ligand, and the product contains aggregated small crystallites.

Crystal Structures. The structures of compounds **1**−**3** all contain two-dimensional layers in which UO_2 cations are linked by benzenedicarboxylate anions. The layers of **1**, **2**, and **2b** as determined from the analysis of X-ray single-crystal data are based on a (6,3) net (Figure 1) with two-fold interpenetration in **1** and without interpenetration in **2** and **2b**. Compounds **2** and **2b** are isostructural except that the potassium cation in **2** is replaced by the guanidinium cation in **2b**. In contrast, compound **3** is based on a (4,4) net where uranyl centers are bridged by a BDC−Br ligand with two different coordination modes.

Compounds 1, 2, and 2b. The coordination environment of the uranium centers in **1**−**2b** are identical. The uranium atoms adopt slightly distorted hexagonal-bipyramidal geometries with the uranyl (UO_2^{2+}) oxygen atoms at the apexes. The short U−O_{axial} bond lengths range between 1.753(12) and 1.765(14) Å for **1**, 1.751(4) to 1.774(3) Å for **2**, and 1.756(4) to 1.757(4) Å for **2b**, in good agreement with the reported average uranyl bond length of 1.758(4) Å. The O−U−O bond angles in the uranyl cations in compound **1** are 178.5(2)° for U1 and 179.1(2)° for U2. In compounds **2** and **2b**, the O−U−O bond angles are 179.7(2)° and 178.6(2)°, respectively. In the equatorial plane, each uranium atom is coordinated by six carboxylate oxygen atoms from three chelating dicarboxylate ligands. The adjacent uranyl cations are bridged by a BDC (**1**) or NDC (**2** and **2b**) ligand. The U−O equatorial bond distances are longer than the axial distances and range from 2.423(19) to 2.504(19) Å for **1**, 2.394(3) to 2.535(3) Å for **2**, and 2.426(3) to 2.553(3) Å for **2b**. The O−U−O bond angles in the equatorial plane, compared to the ideal 60° for a regular hexagonal arrangement, range from 52.0(1)° to 52.7(1)° for **1**, 51.6(1)° to 52.8(1)° for **2**, and 51.8(1)° to 52.3(1)° for **2b**.

In the extended structure, the building units are arranged to generate hexagonal open motifs, which have a large cavity/channel of ca. 22.4−23.1 Å (Figure 1) in **1** and ca. 14.8 Å in **2** and **2b**. The layer in **1** is not flat but adopts a chair configuration with a bend angle of 163.85(2)°, as shown in Figure 2. The bending of the layer is necessary to accommodate the interpenetration of a second layer. Two opposite edges of a six ring in one layer pass through the center of a six ring of the other layer as shown schematically in Figure 3. The resulting structure shows one of four modes of two-

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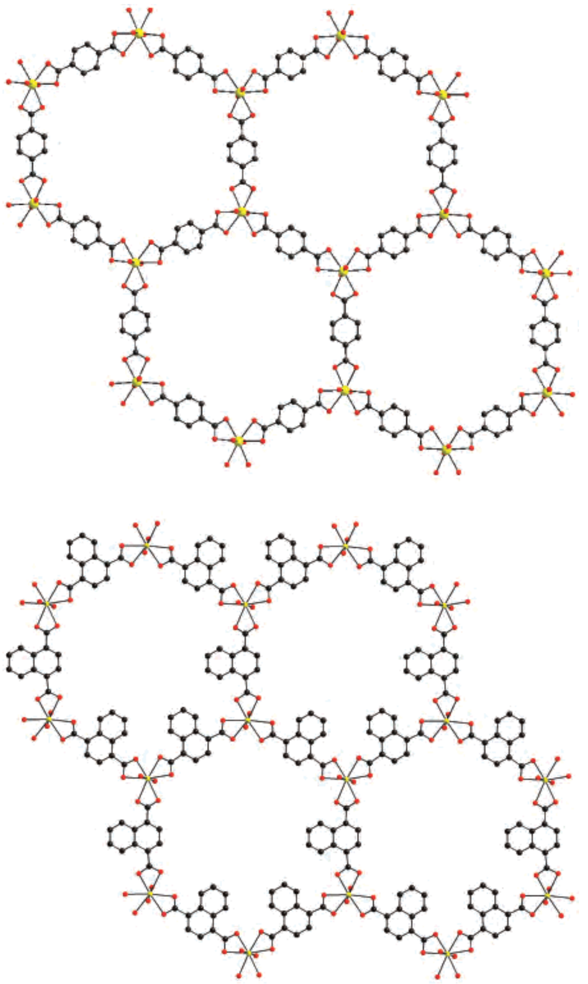

Figure 1. Single layer of the structure of **1** (top) and of **2** and **2b** (bottom). Hydrogen atoms, charge-balancing cations, and guest water molecules are omitted for clarity. U, O, and C atoms are represented by yellow, red, and gray spheres, respectively.

Figure 2. Edge-on view of a single hexagonal unit in **1** showing the chair conformation. U, O, and C atoms are represented by yellow, red, and gray spheres, respectively.

fold parallel interpenetration as discussed by Batten et al.[13] Adjacent double layers in **1** are stacked together, with the disordered guest species located between the layers.

As shown in Figure 3b, compounds **2** and **2b** have a noninterpenetrated (6,3) net and the layers are almost flat with bend angles of 173.77(0)° and 177.12(0)°, respectively. The layers are stacked by $\pi-\pi$ interactions between each NDC ligand from an adjacent layer (Figure 4); the framework stability in this case is maintained by noncovalent interactions instead of by interpenetration.

The space in the six-membered ring is partially occupied by cations (K in **2** and $C(NH_2)_3$ in **2b**), guest water molecules, and three of six extra phenyl rings on the NDC ligands that are directed inside the net. The space available for interpenetration is therefore limited, and the layers in preference adopt a $\pi-\pi$ stacking arrangement to stabilize the overall framework.

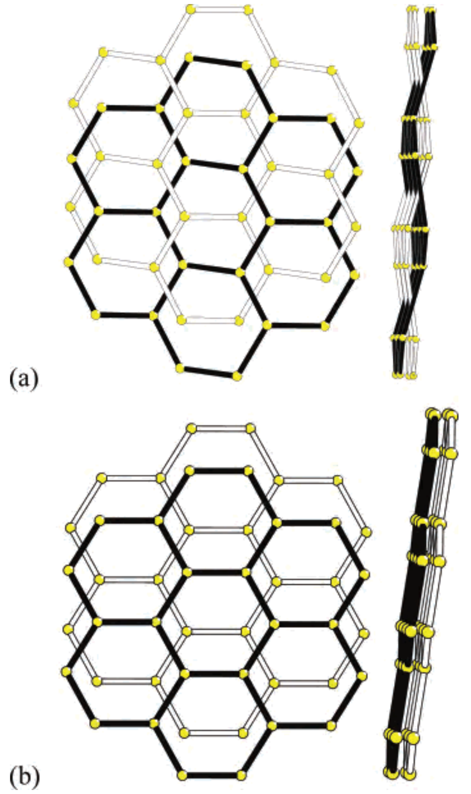

Figure 3. Schematic representation of the two-fold interpenetration of the layers in **1** (a) and the layer stacking without interpenetration in **2** and **2b** (b).

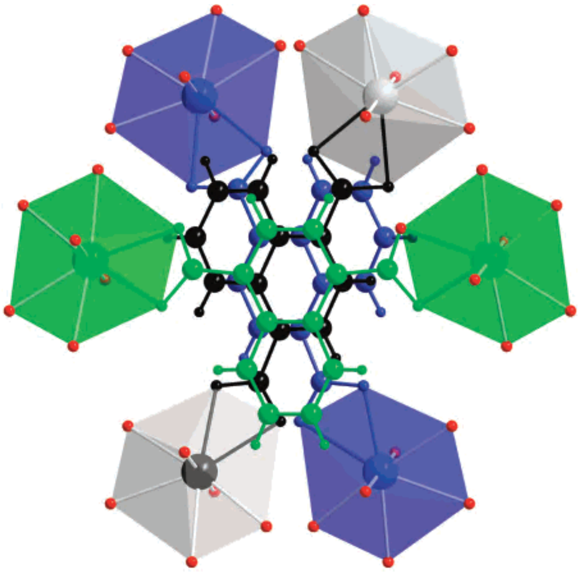

Figure 4. View along the *a* axis showing layers in **2** stacked by face-to-face $\pi-\pi$ interactions. The interlayer distances range from 3.348(2) to 3.473(1) Å. Three different colors represent three adjacent layers: green, top layer; blue, bottom later; and black, middle layer.

Compound **2** has two guest water molecules coordinated to K^+ with well-defined locations. The potassium ion is coordinated by six oxygen atoms (Figure 5); one from a uranyl oxygen atom ($d_{K1-O1} = 2.780(3)$ Å), three from

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(13) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.

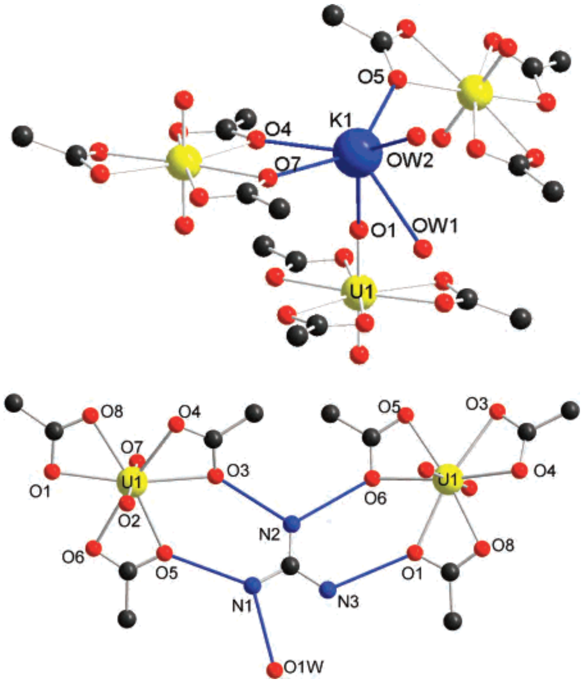

Figure 5. Perspective view of the coordination environment around the potassium atom in **2** (top) and the guanidinium cation in **2b** (bottom).

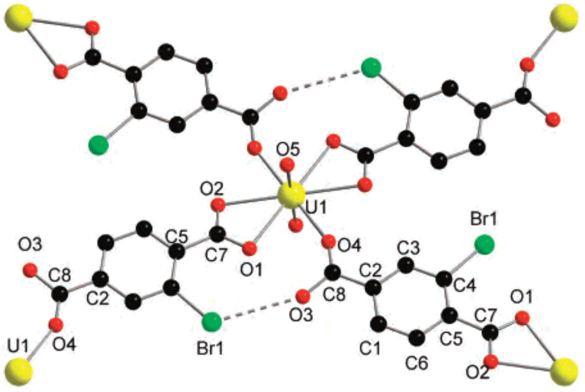

Figure 6. A perspective view of main building unit of **3**. Hydrogen atoms are omitted for clarity.

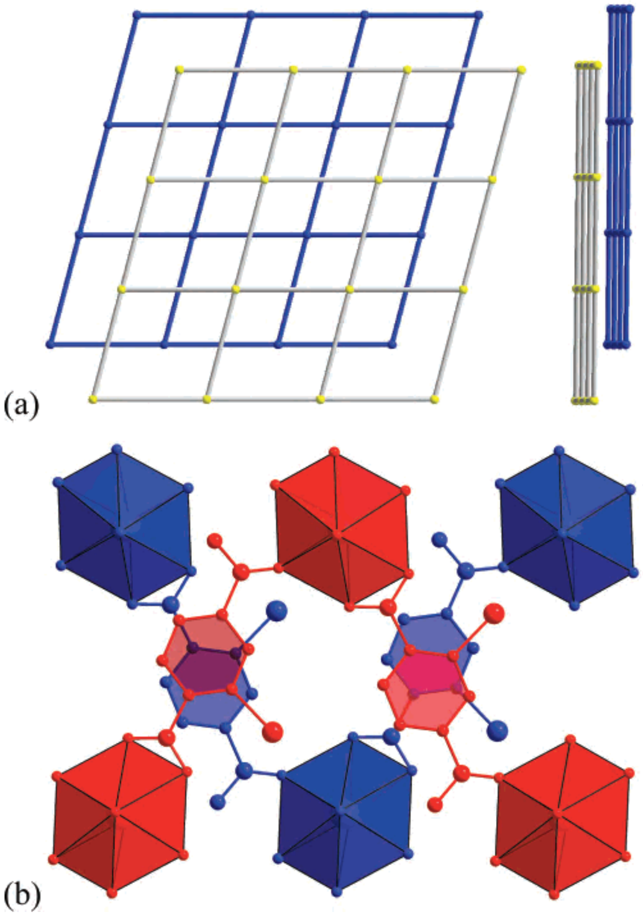

Figure 7. (a) Schematic diagram of the (4,4) net layer stacking in **3** and its side view. (b) A perspective view of two adjacent layers (red, top layer; blue, bottom layer) showing the $\pi-\pi$ interactions of the BDC−Br rings.

carboxylate oxygen atoms of NDC ligands ($d_{\mathrm{K1-O}} = 2.804(3)$, 2.990(3), and 3.032(3) Å), and two from guest water molecules ($d_{\mathrm{O-O1w}} = 2.731(6)$ Å and $d_{\mathrm{O-O2w}} = 3.213(6)$ Å). The potassium cation compensates the negative charge of the $[\mathrm{UO_2(NDC)_{1.5}}]^-$ layer. Three $\mathrm{UO_2O_{6/2}}$ units from three adjacent layers are held together by one potassium ion in addition to the $\pi-\pi$ interactions as shown in Figures 4 and 5. In compound **2b**, the potassium ion is replaced by the guanidinium cation, which holds two $\mathrm{UO_2O_{6/2}}$ units from two adjacent layers and has a strong interaction with a guest water molecule ($d_{\mathrm{O-O1w}} = 2.908(6)$ Å). The distances between the nitrogen atoms of the guanidinium cation to the nearby carboxylate oxygen atoms range from 2.867(5) to 2.932(6) Å, indicating strong hydrogen bonding (Figure 5).

Compound 3. The coordination environment of the uranium center in **3** is similar to that in compounds **1**−**2b**, with slightly distorted hexagonal-bipyramidal geometry (Figure 6). The U−O axial bond distance is 1.712(28) Å and is slightly shorter than the reported average distance (1.758 Å), and the U−O equatorial bond distances range from 2.397(23) to 2.558(20) Å. The O−U−O bond angle in the uranyl cation is 180.0(9)°.

In the equatorial plane, the uranium atom is coordinated by six carboxylate oxygen atoms from two chelating BDC−Br ligands and two monodentate BDC−Br ligands. The bridging BDC−Br ligand adopts two different coordination modes in one molecule, chelating at one end and monodentate at the other end, an arrangement which appears only rarely.[14] The monodentate carboxylic group is protonated, presumably on the noncoordinating O3 atom to balance the layer charge, forming a hydrogen bond between the bromine substituent and the O1 atom ($d_{\mathrm{Br-O3}} = 3.184(9)$ Å and $d_{\mathrm{O1-O3}} = 2.646(14)$ Å) from the chelating carboxylate group. Due to the presence of two monodentate oxygen atoms in the uranyl cation coordination sphere, the O−U−O bond angles in the equatorial plane range from 50.93(27)° to 63.75(27)°, compared to the ideal 60° for a regular hexagonal arrangement.

The extended structure of **3** has layers of four-membered rings (parallelograms) as shown in Figure 7a. The distance between the bromine atom and the carboxylate oxygen atom is 3.184(9) Å, indicative of strong hydrogen bonding. The

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[14] Xu, H. B.; Su, Z. M.; Shao, K. Z.; Zhao, Y. H.; Xing, Y.; Liang, Y. C.; Zhang, H. J.; Zhu, D. X. *Inorg. Chem. Commun.* **2004**, *7*, 260.

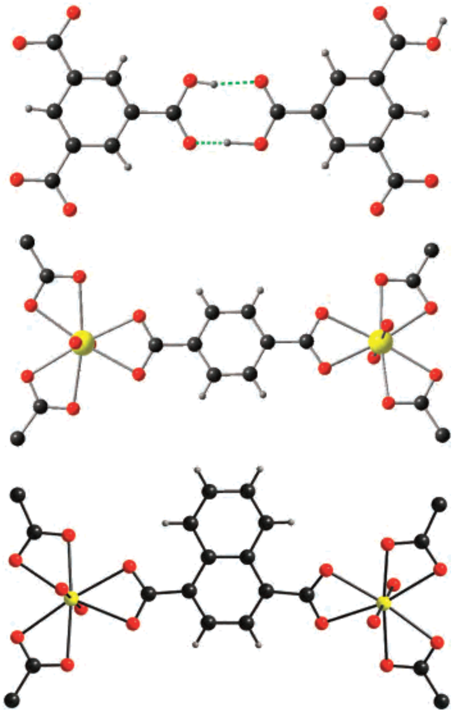

Figure 8. Structural similarity between H_3BTC and $UO_2(BDC)_{1.5}$ and $UO_2(NDC)_{1.5}$.

bromide substituent pulls one carboxylate oxygen atom away from the uranium atom, and the carboxylate ligand switches its coordination mode from chelating to monodentate, allowing the fourth ligand to become involved in the coordination of the uranium atom leading to a (4,4) rather than a (6,3) hexagonal net. The average interlayer distance, i.e., the distance for $\pi-\pi$ interaction between the blue ring and the red ring in Figure 7b, is 3.451(13) Å. The hydrogen-bonded bulky bromine substituents and uncoordinated carboxylate oxygen atoms occupy most of space in the (4,4) net, preventing interpenetration. As in the case of **2** and **2b**, the stacking of layers through $\pi-\pi$ interaction contributes to the stability of the framework.

Coordination frameworks with rigid bridging ligands can form extended structures analogous to known simple hydrogen-bonded organic networks.[15] In this example, **1**−**2b** have similar structural arrangements to that of benzene tricarboxylate (trimesic acid, H_3BTC).[3a] In H_3BTC, the six rings are formed by hydrogen bonding and the interpenetration is more complex than that in **1**. The structural relationship is illustrated in Figure 8, which shows the comparison between two hydrogen-bonded H_3BTC units and two UO_2^{2+} cations bridged by a BDC dianion. The average distance of one side of a six ring in H_3BTC, i.e., the distance between the centroids of two benzene rings connected by hydrogen bonding, is 9.573 Å. The distance between two uranium atoms ranges from 11.376(68) to 11.441(78) Å for **1**, 11.277(1) to 11.440(4) Å for **2**, and 11.363(1) to 11.558(4) Å for **2b**. Other structural parallels between simple hydrogen-bonded organic structures and coordination polymers were described by Zaworotko et al.[2] (e.g., one-dimensional linear chains of H_2BDC, one-dimensional zigzag chains of nitroaniline, and two-dimensional sheets made of cyanuric acid-4,4′-bpy adducts).

Characterization. **Vibrational Spectra.** In the IR spectrum of **1**, the broad band at 3400 cm^{-1} indicates the presence of guest water molecules, in agreement with the X-ray crystal structure. The $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ stretching vibrations at 1533 and 1405 cm^{-1}, respectively, show that all carboxylic groups are chelating. In the IR spectra of **2** and **2b**, the multiple $\nu_{sym}(CO_2)$ stretching bands around 1400 cm^{-1}, which are typical for compounds with mixed coordination modes of carboxylates, are due to the strong interaction of the carboxylate oxygen atoms with the potassium ion (**2**) or the guanidinium ion (**2b**). The strong bands at 3367, 3187, 1680, and 1666 cm^{-1} indicate the presence of the guanidinium ion in compound **2b**. In the IR spectrum of **3**, the strong band at 1673 cm^{-1} indicates the presence of a weakly protonated carboxylic group as indicated in the crystal structure. The rather complicated set of $\nu_{asym}(CO_2)$ stretching bands at 1574−1371 cm^{-1} indicates the mixed coordination of the carboxylates, chelating and monodentate, in addition to the hydrogen bonding with the bromide group of BDC−Br.

Thermal Analysis. Compound **1** shows an immediate weight loss on heating that is complete by 120 °C. This corresponds to the loss of the guest water molecules and indicates that the interactions of these water molecules with the framework are weak. A second weight loss starts at 200 °C and shows a rather complicated weight-loss profile that is complete by 430 °C. Compound **2** loses its guest water molecules slowly until 160 °C (obs. 4.88%, calcd. 5.41%) and decomposes to $KUO_{3.5}$, as identified by X-ray powder diffraction, in one step (onset at 400 °C, completion at 485 °C; obs. 43.26%, calcd. 44.61%). The first weight loss, which ends at somewhat high temperature, indicates the strong interaction of the guest water molecules with the potassium cation, confirming the X-ray structure. Compound **2b** loses first its guest water molecule slowly until 150 °C (obs. 2.77%, calcd. 2.69%) and shows an unexpected two-step weight loss from 300 to 410 °C. The total weight loss corresponds to the decomposition of framework to UO_3 (obs. 54.52%, calcd. 54.58%). Compound **3** is stable up to 325 °C and also shows an unexpected two-step decomposition, which is similar to that of compound **1** and **2b**, to UO_3 from 325 to 450 °C (total weight loss obs. 62.21%, calcd. 62.27%).

Conclusion

The hydrothermal reaction of dicarboxylate ligands with uranyl cation resulted in three extended frameworks with a layer structure based on two-fold interpenetrated (6,3) nets, $NH_4UO_2BDC_{1.5}\cdot 2.5H_2O$ (**1**), and noninterpenetrated (6,3) nets, $KUO_2NDC_{1.5}\cdot 2H_2O$ (**2**) and $[C(NH_2)_3]UO_2NDC_{1.5}\cdot H_2O$ (**2b**). On the other hand, compound **3**, $UO_2(HBDC-Br)_2$, is a noninterpenetrated layer structure based on a (4,4) net

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[15] (a) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120. (b) MacDonald, J. C.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383. (c) Holman, K. T.; Pivovar, A. M.; Swift, J. A.; Ward, M. D. *Acc. Chem. Res.* **2001**, *34*, 107.

instead of a (6,3) net. Frameworks with channels as large as that in **1** (13 Å) tend to adopt interpenetration or entanglement for maximum stability. In our study, we were able to prevent interpenetration by the introduction of bulky substituents in the benzenedicarboxylate ligand, keeping the (6,3) net topology in **2** and **2b** or changing the topology to the (4,4) net in **3**. The stability of a structure with such a large channel in **2** and **2b** was maintained by stacking layers through noncovalent interactions, $\pi-\pi$ or CH$-\pi$ interactions of phenyl rings in the ligand. The extra aromatic rings of the NDC ligands together with the cations and guest water molecules occupy enough space in the ring to prevent interpenetration. The bromide substituent in **3** is strongly hydrogen bonded to a carboxylate oxygen atom ($d_{\mathrm{Br-O}}$ = 3.184 Å) from the nearby BDC−Br ligand. This hydrogen bonding of one of the carboxylate oxygen atoms leads to a monodentate coordination mode instead of all chelating modes as in **1**−**2b**. Therefore, it allows the introduction of the fourth carboxylate group to give four-coordinated vertices at the uranyl cation, leading to a (4,4) net. The bulky bromine substituent limits the space for interpenetration, and the layers are stacked through the $\pi-\pi$ interaction of BDC−Br ligands. The (6,3) honeycomb net structures of **1**−**2b** are related to the hydrogen-bonded network of benzenetricarboxylic acid. The combination of BDC or NDC in which both carboxylate groups are bidentate, with hexagonal-bipyramidal $UO_2O_{6/2}$ building units, provides the two- and three-coordinated vertices necessary to obtain this unusual network.

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Supporting Information Available: X-ray crystallographic data, in CIF format, for the structures of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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