Synthesis, Structural Characterization, and Topological Rearrangement of a Novel Open Framework U–O Material: $(NH_4)_3(H_2O)_2\{[(UO_2)_{10}O_{10}(OH)][(UO_4)(H_2O)_2]\}$

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A novel open framework U–O material with composition $(NH_4)_3(H_2O)_2\{[(UO_2)_{10}O_{10}(OH)][(UO_4)(H_2O)_2]\}$ was synthesized hydrothermally. The structure [monoclinic, $a = 11.627(2)$ Å, $b = 21.161(3)$ Å, $c = 14.706(2)$ Å, $\beta = 103.930(3)°$, $V = 3511.97$ Å³] was solved by direct methods and refined on the basis of F^2 for all 4230 unique reflections in space group $C2/c$ to an agreement factor (R1) of 7.7%, calculated using 2180 unique observed reflections ($|F_o| \geq 4\sigma_F$). The structure contains six symmetrically distinct U^{6+} sites, five of which occur as approximately linear $(UO_2)^{2+}$ uranyl ions that are coordinated by four or five additional ligands, giving square and pentagonal bipyramids. One U^{6+} cation occurs in distorted octahedral coordination. The structure contains β-U_3O_8-type sheets parallel to (001) that are cross-linked through U_2O_{12} pentagonal bipyramid dimers, resulting in an open framework structure composed only of uranium polyhedra. The $(NH_4)^+$ and H_2O groups are located in the interconnected three-dimensional channels along [100] that are bounded by 10-membered rings of uranyl polyhedra. A new layered uranyl material with composition $Cs_3[(UO_2)_3O_2(OH)_3]_2\cdot Cl(H_2O)_3$ was obtained by treatment of the framework phase in CsCl solution at 180 °C for 33 h. The structure [monoclinic, space group $C2$, $a = 19.615(5)$ Å, $b = 7.239(2)$ Å, $c = 12.064(3)$ Å, $\beta = 127.929(4)°$, $V = 1351.2(6)$ Å³] was refined on the basis of F^2 using 2462 unique reflections to R1 = 7.2%, calculated using the 1800 unique observed reflections ($|F_o| \geq 4\sigma_F$). The structure contains α-U_3O_8-type sheets of uranyl pentagonal bipyramids, with two symmetrically distinct Cs cations, a single Cl anion, and two H_2O groups located in the interlayer regions.

Introduction

Recent research concerning the crystal chemistry of actinide-bearing materials (minerals in particular) has demonstrated the presence of a variety of complex structure types and structural building units.[1–5] Much of the impetus for these investigations has stemmed from interest in the long-term geologic disposal of spent nuclear fuel. For example, several U^{6+} phases form on spent nuclear fuel under simulated Yucca Mountain geologic repository conditions.[6,7] An understanding of the structures and properties of such alteration products can thus aid in the assessment and design of storage facilities.

The current study aims to expand on recent studies of the crystal chemistry of uranium and to draw from the growing knowledge base of actinide crystal chemistry and couple it to a template-mediated synthetic incentive, the objective of which is the directed formation of novel open-structured phases. Such materials would be capable of (but certainly not limited to) occluding radionuclides. More broadly, however, there is a fundamental desire to understand the formation pathways and mechanisms of microporous materials in general. Key issues in actinide systems as well as several other families of open-structured materials include building unit speciation,[8] assembly,[9,10] the role(s) of the template,[11] and ion-exchange properties.[12] Reported in this contribution are the hydrothermal synthesis and structural characterization of a novel actinide framework, NDU-2, and its Cs-driven struc-

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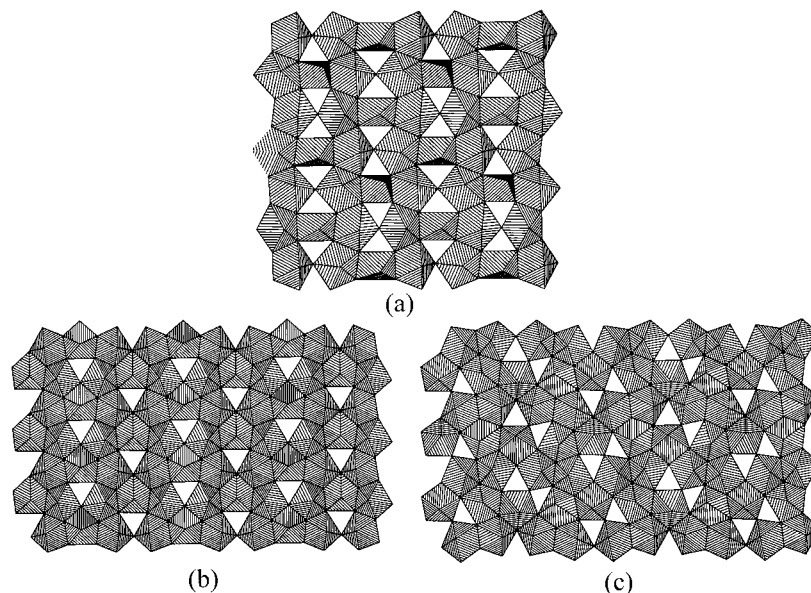
Figure 1. Polyhedral representation of U−O sheet types in (a) NDU-2, (b) NDU-2a, and (c) schoepite.

tural rearrangement to the novel layered cesium uranium oxychloride, NDU-2a.

Experimental Section

Synthesis. Crystals of $(NH_4)_3(H_2O)_2\{[(UO_2)_{10}O_{10}(OH)][(UO_4)(H_2O)_2]\}$ (designated as NDU-2 hereafter) were synthesized hydrothermally in a 23-mL Teflon-lined stainless steel Parr bomb. Uranyl oxyacetate (0.314 g; Alfa) was first dissolved in 4 mL of deionized water, to which 0.144 g of ammonium carbonate [$(NH_4)_2CO_3$; Fisher] was added. The starting materials were transferred to the Parr bomb and heated at 220 °C for 2 weeks. The product, an amber-yellow powder consisting of needlelike crystals, was recovered via filtration, washed with deionized water, and allowed to dry in air. In some preparations, small amounts of dark needle-shaped crystals were observed; powder XRD indicated that these are likely α-UO$_3$.

"Ion-Exchange" Experiments. The ion-exchange properties of NDU-2 with Cs were examined by putting several as-synthesized crystals in a Parr bomb, together with 4 mL of a 2 M CsCl solution, followed by heating at 180 °C for 33 h. This approach has been sucessful in previous studies of uranyl compounds[13] and allows for single-crystal analysis of the exchanged material. Following treatment, both the shape and color of the crystals had changed, resulting in greenish-yellow thin, platy crystals. A full structure determination of this phase (below) was possible via single-crystal X-ray diffraction and indicated that the U−O framework material transformed into a novel layered Cs uranyl oxychloride hydrate (designated as NDU-2a hereafter). In light of this result, a bulk exchange was performed and subsequent X-ray powder diffraction experiments indicated the formation of mixed phase products: NDU-2a and schoepite $\{[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$, PDF# 13-0241}. The structure of schoepite was reported by Finch et al.,[14] as shown in Figure 1c, whereas the crystal structure of NDU-2a has not been previously reported.

Single-Crystal X-ray Diffraction. A single crystal of NDU-2 was mounted on a Bruker three-circle CDD-based X-ray diffractometer operated at 50 kv and 40 mA. A hemisphere of three-dimensional data was collected using monochromatic Mo Kα X-radiation. A frame width of 0.3° in ω and 60 s counting time per frame were used. Final unit cell parameters (Table 1) were refined by least-squares techniques

using 1065 strong reflections selected from the data. The intensity data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT.[15] An empirical absorption correction was applied by modeling the crystal as an ellipsoid. A total of 10 920 reflections was collected, of which there were 4230 unique reflections (R_{int} = 10.7%) with 2180 classed as observed ($|F_o| \geq 4\sigma_F$).

Systematic absences were consistent with space group $C2/c$, and the structure was solved readily using the SHELXTL[16] suite of programs. The uranium atoms were located first, whereas oxygen and nitrogen atoms were found using difference Fourier maps calculated following subsequent refinement cycles. The final structural model was refined on the basis of F^2 for all unique data and included anisotropic displacement parameters for all U atoms. The refinement converged to R1 = 7.7%, calculated for the 2180 unique observed reflections ($|F_o| \geq 4\sigma_F$). Additional information regarding data collection and refinement for NDU-2 is provided in Table 1.

Data collection for NDU-2a was performed in a fashion similar to that for NDU-2 and is summarized in Table 1. Unit cell parameters (Table 1) were refined using 1099 reflections by least-squares techniques. An empirical absorption-correction was done by modeling the crystal as a {100} plate and reduced R_{int} of 612 intense reflections from 12.9% to 10.3%. Reflections with a plate-glancing angle less than 3.0° were discarded. A total of 3750 reflections was collected, of which 2462 were unique (R_{int} = 11.7%), with 1800 considered observed ($|F_o| \geq 4\sigma_F$).

Systematic absences, statistics of intensity distribution, and successful solution and refinement of the structure indicated that the space group of NDU-2a is $C2$. The structure solved readily using direct methods, which provided all U atoms. The O positions were easily found in difference Fourier maps calculated following subsequent least-squares refinement cycles. A single unique Cl site in the interlayer was distinguished from O atoms (H_2O groups) by refining site occupancy factors and displacement parameters. This site gave unreasonably small displacement parameters and a high occupancy factor when treated as an O atom. Designating this site as Cl not only gave a reasonable value for the displacement parameter but also yielded a refined site occupancy of 0.96(3). The presence of Cl in these crystals was confirmed by analysis

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Table 1. Selected Crystallographic Data for Three-Dimensional Ammonium Uranyl Oxide Hydrate (NDU-2) and Two-Dimensional Cs−Uranyl Oxychloride Hydrate (NDU-2a)

	NDU-2	NDU-2a
structural formula	$(NH_4)_3(H_2O)_2\{[(UO_2)_{10}O_{10}(OH)][(UO_4)(H_2O)_2]\}$	$Cs_3[(UO_2)_3O_2(OH)_3]_2Cl(H_2O)_3$
formula weight	3305.53	2274.46
crystal size (mm)	$0.06 \times 0.02 \times 0.02$	$0.05 \times 0.04 \times 0.01$
temp (K)	293(2)	293(2)
crystal system	monoclinic	monoclinic
space group	$C2/c$	$C2$
a (Å)	11.627(2)	19.615(5)
b (Å)	21.161(3)	7.239(2)
c (Å)	14.706(2)	12.064(3)
β (deg)	103.930(3)	127.929(4)
V (Å³), Z	3512.0(9), 4	1351.2(6), 2
μ (mm⁻¹)	50.6	40.0
ρ_{calc} (g/cm³)	6.252	5.590
θ range for data collection	1.92−28.33°	2.14−28.28°
reflections collected	10 920	3750
independent reflections	4230 ($R_{int} = 0.1068$)	2462 ($R_{int} = 0.1170$)
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
goodness-of-fit on F^2	1.009	1.021
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0770, wR2 = 0.1601	R1 = 0.0720, wR2 = 0.1596
R indices (all data)	R1 = 0.1613, wR2 = 0.1812	R1 = 0.1024, wR2 = 0.1705
largest diff peak and hole	7.544 and 8.344 e Å⁻³	4.938 and 4.162 e Å⁻³

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for NDU-2

	x	y	z	$U_{eq}{}^a$
U(1)	2541(1)	907(1)	175(1)	7(1)
U(2)	2500	2500	0	54(1)
U(3)	589(1)	790(1)	201(1)	7(1)
U(4)	5715(1)	784(1)	237(1)	7(1)
U(5)	8197(1)	749(1)	2268(1)	9(1)
U(6)	534(1)	2505(1)	30(1)	6(1)
O(1)	2220(20)	1144(12)	1075(17)	13(6)
O(2)	2820(20)	750(12)	1484(16)	12(5)
O(3)	1180(30)	1917(13)	160(20)	30(8)
O(4)	1200(20)	914(12)	1038(18)	18(6)
O(5)	35(19)	747(11)	1600(16)	9(5)
O(6)	5480(20)	920(11)	1006(18)	17(6)
O(7)	6090(20)	685(12)	1566(18)	17(6)
O(8)	8270(20)	37(12)	2260(19)	17(6)
O(9)	8090(20)	1621(12)	2270(20)	20(7)
O(10)	250(30)	2320(14)	1210(20)	32(8)
O(11)	850(30)	2688(14)	1180(20)	39(9)
O(12)	7707(17)	767(10)	641(14)	2(4)
O(13)	4240(20)	1460(12)	443(18)	18(6)
O(14)	3950(20)	249(12)	35(17)	12(6)
O(15)	960(20)	1468(12)	270(20)	22(7)
O(16)	3670(30)	1914(13)	300(20)	26(7)
O(17)	1010(20)	247(13)	38(19)	23(7)
OH(18)	2500	2500	0	50(14)
OW(19)	1760(30)	2820(18)	1580(30)	66(12)
OW(20)	5000	1600(20)	2500	36(12)
OW(21)^b	6730(50)	2270(30)	2650(40)	20
N(1)	0	1120(20)	2500	18(11)
N(2)	6730(30)	1022(15)	2540(20)	20

^{a} U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^{b} OW(21) occupancy factor = 50%.

Table 3. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for NDU-2a

	x	y	z	$U_{eq}{}^a$
U(1)	7588(1)	2139(2)	9498(2)	9(1)
U(2)	7587(1)	2139(2)	5677(2)	9(1)
U(3)	7797(1)	6426(2)	7798(2)	9(1)
Cs(1)	0(2)	5127(5)	7817(4)	25(1)
Cs(2)	5000	3792(9)	5000	45(2)
Cl(1)	0	2050(30)	0	36(5)
O(1)	6482(18)	2040(50)	5060(30)	24(7)
O(2)	8959(19)	6370(50)	8920(30)	21(7)
O(3)	8661(19)	2010(50)	6280(30)	28(7)
O(4)	6640(20)	6640(60)	6610(40)	44(11)
O(5)	8670(20)	2000(50)	1030(30)	32(8)
O(6)	6519(19)	2080(50)	7910(30)	28(7)
O(7)	7740(20)	5200(50)	6070(30)	19(7)
O(8)	7720(20)	5260(50)	9370(30)	21(8)
OH(9)	7903(19)	8910(40)	6560(30)	15(7)
OH(10)	7955(19)	8850(40)	9380(30)	13(7)
OH(11)	8039(18)	2760(40)	8020(30)	11(6)
OW(12)	40(40)	9170(90)	1890(60)	90(20)
OW(13)	5000	9260(110)	5000	76(24)

^{a} U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TGA in flowing nitrogen. The results showed two distinct weight loss events: a 2.2% loss beginning at approximately 400 °C and a 2% loss beginning at 600 °C. These are likely due to the loss of H_2O and $NH_4{}^+$, respectively. Elemental analysis for N (Galbraith Laboratories) in NDU-2 yielded 1.43 wt % (1.84 wt % NH_4).

X-ray Powder Diffraction. Powder diffraction patterns were collected at room temperature using a Rigaku Miniflex diffractometer (Cu Kα, 3−60° 2θ, 1 s/0.01° step). Calculated diffraction patterns of NDU-2 and -2a were generated with CrystalDiffract 2.1.0.[19] Comparison of observed and calculated patterns, as well as Powder Diffraction File searches, was done with Jade.[20]

Electron Microprobe Analysis. A single crystal of NDU-2a was mounted in epoxy, polished, and coated with carbon. Electron microprobe analyses were done using a Cameca SX-50 operated in wavelength-dispersive spectroscopy (WDS)

using an electron probe (below). The origin of the Cl in NDU-2a is the CsCl solution used for treatment of NDU-2. The final structure model was refined on the basis of F^2 for all unique data, and included anisotropic displacement parameters for all U, Cs, and Cl atoms. The refinement resulted in an R1 of 7.2%, calculated for the 1800 observed reflections. The final atomic coordinators and selected bond lengths and angles for both NDU-2 and NDU-2a are given in Tables 2−5.

IR, TGA, and Elemental Analysis. The infrared spectrum for NDU-2 was obtained using a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Absorption bands around 3200 and 1384 cm⁻¹ may be attributed to characteristic N−H stretching and bending (respectively) modes within the $NH_4{}^+$ group in the structure.[17,18] Thermogravimetric analysis of NDU-2 was performed on a TA Instruments SDT 2960 Simultaneous DTA/

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Table 4. Selected Bond Distances (Å) and Angles (deg) for NDU-2[a]

U(1)−O(1)	1.86(2)	U(2)−O(3)	1.94(3)	U(3)−O(4)	1.81(3)
U(1)−O(2)	1.90(2)	U(2)−O(3)#3	1.94(3)	U(3)−O(5)	2.00(2)
U(1)−O(14)	2.20(2)	U(2)−O(16)	1.97(3)	U(3)−O(12)#5	2.23(2)
U(1)−O(15)	2.22(3)	U(2)−O(16)#3	1.97(3)	U(3)−O(17)	2.25(3)
U(1)−O(17)#1	2.22(3)	U(2)−OW(19)#3	2.37(4)	U(3)−O(17)#1	2.29(3)
U(1)−O(13)	2.25(3)	U(2)−OW(19)	2.37(4)	U(3)−O(15)	2.29(3)
O(1)−U(1)−O(2)	174(1)	$\langle$U(2)$-\phi\rangle$	2.09	U(3)−O(3)	2.48(3)
$\langle$U(1)−O$_{Ur}\rangle$	1.88			O(4)−U(3)−O(5)	173(1)
$\langle$U(1)−O$_{eq}\rangle$	2.22			$\langle$U(3)−O$_{Ur}\rangle$	1.90
				$\langle$U(3)−O$_{eq}\rangle$	2.31
U(4)−O(6)	1.81(3)	U(5)−O(8)	1.67(2)	U(6)−O(10)	1.73(3)
U(4)−O(7)	1.91(3)	U(5)−O(9)	1.85(2)	U(6)−O(11)	1.77(3)
U(4)−O(12)	2.25(2)	U(5)−O(12)	2.32(2)	U(6)−O(15)	2.27(3)
U(4)−O(14)#2	2.27(2)	U(5)−O(5)#7	2.37(2)	U(6)−OH(18)	2.276(1)
U(4)−O(14)	2.30(2)	U(5)−O(2)#7	2.41(2)	U(6)−O(13)#4	2.31(3)
U(4)−O(13)	2.31(3)	U(5)−O(7)	2.42(2)	U(6)−O(3)	2.42(3)
U(4)−O(16)#6	2.49(3)	U(5)−O(5)#6	2.48(2)	U(6)−O(16)#3	2.44(3)
O(6)−U(4)−O(7)	175(1)	O(8)−U(5)−O(9)	179(1)	O(10)−U(6)−O(11)	179(2)
$\langle$U(4)−O$_{Ur}\rangle$	1.86	$\langle$U(5)−O$_{Ur}\rangle$	1.76	$\langle$U(6)−O$_{Ur}\rangle$	1.75
$\langle$U(4)−O$_{eq}\rangle$	2.32	$\langle$U(5)−O$_{eq}\rangle$	2.40	$\langle$U(6)−O$_{eq}\rangle$	2.34

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x$, $-y$, $-z$, #2, $-x + 1$, $-y$, $-z$, #3, $-x - \frac{1}{2}$, $-y + \frac{1}{2}$, $-z$, #4, $-x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z$, #5, $x - 1$, y, z, #6, $x + 1$, y, z, #7, $-x + 1$, y, $-z + \frac{1}{2}$.

Table 5. Selected Bond Distances (Å) and Angles (deg) for NDU-2a[a]

U(1)−O(5)#1	1.76(3)	U(2)−O(3)	1.76(3)	U(3)−O(2)	1.80(3)
U(1)−O(6)	1.77(3)	U(2)−O(1)	1.81(3)	U(3)−O(4)	1.80(4)
U(1)−O(8)#2	2.25(3)	U(2)−O(7)	2.25(3)	U(3)−O(8)	2.17(3)
U(1)−O(8)	2.29(3)	U(2)−O(7)#5	2.27(3)	U(3)−O(7)	2.20(3)
U(1)−OH(11)	2.47(3)	U(2)−OH(11)	2.43(3)	U(3)−OH(9)	2.43(3)
U(1)−OH(10)#2	2.51(3)	U(2)−OH(9)#3	2.48(3)	U(3)−OH(10)	2.47(3)
U(1)−OH(10)#3	2.52(3)	U(2)−OH(9)#5	2.58(3)	U(3)−OH(11)	2.68(3)
O(5)#1−U(1)−O(6)	175(2)	O(3)−U(2)−O(1)	175(2)	O(2)−U(3)−O(4)	176(2)
$\langle$U(1)−O$_{Ur}\rangle$	1.76	$\langle$U(2)−O$_{Ur}\rangle$	1.78	$\langle$U(3)−O$_{Ur}\rangle$	1.80
$\langle$U(1)−O$_{eq}\rangle$	2.41	$\langle$U(2)−O$_{eq}\rangle$	2.40	$\langle$U(3)−O$_{eq}\rangle$	2.39
Cs(1)−OW(12)#6	2.96(6)	Cs(2)−O(1)#7	3.13(3)		
Cs(1)−O(5)#7	3.07(3)	Cs(2)−O(1)	3.13(3)		
Cs(1)−O(3)#8	3.07(3)	Cs(2)−O(6)#7	3.14(3)		
Cs(1)−O(1)#9	3.16(3)	Cs(2)−O(6)	3.14(3)		
Cs(1)−O(2)#8	3.18(3)	Cs(2)−O(4)	3.27(4)		
Cs(1)−O(6)#10	3.24(3)	Cs(2)−O(4)#7	3.27(4)		
Cs(1)−O(2)#4	3.25(3)	Cs(2)−OW(13)#3	3.28(8)		
Cs(1)−Cl(1)#1	3.45(2)	$\langle$Cs(1)$-\phi\rangle$	3.19		
Cs(1)−OW(13)#11	3.45(2)				
Cs(1)−O(7)#8	3.55(3)				
Cs(1)−O(8)#4	3.59(3)				
$\langle$Cs(1)$-\phi\rangle$	3.27				

[a] Symmetry transformations used to generate equivalent atoms: #1, x, y, $z + 1$; #2, $-x + \frac{3}{2}$, $y - \frac{1}{2}$, $-z + 2$; #3, x, $y - 1$, z; #4, $-x + 1$, y, $-z + 2$; #5, $-x + \frac{3}{2}$, $y - \frac{1}{2}$, $-z + 1$; #6, $-x$, y, $-z + 1$; #7, $-x + 1$, y, $-z + 1$; #8, $x - 1$, y, z; #9, $-x + \frac{1}{2}$, $y + \frac{1}{2}$, $-z + 1$; #10, $x - \frac{1}{2}$, $y + \frac{1}{2}$, z, #11, $x - \frac{1}{2}$, $y - \frac{1}{2}$, z.

mode. All analyses were performed with an accelerating voltage of 15 kV and a probe current of 25 nA, with a defocused beam size of 10 μm in diameter. Counting times on peaks and backgrounds were 10 s for Cs(Lα), Cl(Kα), and U(Mα), respectively. Analytical EMPA standards used were Cs-natural pollucite, Cl-synthetic Cl-apatite, and U−UO₂ microspheres from Oak Ridge National Lab. The specimen was found to gradually disintegrate under vacuum, and we were unable to obtain entirely reproducible results over time. Analyses done over the course of several weeks for the same specimen gave progressively lower values for Cs. The average values of four analyses (atomic wt %) conducted initially are U, 62.1; Cl, 1.31; Cs, 13.3. Theoretical values, calculated on the basis of the structural formula, are U, 62.4; Cl, 1.5; Cs, 17.4. In the course of analyses of several other Cs uranyl phases using similar procedures, we found the results for Cs to be consistently about 10% lower than expected, possibly indicating that the standard used was not ideal.

Results

Structure of NDU-2. There are six symmetrically unique U^{6+} positions in the structure of NDU-2. Of these, four [U(3), U(4), U(5), and U(6)] are in pentagonal bipyramidal coordination with either O or OH and can be represented as Ur(3)ϕ_5, Ur(4)ϕ_5, Ur(5)ϕ_5, and Ur(6)ϕ_5, where Ur represents the nearly linear O=U=O uranyl ion, and ϕ = equatorial ligands O, OH, or H_2O (as distinguished via bond-valence summations). Ur(1)ϕ_4 is in a square bipyramidal arrangement with four O atoms, whereas U(2)ϕ_6 is a distorted octahedron with four O atoms and two H_2O groups (OW19, Table 4). Ur(1)ϕ_4, U(2)ϕ_6, Ur(3)ϕ_5, Ur(4)ϕ_5, and Ur(6)ϕ_5 share edges and vertexes, forming sheets parallel to (110) (Figure 1a). The connectivity within these layers and the resulting topology is identical to that found in β-U_3O_8 and is often referred to as the 'β-U_3O_8 sheet type'.[1−3] The sheets are cross-linked via Ur(5)$_2\phi_8$ dimer units, forming an extended framework structure (Figure 2). This cross-linking gives rise to 10-membered channels extending along [100], within which reside NH_4^+ cations and H_2O groups. The dimensions of the channel cross-section are approximately 7.3 × 3.6 Å, as mea-
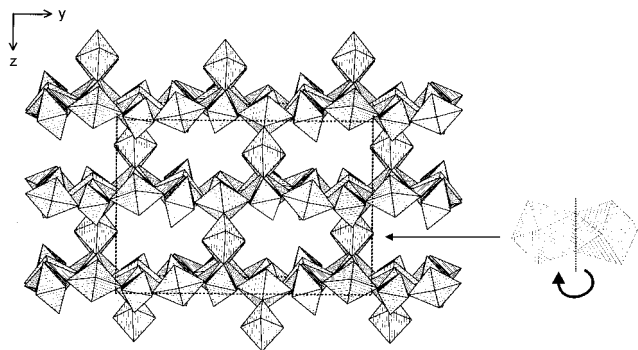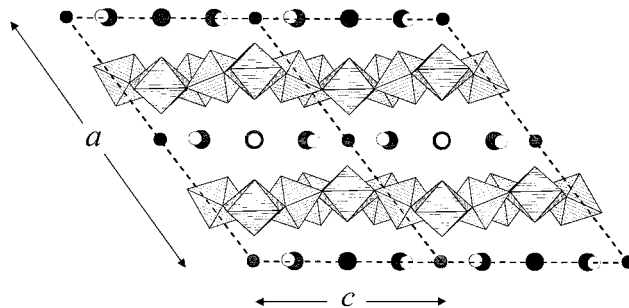
Figure 2. The crystal structure of NDU-2 projected along [100], showing the 3D-framework structure. NH_4^+ and H_2O groups are omitted for clarity. The cross-linking dimer units are shown as an inset to demonstrate connectivity between sheets. The unit cell is shown in dashed lines.

Figure 3. The crystal structure of NDU-2a projected along [010]; large filled circles represent Cs^+, small filled circles Cl^-, and open circles H_2O groups.

sured from the shortest distance between the centers of framework anions.

Bond lengths and angles for NDU-2 (Table 4) are typical of those found in other U−O compounds. The coordination of U(2) (Table 4) to two H_2O groups is unusual, although H_2O is bounded to U^{6+} in the mineral soddyite.[21] Bonding of apical O_{Ur} atoms in square or pentagonal bipyramids to another U^{6+} cation [O(2, 5, 7)] is extremely rare, as these sites are typically satisfied in terms of bond-valence requirements.[1−3] In the structure of NDU-2, this is reflected by a longer than normal U−O_{Ur} distance (∼1.79 Å)[1−3] in the U(1)−O(2) bond at 1.90(2), U(3)−O(5) bond at 2.00(2) Å, and U(4)−O(7) bond at 1.91(3) Å.

Within the channels of NDU-2, there are two independent N sites and two H_2O sites. N(1) and N(2) are part of ammonium cations, as required for charge balance and supported by IR spectroscopy. N(1) is surrounded by eight framework O atoms and N(2) by six framework O atoms and one extraframework H_2O group, with N−O distances ranging from 2.73(4) to 3.39(4) Å. During the crystal structure refinement of NDU-2, one of the N sites [N(2)] exhibited unusually small displacement parameters and an abnormal occupancy factor. Elemental analysis of the compound to check for possible contaminents was done, but yielded no indication of any heavier elements that would be compatible with this site. Also, in the initial stages of the refinement, the displacement parameter for OW(21) was large and thus prompted occupancy factor refinement that resulted in nearly half-occupancy. Therefore, in the final structural model, the displacement parameter and site occupancy factor were fixed at 0.02 and 1.0 for N(1) and 0.02 and 0.50 for OW(21), respectively. Considering both the framework and extraframework species in NDU-2, the structural formula should be written as $(NH_4)_3(H_2O)_2\{[(UO_2)_{10}O_{10}(OH)][(UO_4)(H_2O)_2]\}$, where the framework composition is contained in brackets.

Structure of NDU-2a. There are three symmetrically unique U^{6+} cations in the structure of NDU-2a, all of which are in $Ur\phi_5$ uranyl pentagonal bipyramidal coordinations with O or OH. The uranyl polyhedra share edges, forming sheets (Figure 1b) parallel to the (011)

plane, within which the connectivity is identical to that found in α-U_3O_8. Oxygen sites were distinguished from OH groups via bond-valence summations. Bond lengths within the polyhedra range from 1.76 to 2.68 Å (Table 5) and are consistent with many other materials containing U in this arrangement.[2,3]

The interlayer region of NDU-2a hosts two unique Cs cation sites, one Cl, and two H_2O sites (Figure 3). Cs(1) is coordinated to eleven anions with $\langle Cs(1)-\phi \rangle = 3.27$ Å (ϕ, O^{2-}, Cl^-, and H_2O), and Cs(2) is bonded to seven anions with $\langle Cs(2)-\phi \rangle = 3.19$ Å. Cs polyhedra in the interlayer share edges and faces, forming chains parallel to the c axis (Figure 3). Cl is weakly bonded to two Cs(1) atoms at a distance of 3.45 Å and is held in place by O···H···Cl hydrogen bonds (Cl−OH(11); ∼3.1 Å). Considering both the composition of the sheets and the interlayer region, the formula of NDU-2a is thus $Cs_3[(UO_2)_3O_2(OH)_3]_2Cl(H_2O)_3$, with the sheet composition enclosed in brackets. This formula suggests that Cl accounts for 1.56 wt % of NDU-2a, in agreement with the value obtained from the electron microprobe analysis.

Discussion

The structure of NDU-2 can best be described as a series of parallel β-U_3O_8-type layers cross-linked through edge-sharing dimers, resulting in a 3-D framework. This connectivity exhibits a number of interesting topological features, the most notable of which is the bridging through apical (Ur) oxygen atoms (O2, O5, and O7, Table 4) that link subsequent sheets together. This is a very unusual situation and appears to be unprecedented in hydrous uranyl phases. Thus a new bonding mechanism in U−O materials has been observed and introduces a challenge for synthetic efforts to delineate experimental conditions that produce this type of topology. As the vast majority of U^{VI}−O materials in fact consist of layered structures, the potential to create an entirely new family based on the polymerizing of known layer types is enormous.

It is likely that the ammonium cations play a key role in directing the formation of NDU-2. Aside from the charge balancing role of the ammonium cations, more experiments are needed to specify any additional functions, i.e., as outlined by Davis as space filling, structure directing, or "true templating".[11] There are several reports of other systems that have made use of NH_4^+ as a template (or, more generally, a structure directing agent) including cobalt aluminum phophates (CoAPOs), germanates, and iron phosphates, yet these have com-

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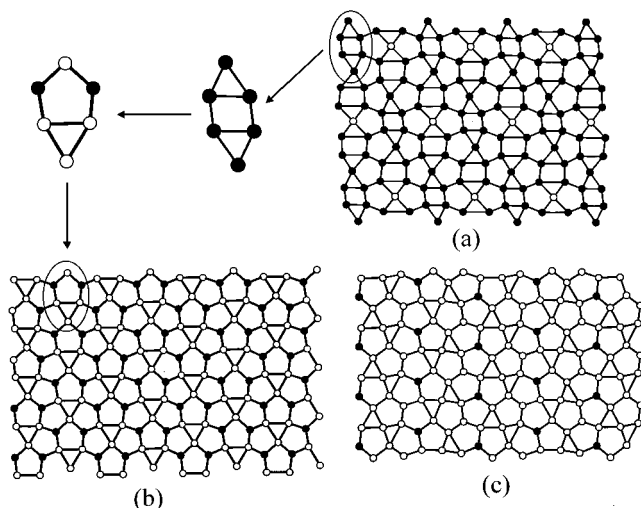
Figure 4. Corresponding sheet anion topology for (a) NDU-2, (b) NDU-2a, and (c) schoepite. The positions of the O^{2-} and $(OH)^-$ are designated by filled and open circles, respectively.

mented little on its exact function and subsequent assembly mechanisms.[17,22,23]

Attempts at Cs exchange of NDU-2 resulted in a radical change in topology from framework to layered in NDU-2a. This is likely driven by the size of the Cs^+ ion, as similar experiments (although preliminary) with K^+ and Na^+ resulted in little structural change. One can speculate on the integrity of the NDU-2 framework in light of this observation; it is possible that the interlayer linkage is not robust. In other words, the normally terminal uranyl ion O atoms that are in this case bridging to the $Ur(5)O_8$ dimer may be a "weak link" in the framework. A stronger framework would have excluded the Cs^+ ions rather than rearranged to accommodate them. This observation may be supported by the fact that this mode of connectivity has not been observed in uranyl minerals and perhaps results only from a narrow range of formation conditions.

The transition from the β-U_3O_8-type sheet in NDU-2 to the α-U_3O_8-type sheet in NDU-2a is shown via the anion topology representation[1] in Figure 4. From this figure, it is clear that the structural rearrangement within the sheets is fairly minor, involving only a slight displacement of anions in the β-U_3O_8-type sheet to result in the α-U_3O_8 topology. The formation of schoepite in bulk exchange experiments, however, may be the result of a reassembly of the dimer units displaced from the NDU-2 framework. Thus an overall transition mechanism can be envisaged as a "pseudo-intercalation" process in which the Cs^+ cations of NDU-2a displaced the cross-linking $Ur(5)O_8$ dimers of NDU-2. The dimer species are then free to recombine and in this system do so as schoepite.

NDU-2a is a member of a family of uranyl materials, including minerals and synthetic phases, in which uranyl polyhedra polymerize to form sheets based on

the α-U_3O_8 topology. Other materials include becquerelite, $Ca[(UO_2)_3O_2(OH)_3]_2(H_2O)_8$; billietite, $Ba[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$; protasite, $Ba[(UO_2)_3O_3(OH)_2](H_2O)_3$;[24] compreignacite, $K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$;[25] richetite, $M_xPb_{8.57}[(UO_2)_{18}O_{18}(OH)_{12}]_2(H_2O)_{45}$;[26] agrinerite, $K_2(Ca_{0.65}Sr_{0.35})[(UO_2)_3O_3(OH)_2]_2(H_2O)_5$;[27] masuyite, $Pb[(UO_2)_3O_3(OH)_2](H_2O)_3$;[28] and $Cs_3[(UO_2)_{12}O_7(OH)_{13}](H_2O)_3$.[29] The compounds differ from one another not only in interlayer composition but also in distribution of hydroxyl groups within the sheets themselves. NDU-2a is unique in this system in that it is the first layered uranyl material to incorporate anionic species (Cl) in its interlayer region, yet its hydroxyl arrangement is equivalent to that of becquerelite, billietite, and compreignacite. Interestingly, becquerelite and compreignacite have been found to form as alteration phases on spent nuclear fuel under simulated geologic repository conditions.[6] Further, radionuclide release fractions obtained from these studies indicate that ^{137}Cs is incorporated into or onto alteration products.[6] As NDU-2a is closely related to these phases, it is plausible that its existence could impact the release of ^{137}Cs and ^{135}Cs if it forms under repository conditions.

Conclusions

A novel open framework actinide material (NDU-2) that exhibits very unusual bridging uranyl oxygen atoms has been synthesized. The existence of such a bonding mechanism indicates the potential for synthesis of a range of framework materials in the U−O system. Ion-exchange experiments have demonstrated that in order to accommodate Cs, NDU-2 undergoes a structural rearrangement to a layered cesium uranyl oxychloride phase, NDU-2a. Further, NDU-2a is the first example of a layered uranyl material that contains an anionic species in its interlayer region (Cl). The formation of both of these materials under hydrothermal conditions, as well as their structural relationships to known alteration phases of spent nuclear fuel, suggests their possible formation under the conditions of the proposed geologic repository for spent nuclear fuel at Yucca Mountain, Nevada.

Supporting Information Available: A file of X-ray crystallographic data for NDU-2 and NDU-2a in CIF format. This material is available free of charge via the Internet at http/::pubs.acs.org.

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