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Hydrothermal Preparation of Nickel(II)/Uranium(IV) Fluorides with One-, Two-, and Three-Dimensional Topologies

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A modified compositional diagram for the reactions of $Ni(C_2H_3O_2)_2{\cdot}4H_2O$ with $UO_2(C_2H_3O_2)_2{\cdot}2H_2O$ and HF in aqueous media under mild hydrothermal conditions (200 °C) has been completed to yield three Ni(II)/U(IV) fluorides, $Ni(H_2O)_4UF_6{\cdot}1.5H_2O$ (**1**), $Ni_2(H_2O)_6U_3F_{16}{\cdot}3H_2O$ (**2**), and $Ni(H_2O)_2UF_6(H_2O)$ (**3**). The structure of **1** consists of one-dimensional columns constructed from two parallel chains of edge-sharing dodecahedral $[UF_8]$ units. The sides of the columns are terminated by octahedral Ni(II) units that occur as *cis*-$[Ni(H_2O)_4F_2]$ polyhedra. In contrast, the crystal structure of **2** reveals a two-dimensional Ni(II)/U(IV) architecture built from edge-sharing tricapped trigonal prismatic $[UF_9]$ units. The top and bottom of the sheets are capped by *fac*-$[Ni(H_2O)_3F_3]$ octahedra. The structure of **3** is formed from $[UF_8(H_2O)]$ tricapped trigonal prisms that edge share with one another to form one-dimensional chains. These chains are then joined together into a three-dimensional network by corner sharing with *trans*-$[Ni(H_2O)_2F_4]$ octahedra. Crystallographic data: **1**, orthorhombic, space group *Cmcm*, $a = 14.3383(8)$ Å, $b = 15.6867(8)$ Å, $c = 8.0282(4)$ Å, $Z = 8$; **2**, hexagonal, space group $P6_3/mmc$, $a = 7.9863(5)$ Å, $c = 16.566(1)$ Å, $Z = 2$; **3**, monoclinic, space group $C2/c$, $a = 12.059(1)$ Å, $b = 6.8895(6)$ Å, $c = 7.9351(7)$ Å, $\beta = 92.833(2)°$, $Z = 4$.

Introduction

In recent years the synthesis of organically templated uranium fluorides has been the focus of considerable interest, owing to both the diversity of structures observed and the physicochemical properties that these compounds display.[1−11] For instance, the one-dimensional homopiperazinium-templated U(IV) fluoride $(C_5H_{14}N_2)_2U_2F_{12}{\cdot}2H_2O$ exhibits metamagnetic behavior.[7] Likewise, unusual short-range ferromagnetic coupling is found in two-dimensional $(C_2H_{10}N_2)U_2F_{10}$.[7] Ion-exchange properties are also known for a series of U(IV) fluorides with sheet topologies similar to those observed in $(C_2H_{10}N_2)U_2F_{10}$.[1,12] In addition, several porous and three-dimensional network structures with U(VI) have been isolated with fluoride and other hard anions. These compounds include $[C_6H_{14}N_2][(UO_2)_2F_6]$,[11] $[C_4H_{12}N_2][U_2O_4F_6]$,[4,5] $[(C_2H_5)_2NH_2]_2[(UO_2)_5(PO_4)_4]$,[13] $Na_2(UO_2)(Si_4O_{10}){\cdot}2.1H_2O$,[14] $RbNa(UO_2)(Si_2O_6){\cdot}H_2O$,[14] $[C_4H_{12}N_2][(UO_2)_2(PO_3H)_2\{PO_2(OH)H\}_2]$,[15] and $[NH_4]_3[(UO_2)_{10}O_{10}(OH)][(UO_4(H_2O)_2]{\cdot}2H_2O$.[16] On the basis of these works, the possibility of preparing uranium-based materials with zeolitic topologies is starting to become a reality.

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(1) Francis, R. J.; Halasyamani, P. S.; O'Hare, D. *Chem. Mater.* **1998**, *10*, 3131.
(2) Francis, R. J.; Halasyamani, P. S.; O'Hare, D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2214.
(3) Francis, R. J.; Halasyamani, P. S.; Bee, J. S.; O'Hare, D. *J. Am. Chem. Soc.* **1999**, *121*, 1609.
(4) Halasyamani, P. S.; Walker, S. M.; O'Hare, D. *J. Am. Chem. Soc.* **1999**, *121*, 7415.
(5) Walker, S. M.; Halasyamani, P. S.; Allen, S.; O'Hare, D. *J. Am. Chem. Soc.* **1999**, *121*, 10513.
(6) Almond, P. M.; Deakin, L.; Porter, M. J.; Mar, A.; Albrecht-Schmitt, T. E. *Chem. Mater.* **2000**, *12*, 3208.
(7) Talley, C. E.; Bean, A. C.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2000**, *39*, 5174.
(8) Almond, P. M.; Deakin, L.; Mar, A.; Albrecht-Schmitt, T. E. *J. Solid State Chem.* **2001**, *158*, 87.
(9) Almond, P. M.; Deakin, L.; Mar, A.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2001**, *40*, 866.
(10) Almond, P. M.; Talley, C. E.; Bean, A. C.; Peper, S. M.; Albrecht-Schmitt, T. E. *J. Solid State Chem.* **2000**, *154*, 635.
(11) Cahill, C. L.; Burns, P. C. *Inorg. Chem.* **2001**, *40*, 1347.
(12) Sykora, R. E.; Albrecht-Schmitt, T. E. *Chem. Mater.* **2001**, *13*, 4399.
(13) Danis, J. A.; Runde, W. H.; Scott, B.; Fettinger, J.; Eichhorn, B. *Chem. Commun.* **2001**, *22*, 2378.
(14) (a) Li, Y.; Burns, P. C. *J. Nucl. Mater.* **2001**, *299*, 219. (b) Wang, X.; Haung, J.; Liu, L.; Jacobson, A. J. *J. Mater. Chem.* **2002**, *12*, 406.
(15) Doran, M.; Walker, S. M.; O'Hare, D. *Chem. Commun.* **2001**, 1988.
(16) Li, Y.; Cahill, C. L.; Burns, P. C. *Chem. Mater.* **2001**, *13*, 4026.

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Despite these widespread efforts to understand the hydrothermal chemistry of uranium, mixed-metal compounds derived from hydrothermal conditions are lacking. In fact, they can be largely restricted to U(VI) chromates and molybdates that are known with both organic structure-directing agents[17] and inorganic cations.[18−29] In the latter case, however, the transition metal does not impart desirable electronic properties associated with unpaired electrons on the metal centers. Therefore, the preparation of mixed-metal uranium compounds with transition metals bearing d electrons can be viewed as an important synthetic challenge that may give rise to mixed-metal compounds with atypical electronic properties. The majority of well-characterized representatives of transition metal/uranium fluorides are found to contain transition metals in the +2 oxidation state, especially Ni(II), and U(VI) in the form of uranyl, UO_2^{2+}, cations. Members of this group include $[Ni(H_2O)_6]_2[(UO_2)_2F_8]\cdot 2H_2O$,[30] $[Ni(H_2O)_6]_3[(UO_2)_4F_{14}]$,[31] and $[NH_4]_2[Ni(H_2O)_6][(UO_2)_2F_8]$.[32] Limited crystallographic information has also been reported for the mixed-metal U(IV) fluorides $[M(H_2O)_6][U_2F_{10}]\cdot 2H_2O$ (M = Co, Ni, Cu).[33] The common feature of both of these Ni(II)/U(IV)/F and Ni(II)/U(VI)/F systems is that the transition metals are fully hydrated and are essentially serving as counterions that are not directly incorporated into the uranium fluoride extended or molecular structures.

In this report we detail the preparation of three new Ni(II)/U(IV) fluorides, $Ni(H_2O)_4UF_6\cdot 1.5H_2O$ (**1**), $Ni_2(H_2O)_6U_3F_{16}\cdot 3H_2O$ (**2**), and $Ni(H_2O)_2UF_6(H_2O)$ (**3**), which formed under mild hydrothermal conditions. These compounds display dimensionalities ranging from one-dimensional chains to two-dimensional layers to three-dimensional networks created through the combination of a variety of U(IV) polyhedra with various isomers of $Ni(H_2O)_{6-x}F_x$ octahedra, where there are linkages between Ni(II) and U(IV) via bridging fluoride anions.

Experimental Section

Syntheses. $UO_2(C_2H_3O_2)_2\cdot 2H_2O$ (98%, Alfa-Aesar), $Ni(C_2H_3O_2)_2\cdot 4H_2O$ (98%, Aldrich), and HF (48 wt %, Aldrich) were used as received. Distilled and Millipore filtered water was used in all reactions. The resistance of the water was 18.2 MΩ. The PTFE liners used to contain these reactions were cleaned of contaminants by heating with distilled and Millipore filtered water at 200 °C for 3 d prior to use. *While the UO_3 contains depleted U, standard precautions for handling radioactive materials should be followed. Old sources of depleted U should not be used, as the daughter elements of natural decay are highly radioactive and present serious health risks.* SEM/EDX analyses were performed using a JEOL 840/Link Isis instrument. The reported preparations given herein are taken from a modified compositional diagram and represent the highest yields of pure phases obtained where possible.

$Ni(H_2O)_4UF_6\cdot 1.5H_2O$ (1) and $Ni(H_2O)_2UF_6(H_2O)$ (3). $UO_2(C_2H_3O_2)_2\cdot 2H_2O$ (212 mg, 0.500 mmol) and $Ni(C_2H_3O_2)_2\cdot 4H_2O$ (373 mg, 1.5 mmol) were loaded in a 23 mL PTFE-lined autoclave. Water (1 mL) was then added to the solids followed by the dropwise addition of HF (0.73 mL, 20 mmol). The autoclave was sealed and placed in a box furnace and heated to 200 °C. After 72 h the furnace was cooled at 9 °C/h to 23 °C. The product consisted of an aquamarine solution over pale green tablets of **1** and large, dark green, roughly hexagonal blocks of **3**. The mother liquor was decanted from the crystals, which were then washed with water and methanol, and allowed to dry. Yield of **1**: 150 mg (62% yield based on U). Yield of **3**: 30 mg (12% yield based on U). EDX analysis for $Ni(H_2O)_4UF_6\cdot 1.5H_2O$ (**1**) and $Ni(H_2O)_2UF_6(H_2O)$ (**3**) both provided a Ni:U ratio of 1:1.

$Ni_2(H_2O)_6U_3F_{16}\cdot 3H_2O$ (2). $UO_2(C_2H_3O_2)_2\cdot 2H_2O$ (170 mg, 0.4 mmol) and $Ni(C_2H_3O_2)_2\cdot 4H_2O$ (299 mg, 1.2 mmol) were loaded in a 23 mL PTFE-lined autoclave. Water (1 mL) was then added to the solids followed by the dropwise addition of HF (0.73 mL, 20 mmol). The autoclave was sealed, placed in a box furnace, and heated to 200 °C. After 72 h the furnace was cooled at 9 °C/h to 23 °C. The product consisted of a green solution over light green hexagonal tablets of **2**. The mother liquor was decanted from the crystals, which were then washed with water and methanol and allowed to dry. Yield: 333 mg (67% yield based on U). EDX analysis for $Ni_2(H_2O)_6U_3F_{16}\cdot 3H_2O$ provided a Ni:U ratio of 2:3.

Crystallographic Studies. Single crystals of $Ni(H_2O)_4UF_6\cdot 1.5H_2O$ (**1**), $Ni_2(H_2O)_6U_3F_{16}\cdot 3H_2O$ (**2**), and $Ni(H_2O)_2UF_6(H_2O)$ (**3**) were carefully selected and mounted on thin glass fibers with epoxy. The mounted crystals were cooled to −80 °C using an Oxford Cryostream and optically aligned on a Bruker SMART APEX CCD X-ray diffractometer. Intensity measurements were performed using graphite-monochromated Mo Kα radiation from a sealed tube with a monocapillary collimator. SMART was used for preliminary determination of the cell constants and data collection control. For all compounds, the intensities of reflections of a sphere were collected by a combination of three sets of exposures (frames). Each set had a different ϕ angle for the crystal, and each exposure covered a range of 0.3° in ω. A total of 1800 frames were collected with an exposure time per frame of 30 s.

For all compounds, determination of integral intensities and global cell refinement were performed with the Bruker SAINT (version 6.02) software package using a narrow-frame integration algorithm. A face-indexed analytical absorption correction was

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(17) Halasayamani, P. S.; Francis, R. J.; Walker, S. M.; O'Hare, D. *Inorg. Chem.* **1999**, *38*, 271.

(18) Rastsvetaeva, R. K.; Barinova, A. V.; Fedoseev, A. M.; Budantseva, N. A.; Nekrasov, Yu. V. *Dokl. Akad. Nauk* **1999**, *365*, 68.

(19) Krivovichev, S. V.; Burns, P. C. *Can. Mineral.* **2000**, *38*, 847.

(20) Khrustalev, V. N.; Andreev, G. B.; Antipin, M. Yu.; Fedoseev, A. M.; Budantseva, N. A.; Shirokova, I. B. *Zh. Neorg. Khim.* **2000**, *45*, 1996.

(21) Andreev, G. B.; Antipin, M. Yu.; Fedoseev, A. M.; Budantseva, N. A. *Koord. Khim.* **2001**, *27*, 227.

(22) Krivovichev, S. V.; Burns, P. C. *Can. Mineral.* **2001**, *39*, 207.

(23) Krivovichev, S. V.; Burns, P. C. *Can. Mineral.* **2001**, *39*, 197.

(24) Krivovichev, S. V.; Finch, R. J.; Burns, P. C. *Can. Mineral.* **2002**, *40*, 193.

(25) Krivovichev, S. V.; Burns, P. C. *Can. Mineral.* **2002**, *40*, 201.

(26) Krivovichev, S. V.; Cahill, C. L.; Burns, P. C. *Inorg. Chem.* **2002**, *41*, 34.

(27) Krivovichev, S. V.; Burns, P. C. *Inorg. Chem.* **2002**, *41*, 4108.

(28) Sykora, R. E.; Wells, D. M.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2002**, *41*, 2304.

(29) Sykora, R. E.; McDaniel, S. M.; Wells, D. M.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2002**, *41*, 5126.

(30) Ivanov, S. B.; Mikhailov, Y. N.; Davidovich, R. L. *Koord. Khim.* **1982**, *8*, 1250.

(31) Ivanov, S. B.; Mikhailov, Y. N.; Kuznetsov, V. G.; Davidovich, R. L. *J. Struct. Chem.* **1981**, *22*, 302.

(32) Mikhailov, Y. N.; Udovenko, A. A.; Kuznetsov, V. G.; Butman, L. A.; Kokh, L. A. *Zh. Strukt. Khim.* **1973**, *14*, 170.

(33) Charpin, P.; Montoloy, F.; Nierlich, M. *C. R. Acad. Sci., Paris, Ser. C* **1968**, *266*, 1685.

Table 1. Crystallographic Data for $Ni(H_2O)_4UF_6{\cdot}1.5H_2O$ (**1**), $Ni_2(H_2O)_6U_3F_{16}{\cdot}3H_2O$ (**2**), and $Ni(H_2O)_2UF_6(H_2O)$ (**3**)

	1	**2**	**3**
formula	$Ni(H_2O)_4UF_6{\cdot}1.5H_2O$	$Ni_2(H_2O)_6U_3F_{16}{\cdot}3H_2O$	$Ni(H_2O)_2UF_6(H_2O)$
formula mass	509.79	1297.65	464.79
cryst syst	orthorhombic	hexagonal	monoclinic
space group	*Cmcm* (No. 63)	$P6_3/mmc$ (No. 194)	*C*2/*c* (No. 15)
a (Å)	14.3383(8)	7.9863(5)	12.059(1)
b (Å)	15.6867(8)	7.9863(5)	6.8895(6)
c (Å)	8.0282(4)	16.566(1)	7.9351(7)
α (deg)	90	90	90
β (deg)	90	90	92.833(2)
γ (deg)	90	120	90
V (Å^3)	1805.7(2)	915.0(1)	658.5(1)
Z	8	2	4
T (°C)	−80	−80	−80
λ (Å)	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	3.883	4.644	4.689
μ(Mo Kα) (cm^{-1})	201.13	286.67	275.07
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$	0.0252	0.0237	0.0330
$R_w(F_o^2)^b$	0.0692	0.0648	0.0878

^{a} $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w(F_o^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma\, wF_o^4]^{1/2}$.

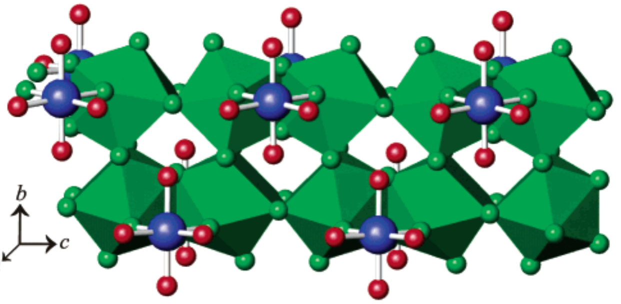

Figure 1. View of the zigzagging chains of edge-sharing dodecahedral $[UF_8]$ units that are linked to form columns in $Ni(H_2O)_4UF_6{\cdot}1.5H_2O$ (**1**). The periphery of these U(IV) fluoride columns are lined with *cis*-$[Ni(H_2O)_2F_4]$ octahedra.

initially applied using XPREP.[34] Individual shells of unmerged data were corrected analytically and exported in the same format. These files were subsequently treated with a semiempirical absorption correction with SADABS using a $\mu{\cdot}t$ parameter of 0.[35] The program suite SHELXTL (version 5.1) was used for space group determination (XPREP), direct methods structure solution (XS), and least-squares refinement (XL).[34] Hydrogen atom positions were not located from the difference maps and were not included in the final refinements. The final refinements included anisotropic displacement parameters for all non-hydrogen atoms that are a part of the nickel(II)/uranium(III) frameworks and a secondary extinction parameter.

Crystallographic data for **1**−**3** are given in Table 1.

Results and Discussion

Syntheses. The preparation of $Ni(H_2O)_4UF_6{\cdot}1.5H_2O$ (**1**), $Ni_2(H_2O)_6U_3F_{16}{\cdot}3H_2O$ (**2**), and $Ni(H_2O)_2UF_6(H_2O)$ (**3**) was accomplished by reacting $Ni(C_2H_3O_2)_2{\cdot}4H_2O$ with $UO_2(C_2H_3O_2)_2{\cdot}2H_2O$ and HF in aqueous media at 200 °C for 3 days followed by slow cooling to promote the growth of high-quality single crystals. In this system use was made of a modified compositional diagram[5,7−10,36−39] to determine the conditions under which various U(IV) solids crystallize. In the course of these studies it was determined that the formation of **1**−**3** is remarkably sensitive to scale, and consistent isolation of solid U(IV) products could only be ensured by maintaining 20 mmol of HF in the reaction mixtures. The most commonly observed crystalline solids were the less interesting U(IV) fluorides $UF_4{\cdot}{}^1/_3H_2O$ and $[Ni(H_2O)_6][U_2F_{10}]{\cdot}2H_2O$.[33] When the reactions were run at increased temperatures or with increased duration, the occurrence of these last two compounds dominated compositional space, implying that these may be the result of thermodynamic control, whereas **1**−**3** are likely kinetic products. There is no obvious correlation between product and reaction stoichiometry.

A series of control reactions were conducted to determine that the reduction of U(VI) to U(IV) in these syntheses is acid and acetate dependent and likely corresponds to a decarboxylation reaction of the acetate anion. Reduction of U(VI) to U(IV) has also been observed in the preparation of organically templated U(IV) fluorides.[1−3,5,6,8,9,11] In these latter syntheses, aliphatic amines are apparently the reducing agents.[7] For example, the reaction of excess ethylenediamine with UO_3 and HF under hydrothermal conditions results in the reduction of U(VI) to U(IV) and the crystallization of $(C_2H_{10}N_2)U_2F_{10}$ in nearly quantitative yield.[6]

Structures. $Ni(H_2O)_4UF_6{\cdot}1.5H_2O$ (1). The structure of **1** consists of one-dimensional columns constructed from two interconnected, zigzagging chains of edge-sharing dodecahedral $[UF_8]$ units, as shown in Figure 1. The sides of the columns are terminated by octahedral Ni(II) that occur as *cis*-$[Ni(H_2O)_4F_2]$ polyhedra. The individual chains that edge share to form the columns of **1** are similar to the one-dimensional ${}^1_\infty[MF_{4/1}F_{4/2}]^{4-}$ (M = Zr, U) chains found in

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(34) Sheldrick, G. M. SHELXTL PC, Version 5.0, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994.

(35) SADABS is a program for absorption correction using SMART CCD based on the method of Blessing: Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(36) Halasyamani, P. S.; Willis, M. J.; Lundquist, P. M.; Stern, C. L.; Wong, G. K.; Poeppelmeier, K. R. *Inorg. Chem.* **1996**, *35*, 1367.

(37) Harrison, W. T. A.; Dussack, L. L.; Jacobson, A. J. *J. Solid State Chem.* **1996**, *125*, 234.

(38) Norquist, A. J.; Heier, K. R.; Stern, C. L.; Poeppelmeier, K. R. *Inorg. Chem.* **1998**, *37*, 6495.

(39) Welk, M. E.; Norquist, A. J.; Stern, C. L.; Poeppelmeier, K. R. *Inorg. Chem.* **2000**, *39*, 3946.

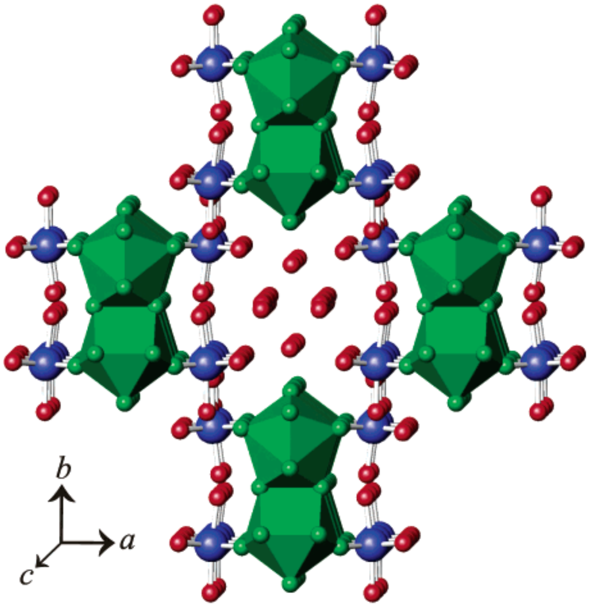

Figure 2. View of the channel structure of $Ni(H_2O)_4UF_6 \cdot 1.5H_2O$ (**1**) formed by the interdigitation of the $Ni(H_2O)_4UF_6$ columns. Ordered and disordered water molecules fill the channels in this compound.

several inorganic and organically templated U(IV) and Zr(IV) fluorides.[5,40−46]

The nature of the edge-sharing of the $[UF_8]$ units is such that opposite edges are shared to create the one-dimensional chains running along the *c* axis, and a single edge approximately orthogonal to the direction of chain propagation is shared to link two such chains together. Therefore, six of the eight fluoride anions surrounding each U(IV) center are utilized in the formation of the uranium fluoride columns. The two remaining fluoride anions are used to bind the octahedral Ni(II) atoms to the periphery of the columns. The remaining four sites around the Ni(II) centers are occupied by terminal water molecules. This requires the $[Ni(H_2O)_4F_2]$ polyhedra to have a *cis* geometry. The ${}^{1}_{\infty}[Ni(H_2O)_4UF_6]$ columns are packed together in an interdigitated fashion and combine to form a channel structure where the channels are filled with occluded water molecules. A view of the channel structure of **1** is shown in Figure 2. There are two crystallographically unique water molecules within the channels; one of these is ordered and the other is disordered. The U−F bond distances are within normal ranges and occur from 2.220(4) to 2.425(2) Å. The $Ni-O(H_2O)$ distances of 2.072(5), 2.056(3) (×2), and 2.081(4) Å are uniformly longer than the two Ni−F distances of 2.003(3) Å and compare well with those found in $[Ni(H_2O)_6][M_2F_{10}] \cdot 2H_2O$ (M = Ce, U).[12,33] Selected bond distances are summarized in Table 2.

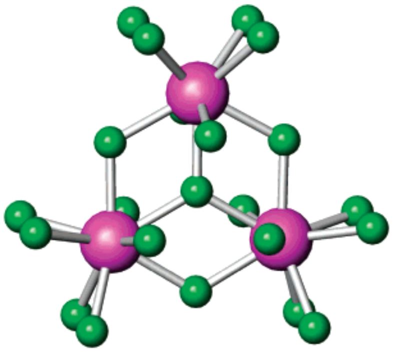

Figure 3. Depiction of the cyclic trimer formed from the edge-sharing of three $[UF_9]$ tricapped trigonal prisms in $Ni_2(H_2O)_6U_3F_{16} \cdot 3H_2O$ (**2**).

Table 2. Selected Bond Distances (Å) for $Ni(H_2O)_4UF_6 \cdot 2.5H_2O$ (**1**)

U(1)−F(1) (×2)	2.252(3)	U(1)−F(6) (×2)	2.390(2)
U(1)−F(2)	2.357(3)	U(1)−F(4) (×2)	2.425(2)
U(1)−F(3)	2.220(4)	U(1)−F(5)	2.303(3)
Ni(1)−F(1) (×2)	2.003(3)	Ni(1)−O(2) (×2)	2.056(3)
Ni(1)−O(1)	2.072(5)	Ni(1)−O(3)	2.081(4)

These bond distances were used to calculate the bond valence sums for the Ni(II) and U(IV) atoms with values of 1.98 and 4.07 Å being found, respectively.[47,48]

$Ni_2(H_2O)_6U_3F_{16} \cdot 3H_2O$ (2). In contrast to the one-dimensional features found for **1**, the crystal structure of **2** reveals a highly symmetric two-dimensional Ni(II)/U(IV) architecture built from edge-sharing tricapped trigonal prismatic $[UF_9]$ units. The sheets are capped on both sides by $[Ni(H_2O)_3]$ moieties. In this compound a hexagonal planar $[U_3F_3]$ ring is found to repeat throughout the layers. In the center of this ring is a μ_3-F atom residing on a $\bar{6}m2$ special position. This central atom also represents the core atom utilized in the simultaneous edge-sharing of three $[UF_9]$ tricapped trigonal prisms, where each of these units shares two common edges with each other to form a trimer as shown in Figure 3. Therefore, while the structure is derived from a single $[UF_9]$ tricapped trigonal prism, the trimer is more useful for visualizing the repeating pattern in the layers. The formation of this fluoride-centered ring utilizes three of the nine fluoride anions surrounding each U(IV) center. For each $[UF_9]$ unit an additional four fluoride atoms are occupied in edge sharing with two neighboring trimers to form the two-dimensional ${}^{2}_{\infty}[U_3F_{16}]^{4-}$ sheets depicted in Figure 4.

The remaining two fluoride atoms in each $[UF_9]$ tricapped trigonal prism are directed above and below each layer. The trimer of edge-sharing $[UF_9]$ therefore has three fluoride atoms arranged above and below the rings for the binding of the Ni(II) centers. This necessitates that the $[Ni(H_2O)_3F_3]$ octahedra have a *fac* geometry. The Ni(II) atoms reside directly above and below the μ_3-F atoms in the center of $[UF_{2/1}F_{6/2}F_{1/3}]_3$ trimers and are located on $3m$ sites. A view down the *c* axis showing the capping of a ${}^{2}_{\infty}[U_3F_{16}]^{4-}$ sheet with *fac*-$[Ni(H_2O)_3F_3]$ octahedra is shown in Figure 5. The remaining water molecules in **2** are located between the

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(40) Ross, C. R., II; Paulsen, B.; Nielson, R. M.; Abrahams, S. C. *Acta Crystallogr.* **1998**, *B54*, 417.

(41) Gerasimenko, A. V.; Bukvetskii, B. V.; Davidovich, R. L.; Kondratyuk, N. P. *Koord. Khim.* **1989**, *15*, 130.

(42) Penneman, R. A.; Ryan, R. R.; Rosenzweig, A. *Struct. Bonding* **1973**, *13*, 1.

(43) Laval, J. P.; Mercurio-Lavaud, D.; Gaudreau, B. *Rev. Chim. Mineral.* **1974**, *11*, 742.

(44) Hoppe, R.; Mehlhorn, B. *Z. Anorg. Allg. Chem.* **1976**, *425*, 200.

(45) Sykora, R. E.; Ruf, M.; Albrecht-Schmitt, T. E. *J. Solid State Chem.* **2001**, *159*, 198.

(46) Laval, J. P.; Papiernik, R.; Frit, B. *Acta Crystallogr.* **1978**, *B34*, 1070.

(47) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

(48) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

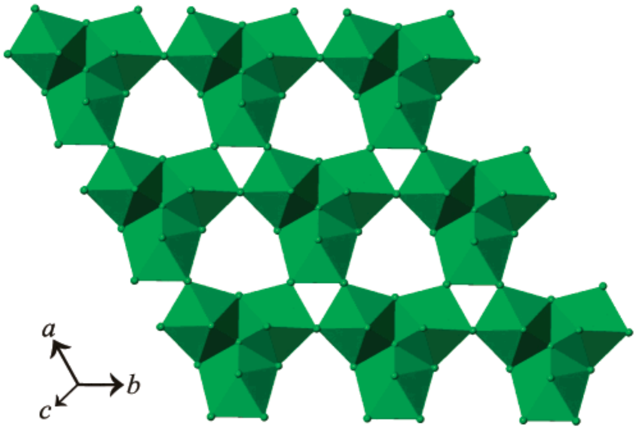

Figure 4. Representation of the two-dimensional $^{2}_{\infty}[U_3F_{16}]^{4-}$ sheets created from the edge-sharing of $[UF_9]$ tricapped trigonal prisms with two neighboring trimers formed from these same $[UF_9]$ units in $Ni_2(H_2O)_6U_3F_{16}\cdot3H_2O$ (**2**).

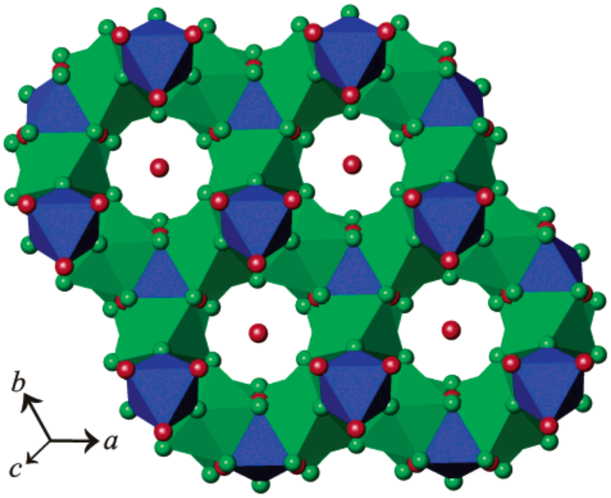

Figure 5. View down the *c* axis showing the capping of a $^{2}_{\infty}[U_3F_{16}]^{4-}$ sheet with *fac*-$[Ni(H_2O)_3F_3]$ octahedra. Occluded water molecules in **2** are located between the layers in channels that run along the *c* axis.

Table 3. Selected Bond Distances (Å) for $Ni_2(H_2O)_6U_3F_{16}\cdot3H_2O$ (**2**)

U(1)−F(1) (×2)	2.354(3)	U(1)−F(3) (×4)	2.363(2)
U(1)−F(2)	2.3261(3)	U(1)−F(4) (×2)	2.222(4)
Ni(1)−F(4) (×3)	2.017(4)	Ni(1)−O(1) (×3)	2.061(5)

layers in channels that run along the *c* axis. The U−F bond distances range from 2.222(4) to 2.354(3) Å. The three Ni−O(H_2O) distances of 2.061(5) Å are again longer than the three Ni−F bond distances of 2.017(4) Å. Selected bond distances for **2** are summarized in Table 3. The bond valence sums for the Ni(II) and U(IV) atoms in **2** were calculated to be 1.97 and 4.14, respectively.[47,48]

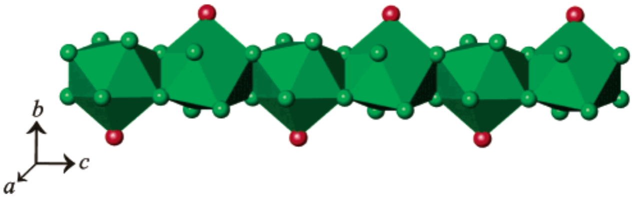

Figure 6. $[UF_8(H_2O)]$ tricapped trigonal prisms in $Ni(H_2O)_2UF_6(H_2O)$ (**3**) edge-sharing with one another to form one-dimensional chains.

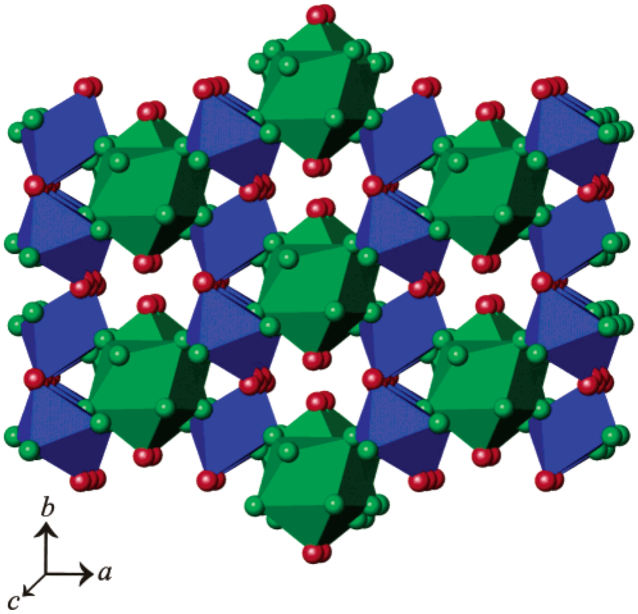

Figure 7. View down the *c* axis of the three-dimensional network structure of $Ni(H_2O)_2UF_6(H_2O)$ (**3**), demonstrating that both the water molecules bound to the Ni(II) centers and the water molecules ligating the U(IV) atoms reside within channels running along this same axis.

Table 4. Selected Bond Distances (Å) for $Ni(H_2O)_2UF_6(H_2O)$ (**3**)

U(1)−F(1) (×2)	2.244(4)	U(1)−F(3)′ (×2)	2.392(4)
U(1)−F(2) (×2)	2.292(4)	U(1)−O(2)	2.543(9)
U(1)−F(3) (×2)	2.306(3)		
Ni(1)−F(1) (×2)	1.990(3)	Ni(1)−O(1) (×2)	2.070(6)
Ni(1)−F(2) (×2)	2.006(3)		

$Ni(H_2O)_2UF_6(H_2O)$ (3). The tricapped trigonal prismatic geometry observed for U(IV) in **2** is observed again in **3**. However, one of the fluoride anions has been replaced by a water molecule to yield $[UF_8(H_2O)]$ units. The assignment of this ligand as water can be inferred from its U−O bond distance of 2.543(9) Å, which is considerably longer than the average U−F distance of 2.309(4) Å in this compound. This designation is also supported by the bond valence sum of the O atom at 0.31, which is well within normal range for bound water molecules. The $[UF_8(H_2O)]$ tricapped trigonal prisms edge share with one another to form one-dimensional chains, as shown in Figure 6. Unlike the zigzagging one-dimensional chains found in **1**, the chains of **3** are approximately linear. These chains are in turn linked together by corner sharing with *trans*-$[Ni(H_2O)_2F_4]$ octahedra into a three-dimensional network. When viewed down the *c* axis, as shown in Figure 7, it can be seen that both the water molecules bound to the Ni(II) centers and the water molecule ligating the U(IV) atoms are located within channels running down the *c* axis. The water molecules are sufficiently separated from one another to preclude hydrogen bonding being the driving force behind the formation of this particular structure type. Selected bond distances for **3** are summarized in Table 4. The bond valence sums for the Ni(II) and U(IV) atoms in **3** were calculated to be 2.01 and 4.16, respectively.[47,48] An analysis of the bond valence sums for **1**−**3** reveals little variance in the sums for Ni(II) and U(IV) and supports their assignment in these oxidation states.

Conclusions

This present study represents the first in a series of investigations that have demonstrated that mixed-metal 3d transition metal/U(IV) fluorides with a wide range of structures can be prepared under mild hydrothermal conditions. This preparative and structural study has given rise to ongoing magnetic susceptibility measurements, whose goal is to determine whether coupling between the expanded 5f orbitals of uranium and *n*d orbitals of transition metals can be mediated by bridging fluoride anions.

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Supporting Information Available: Thermal ellipsoid plots for $Ni(H_2O)_4UF_6{\cdot}1.5H_2O$ (**1**), $Ni_2(H_2O)_6U_3F_{16}{\cdot}3H_2O$ (**2**), and $Ni(H_2O)_2UF_6(H_2O)$ (**3**) and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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