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Structural Studies Coupling X-ray Diffraction and High-Energy X-ray Scattering in the UO_2^{2+}−HBr_{aq} System

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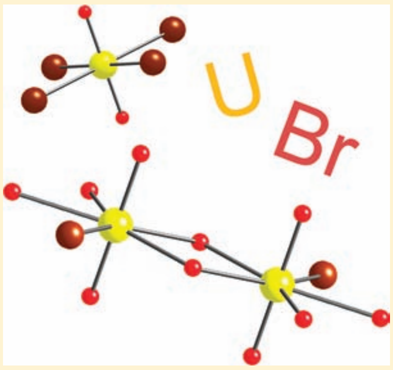
Supporting Information

ABSTRACT: The structural chemistry of uranium(VI) in concentrated aqueous hydrobromic acid solutions was investigated using both single crystal X-ray diffraction and synchrotron-based high-energy X-ray scattering (HEXS) to reveal the structure of the uranium(VI) complexes in solution prior to crystallization. The crystal structures of a series of uranyl tetrabromide salts are reported, including $Cs_2UO_2Br_4$, $Rb_2UO_2Br_4 \cdot 2H_2O$, $K_2UO_2Br_4 \cdot 2H_2O$, and $(NH_4)_2UO_2Br_4 \cdot 2H_2O$, as well as a molecular dimer of uranium(VI), $(UO_2)_2(OH)_2Br_2(H_2O)_4$. Limited correspondence exists between the structures observed in the solid state and those in solution. Quantitative analysis of the HEXS data show an average U−Br coordination number of 1.9(2) in solution, in contrast to the U−Br coordination number of 4 in the solid salts.



INTRODUCTION

The structural chemistry of metal ions and their complexes in both the solid and solution states underpins the comprehensive chemical understanding necessary for predictive chemical modeling. Understanding the solution speciation of solute metal ions is requisite for manipulating their chemistry to achieve deliberate chemical control as exemplified by either a chemical separation or a rational chemical synthesis. In the solid precipitate, correlating the solution speciation with a structural or functional material is developing as a desirable path toward rational materials synthesis. While much is currently known regarding transition metal coordination chemistry, fewer studies have focused on the actinide elements despite the complexity of their chemistry and their technological importance for energy production.

Historically, anionic metal complexes have been used as targets in separations schemes, particularly for ion-exchange-based separations on solid supports or in liquid−liquid extractions.[1−3] More recently, anionic metal complexes are being targeted in a synthon−tecton approach to materials synthesis coupling the anionic metal complexes to each other through cationic organic linkages exploiting noncovalent ionic and hydrogen-bonding interactions.[4−6] A common set of ligands used in the formation of these complexes are halide anions. The halides provide a suite of ligands to study the structural chemistry of metal−ligand interactions in both the solution and solid states. The strength of the metal−ligand interaction for a given metal ion usually decreases as one progresses down the halogen group, and for the heaviest of the halogens, bromine and iodine, one would expect the interaction to be quite small, an effect which is exploited in the use of heavier metal−halide complexes as starting materials in organometallics and nonaqueous chemical syntheses.[7] Conversely, as one proceeds across the actinide series, the strength of these actinide−halide interactions increases for a given halogen.[8] In consideration of the weak metal−ligand interactions expected for bromide ions with metal ions, we have undertaken a study aimed at isolating uranyl bromide complexes in the solid state and attempting to correlate their structures with the species seen in solution.

Hexavalent uranium in aqueous solution exists as a linear dioxo cation, its coordinating ligands confined, for the most part, to the plane perpendicular to the linear uranyl moiety $[O{=}U{=}O]^{2+}$ and generally numbering between four and six.[9] This is in contrast to the spherical cations of the tri- and tetravalent actinide ions, whose coordination geometries and numbers are exceptionally diverse. The confinement of the ligand coordination in uranyl and the other actinyl ions therefore makes them good entry points to studying both the solid-state and solution-state structures of their complexes.

Herein we report the solid-state structures of uranyl complexes isolated from concentrated aqueous hydrobromic acid. The structures include a series of uranyl tetrabromide salts and a uranyl hydroxo-bridged dimer; the structures of the cesium and ammonium bearing salts have been previously reported and are included here for completeness.[10,11] Previous studies aimed at measuring the stability constants of these complexes in aqueous

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Table 1. Crystallographic Details for the Uranyl Bromide Structures

	$(NH_4)UO_2Br_4\cdot 2H_2O$ (**1**)	$K_2UO_2Br_4\cdot 2H_2O$ (**2**)	$Rb_2UO_2Br_4\cdot 2H_2O$ (**3**)	$Cs_2UO_2Br_4$ (**4**)	$(UO_2)_2(OH)_2Br_2(H_2O)_4$ (**5**)
a (Å)	6.777(1)	6.753(1)	6.862(1)	6.350(1)	9.840(2)
b (Å)	6.822(1)	6.825(1)	6.925(2)	9.742(2)	6.320(1)
c (Å)	7.680(1)	7.573(3)	7.736(3)	9.927(2)	10.850(2)
α (deg)	98.08(1)	93.97(1)	93.754(4)	90.00	90.00
β (deg)	95.04(1)	99.49(1)	99.142(4)	104.51(2)	115.65(3)
γ (deg)	116.49(1)	117.48(1)	117.360(3)	90.00	90.00
V (Å3)	310.1(1)	301.1(1)	318.28(16)	594.5(2)	608.3(3)
Z	1	1	1	2	2
MW (g mol^{-1})	649.65	699.83	792.57	855.49	795.88
space group	$P\bar{1}$ triclinic	$P\bar{1}$ triclinic	$P\bar{1}$ triclinic	$P2_1/c$ monoclinic	$P2_1/c$ monoclinic
T (°C)	−173	−173	−173	−173	−173
λ (Å) [Mo Kα]	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calc} (g cm^{-3})	3.479	3.859	4.135	4.779	4.345
μ (mm^{-1})	25.954	27.408	32.874	33.079	33.185
$R(F_0)$, $wR(F_0^2)$	0.030, 0.072	0.030, 0.075	0.044, 0.105	0.031, 0.071	0.040, 0.070

solution have shown the uranyl—bromide interaction to be weak.[8] Published attempts to synthesize uranyl halide complexes as starting materials for nonaqueous and organometallic syntheses have demonstrated these complexes to be particularly labile.[7] To probe the uranyl bromide complexes existing in solution, their impact on uranyl solution chemistry, and their relationship to the compounds that precipitate, we have studied crystal supernates using high-energy X-ray scattering (HEXS), a technique previously demonstrated to be useful in relating solid-state structures with correlations existing in solution.[12−14]

■ EXPERIMENTAL METHODS

Caution! ^{238}U is an α-emitting radionuclide. All preparations were carried out using strict radiological controls in specially designed facilities for the manipulation of α-emitting radionuclides.

Synthesis of $Cs_2UO_2Br_4$ and $M_2UO_2Br_4\cdot 2H_2O$ (M = NH_4, K, Rb). A 1 m (mol/kg H_2O) solution of UO_2^{2+} in aqueous hydrobromic acid was prepared by the dissolution of UO_3 (572 mg) in aqueous hydrobromic acid (2.552 mL), accounting for the formation of water during the dissolution reaction of UO_3 with HBr_{aq}. The HBr_{aq} was brought to its constant boiling azeotrope before use (48% HBr wt/wt, ρ = 1.48 g mL^{-1}). Saturated solutions of NH_4Br, KBr, RbBr, and CsBr were prepared by dissolution of the salts in aqueous hydrobromic acid. Equal volumes of the 1 m UO_2^{2+} solution and the saturated salt solutions were combined and allowed to evaporate. In the case of the Rb and Cs preparations, crystals suitable for single crystal X-ray diffraction studies formed within 1 h. Larger crystals, >1 mm, could be prepared by decreasing the alkali metal concentration to 0.5−1 m in concentrated HBr_{aq}, allowing for slower crystal growth. No attempt was made to control the hydration state of the resulting complexes. Attempts to produce crystals of Na or Li containing salts were unsuccessful.

Synthesis of $(UO_2)_2(OH)_2Br_2(H_2O)_4$. To prepare single crystals of $(UO_2)_2(OH)_2Br_2(H_2O)_4$, a 1 mL aliquot of the 1 m UO_2^{2+} solution in concentrated HBr was allowed to concentrate by evaporation at room temperature. Crystals suitable for X-ray diffraction studies developed after several weeks, by which time more than 90% of the solution volume had evaporated, leaving a viscous yellow-red solution as a supernatant with the crystals.

Single Crystal X-ray Diffraction. Single crystals of the reported compounds were sorted under inert oil and mounted on glass fibers using a quick drying epoxy as a fixative. Diffraction data were collected on a Bruker APEX II diffractometer using Mo Kα radiation (λ = 0.71073 Å). The data were collected at 100 K using an Oxford Cryostream, and corrections for absorption in the crystals were applied using the program SADABS.[15] Structure solutions were performed with direct methods using SHELXS and subsequent structural refinements performed using SHELXL.[16] Attempts to locate the hydrogen atom positions (using difference Fourier maps) associated with either the ammonium cations or the water molecules were unsuccessful.

Raman Spectroscopy. Raman spectra were collected on liquid samples of 1 m UO_2^{2+} in 11 m HBr, 1 m UO_2^{2+} in 3 m $HClO_4$ and powders of the reported salts using a Renishaw inVia Raman Microscope with an excitation line of 532 nm. Liquid samples were enclosed in a standard optical cuvette for measurement. Solid powders were mounted on standard microscope slides using a coverslip affixed with epoxy.

High-Energy X-ray Scattering. High-energy X-ray scattering data were collected on a 1 m UO_2^{2+} solution in concentrated HBr_{aq} (11 m) and a sample containing the viscous mother liquor that coexisted with crystals of $(UO_2)_2(OH)_2Br_2(H_2O)_4$. Samples were selaed in a polyimide capillary with epoxy and packaged as required for radiological samples. The data were collected at the Advanced Photon Source, Argonne National Laboratory, on beamline 11-ID-B using a 91 keV (λ = 0.13702 Å) monochromatic X-ray beam and collected using an amorphous silicon flat panel detector. Analogous data reduction and analysis has been described previously.[13,17,18]

■ RESULTS AND DISCUSSION

Structural Details. Crystallographic details for all of the reported structures are presented in Table 1. All of the tetrabromide complexes contain a $UO_2Br_4^{2-}$ dianion in the structure. The local coordination environment about the uranium atom is a square bipyramid of approximately D_{4h} symmetry, containing the two axial "yl" oxygen atoms with U—O bond distances consistent with those measured in other uranium(VI) complexes as well the four bromide anions. For the four uranyl tetrabromide complexes, the average axial U—O bond distance is 1.77(1) Å, consistent with other uranyl-containing structures.[9] The U—Br bond distances in the four tetrabromide structures average 2.82(1) Å, closely matching those reported for other tetrabromide complexes of uranium(VI).[4,10,11,19] Relevant bond distances for each of the individual complexes are presented in Table 2. For this set of compounds, only minor distortions about the square bipyramids exist with respect to both the bond angles

Table 2. Relevant Bond Distances (Å) for the Reported Structures

bond	1	2	3	4	5
U−O$_{yl}$	1.772(3)	1.772(3)	1.759(5)	1.777(4)	1.758(4) 1.777(4)
U−Br	2.814(1) 2.819(1)	2.815(1) 2.816(1)	2.812(1) 2.815(2)	2.820(1)	2.927(2)
U−OH,					2.375(4) 2.367(4)
U−OH$_2$					2.411(4) 2.477(5)
U−U					3.927(1)

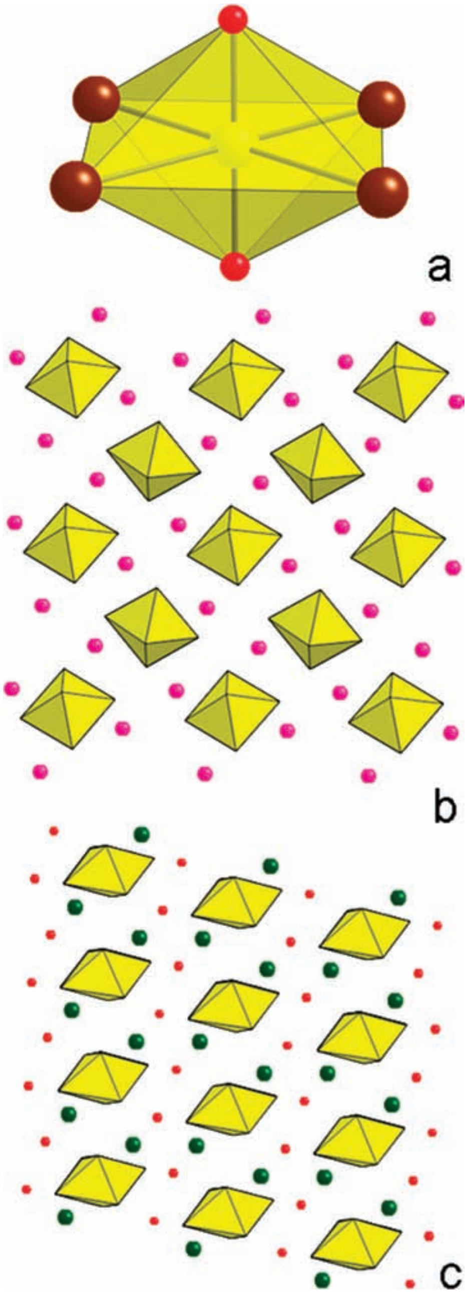

Figure 1. (a) The $UO_2Br_4^{2-}$ dianion common to all structures highlighting the linear O═U═O uranyl moiety and the square bipyramid geometry introduced by the coordination of four bromide ions; oxygen atoms are red and bromine in brown. (b) A packing diagram of $Cs_2UO_2Br_4$, with yellow $UO_2Br_4^{2-}$ polyhedra and magenta Cs^+ spheres. (c) The packing diagram for the isostructural group of $M_2UO_2Br_4 \cdot 2H_2O$, ($M = NH_4^+$, K^+, Rb^+), with yellow $UO_2Br_4^{2-}$ polyhedra, water molecules as red spheres, and the cations represented by the green spheres.

and bond distances present in the structures, despite varying hydration states and different charge compensating cations. Figure 1 shows the square bipyramidal arrangement common to the structures as well as the different packing arrangements about the uranyl polyhedra with their water molecules of hydration and charge compensating cations.

The NH_4^+-, K^+-, and Rb^+-bearing salts are isostructural. The cations have six bromide neighbors from four uranyl tetrabromide anions, with average distances of interaction of 3.63(10), 3.61(8), and 3.66(6) Å, respectively. For comparison, the M−Br interaction in their binary salts are 3.45 Å (NH_4Br), 3.30 Å (KBr), and 3.43 Å (RbBr). There are four closer interactions between the countercations and the hydrating water molecules in these structures as well as interactions between the countercations and the axial oxygen atoms of the uranyl moiety. The M−OH_2 average distances are 2.87(2), 2.75(1), and 2.91(2) Å for $M = NH_4^+$, K^+, and Rb^+, respectively. The M−O$_{yl}$ distances are 3.07(1), 2.98(6), and 3.07(1) Å, respectively, and perfectly opposed due to symmetry. The changes in distances and lattice parameters track well with the size of the countercations present in these salts. It is worth noting that crystallization of the isostructural series to Rb aided in assignment of the water molecule arrangement versus the lighter ammonium and potassium cations in these lattices.

For the $Cs_2UO_2Br_4$ salt, which has been previously reported[11] and included here for completeness, the cesium cations have eight bromide neighbors and two closer interactions with the uranyl axial oxygens. The average Cs−Br interaction in this compound is at 3.75(9) Å, and that in CsBr is 3.70 Å . The average Cs−O$_{yl}$ distance in $Cs_2UO_2Br_4$ is 3.30(5) Å.

Previously, a variety of hydrogen bonding and donor−acceptor interactions have been identified between the charge compensating cations and the uranium anion complexes. Using a series of linear bipyridyl cations to explore the extent to which hydrogen bonding and ionic interactions could be used as structure-directing tools in uranium-based coordination polymers, Deifel and Cahill demonstrated that the hydrogen-bonding interaction between the protonated bipyridyl ligands often bifurcates the Br−U−Br and Cl−U−Cl angle, while for nonlinear or branched bipyridyl cations no such interactions existed.[4,5] In a study investigating the complexes of uranyl perhalo anions and alkali−metal crown ether complexes, three different interaction modes were noted depending on the identity of the alkali metal cation.[20] In the complexes reported here, the geometry of the interaction between the charge compensating cations and the $UO_2Br_4^{2-}$ anion most closely resembles a bifurcation of the Br−U−Br angle, although the cations are not coplanar with the U−Br_4 plane. Other interactions between the countercations and the $UO_2Br_4^{2-}$ anion occur through an interaction between the cations and the axial oxygen atoms of the uranyl unit. Interactions between countercations and the axial oxygen atoms of actinyl ions are not infrequent.[21−23]

$(UO_2)_2(OH)_2Br_2(H_2O)_4$ forms upon evaporation of a HBr_{aq} solution containing UO_2^{2+}. Depicted in Figure 2, the complex is best described as two nearly coplanar uranyl pentagonal

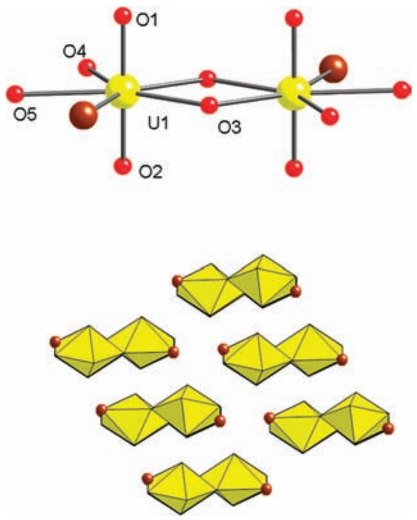

Figure 2. Structure and packing diagram of the $(UO_2)_2(OH)_2Br_2(H_2O)_4$ molecule; uranium is in yellow, oxygen in red, bromine in brown.

biypramids, edge sharing through two μ_2-OH groups to form a molecular dimer in a manner similar to the previously reported chloride-containing dimer.[24] The U—U bond distance in $(UO_2)_2(OH)_2Br_2(H_2O)_4$ is 3.927(5) Å. The uranyl bond distances are 1.758(5) and 1.777(5) Å and nearly perfectly opposed with an O—U—O bond angle of 178°. The bond distances between the uranium atom and the two water molecules in the equatorial plane are 2.412(5) and 2.477(5) Å. The U—OH bond distances are expectedly shorter at 2.367(4) and 2.375(4) Å. Assignment of the bridging O-atoms as OH^- and not O^{2-} is aided by the existence of the isostructural Cl bearing salt and the significantly longer bond distances in the molecule reported here relative to a uranium oxide bond of ~2.23 Å, such as exists in meta-schoepite.[24] The U—Br distance of 2.913(1) Å in this complex is nearly 0.1 Å longer than those of the tetrabromide salts. This significant increase in the bond distance may be an effect of the higher coordination number, 5, about the equatorial plane of the uranyl in comparison to the 4-coordinate tetrabromide salts. Previous reports of the crystal structures and syntheses of $UO_2(H_2O)_3Br_2$ and $(UO_2)_2(H_2O)_4Br_4$ demonstrated average U—Br bond distances of 2.90(1) and 2.89(7) Å, respectively, for these pentacoordinate complexes.[7] Interestingly, no clear hydrogen-bonding interactions are evident in the packing arrangement of $(UO_2)_2(OH)_2Br_2(H_2O)_4$. The nearest donor—acceptor distances in the crystal structure are between the uranyl oxygen atoms and the coordinated water and bromide ions of the nearest neighbor dimers.

Raman Spectroscopy. The Raman spectra of solutions containing 1 *m* UO_2^{2+} in 3 *m* $HClO_4$ and 1 *m* UO_2^{2+} in 11 *m* HBr are shown in Figure 3a. The lower trace in Figure 3 shows the Raman spectrum of UO_2^{2+} in 3 *m* $HClO_4$. The major bands occur at 873 cm^{-1}, attributed to the symmetric stretch (ν_1) of the uranyl, and 933 cm^{-1}, attributable to the (ν_1) mode of the perchlorate anion.[25] In the top trace of Figure 3 is the Raman spectrum of 1 *m* UO_2^{2+} in 11 *m* HBr. The major band is assigned to the symmetric stretch of the uranyl moiety at 863 cm^{-1}. Relative to its position in the perchlorate solution, the ν_1 band in the bromide solution is shifted to lower energy by 10 cm^{-1} and exhibits marked broadening and asymmetry not present in the $UO_2^{2+}/HClO_4$ spectrum. This result is inconsistent with a previous report that the uranyl frequency does not shift in systems containing Br^- at concentrations as high as 5 *m*.[25] This shift is a result of the interaction of bromide with the uranyl unit. Shifts of the uranyl frequency have been demonstrated to be highly correlated with the strength of the uranyl—ligand interaction as well as the number of interacting ligands.[25] Previous studies have shown that in high concentrations of chloride and nitrate in solution the

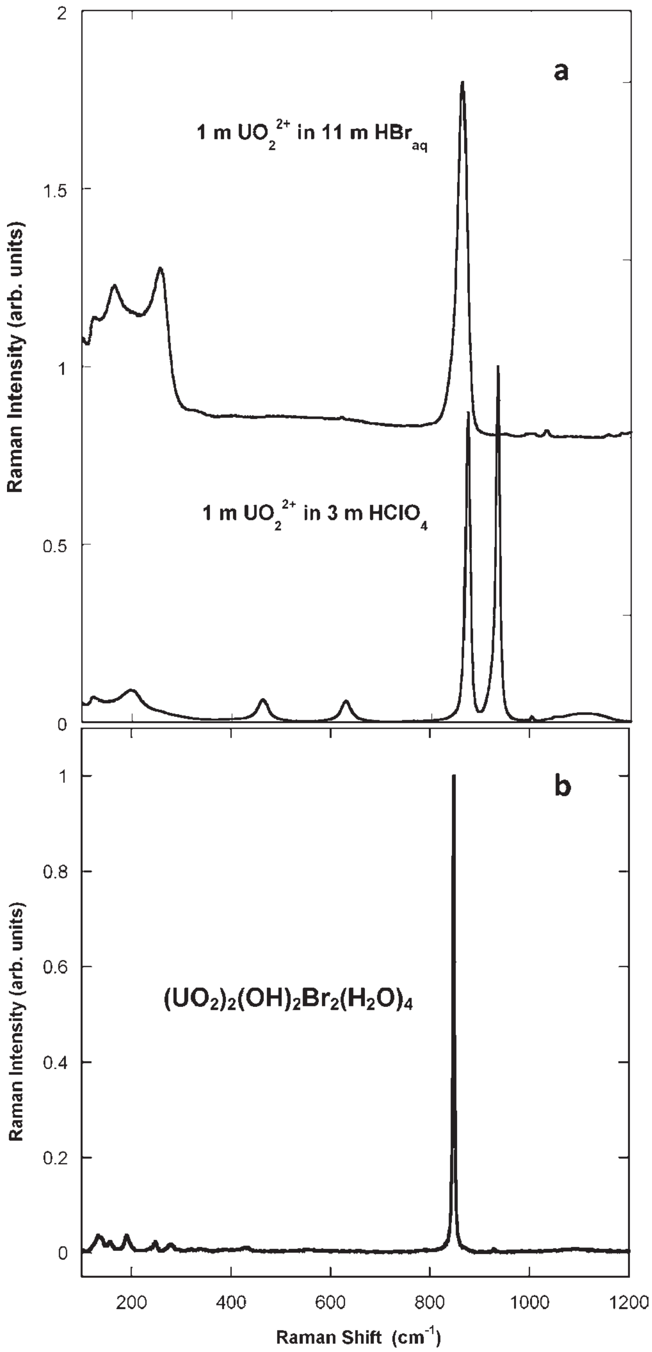

Figure 3. (a) Raman spectra of 1 *m* UO_2^{2+} solutions in 3 *m* $HClO_{4(aq)}$ (bottom) and 11 *m* HBr_{aq} (top) using and excitation wavelength of 532 nm. For the $[O{=}U{=}O]^{2+}$ symmetric stretch, ν_1 is observed to shift and broaden, indicating UO_2—Br interactions, 873 cm^{-1} ($HClO_{4(aq)}$) and 863 cm^{-1} (HBr_{aq}). (b) Raman spectrum from a powdered sample of $(UO_2)_2(OH)_2Br_2(H_2O)_4$; the symmetric stretch is observed at 847 cm^{-1}.

mode associated with the symmetric stretch of the uranyl moiety shifts to 834 and 871 cm^{-1}, respectively.[25] The magnitude of these shifts is indicative of weakly complexing ligands in aqueous solution.

The Raman spectra of the tetrahalide salts show a shift of the uranyl symmetric stretch to 833 cm^{-1}, in good agreement with previously reported data.[26] The Raman spectrum of the uranyl dimer, Figure 3b, shows a uranyl stretching band centered at 847 cm^{-1} intermediate to the aquated ion in 3 *m* $HClO_4$, 873 cm^{-1}, and the uranyl band of the tetrabromides at 833 cm^{-1}, which is expected since the shift should correlate with the total bromide coordination number.

Solution Correlations. The five compounds reported herein were all isolated from the same UO_2^{2+}—HBr_{aq} stock solution, thus provoking interest in the uranyl speciation prior to crystallization. Energetics for aqueous uranyl bromide complexes have been studied previously using potentiometric[27] and spectrophotometry[28] from which was obtained the only currently reviewed stability constant for the formation of UO_2Br^+, 1.66 kg mol^{-1}.[8] None are available for the dibromo or any higher species. Any higher bromide complexes, which have not been reported, should be weaker according to the usually observed stepwise formation constants. Numerous solid-state tetrahalide complexes of uranium, synthesized from aqueous solutions, have been reported both for chloride[29,30] and bromide,[10,11,31] suggesting that higher uranyl bromide complexes may be present in the solutions used for their syntheses, which are very far from the zero-ionic-strength ideal applicable to the thermodynamic description. In order to investigate solution-state uranyl correlations present under the conditions of our synthesis, we employed synchrotron-based high-energy X-ray scattering (HEXS). Following appropriate scattering-data corrections and Fourier transforming of the data, a pair-distribution function (PDF) is obtained in which the peak positions correspond to the distance between atomic pairs in solution and their intensities relate to the total number of electrons involved in each pair.[17,18,32]

The PDF shown in Figure 4a is obtained from the stock solution used for the crystal syntheses (1 *m* UO_2^{2+} in 11 *m* HBr), after subtracting a background spectrum. In this case, the background used was a concentrated solution of HBr. Differences in the solvent correlations with and without uranyl are visible in the PDF as slightly high backgrounds in the lower *r* region and contribute to the reported errors in the fitted intensities. Also shown in the figure are the Gaussians used to fit the atomic correlations. The fitted Gaussian parameters and their assignments are listed in Table 3.

In Figure 4b, the PDF acquired from the viscous mother liquor that the crystals of $(UO_2)_2(OH)_2Br_2(H_2O)_4$ were drawn from is presented. There is no evidence in this data, or the data in Figure 4a, for a U—U interaction at about 3.9 Å that could be assigned to the presence of a dimeric species, despite the isolation of $(UO_2)_2(OH)_2Br_2(H_2O)_4$ from these solutions. This is in contrast to previous results in which oligomeric interactions seen in the single crystals preform in the solutions from which the solids precipitate.[33,34]

The first peak in the PDF in Figure 4a (1 *m* UO_2^{2+} in 11 *m* HBr), at 1.77(5) Å results from the correlation between the uranium and the oxygen atoms within the uranyl unit. The second feature is centered at 2.44(5) Å and assigned to 2.0(5) waters in the equatorial plane of the uranyl unit. Also in the uranyl first coordination sphere are 1.9(1) bromide atoms at a distance of 2.88(5) Å. These results are consistent with a uranyl inner-sphere coordination of two waters and two bromide ions. Thus, even in solutions with very high Br^- concentration the actinyl ion has only on average two coordinating halide ligands, compared with the four bromides seen in the uranyl bromide structures described herein. The U—Br bond distances in the solid-state structures, ~2.81 Å, are shorter than the 2.88 Å observed in solution. Comparative longer distances have been observed in solid-state uranyl dibromide complexes $UO_2(H_2O)_3Br_2$ and $(UO_2)_2(H_2O)_4Br_4$, with average U—Br bond lengths of 2.90(1) and 2.89(7) Å, respectively, but the uranyl possesses 5-fold coordination in the equatorial plane.[7] The HEXS data obtained from solution have peak intensities that are inconsistent with a 5-coordinate uranyl species. It should be noted that shortening of bond distances in solution versus solid-state structures has been previously observed.[12]

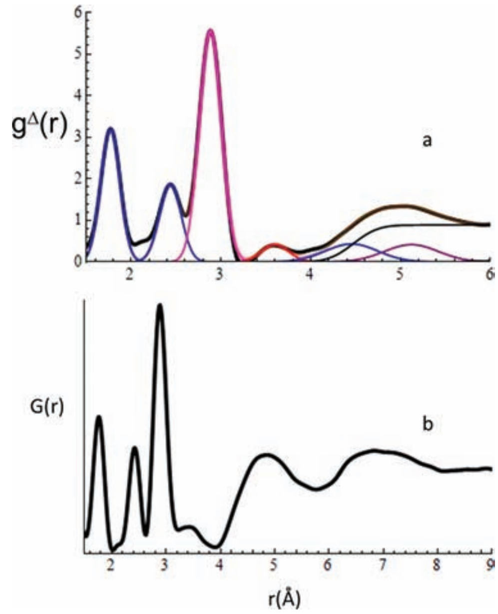

Figure 4. (a) The Fourier transformed high-energy X-ray scattering data (PDF) from a background-subtracted 1 *m* UO_2^{2+} in 11 *m* HBr_{aq} solution (thick black). The data are fitted by a series of Gaussians with intensities attributed to U correlations with oxygen (blue), bromine (magenta), hydrogen (red), solution disorder (thin black), and a peak at 5.1 Å (purple) assigned as discussed in the text. The fit is depicted in brown but not visible in the figure because it overlaps with the data, except at lower *r*, as discussed in the text. (b) The PDF from the mother liquor solution from which the uranyl dimer was isolated, demonstrating the lack of U—U correlations in the mother liquor.

Table 3. Metrical Data from the Fitting and Analysis of the 1 *m* UO_2^{2+} in 11 *m* HBr_{aq} Pair-Distribution Function

peak position (Å)	peak width ($2\sigma^2$)	intensity (electrons)	assignment
1.77(5)	0.011	13(4)	2.0(5) O from UO_2^{2+}
2.44(5)	0.014	16(4)	2.0(5) equatorial O as H_2O
2.88(5)	0.015	65(4)	1.9(2) Br^- as U—Br
3.6(1)	0.023	9(2)	9(2) H as U—OH_2
4.5(2)	0.087	28(4)	2.8(4) second coordination sphere H_2O
5.1(2)	0.091	39(4)	see the text
6.6(3)	0.2	15(5)	unassigned

The fitted peaks at distances longer than 3 Å are attributable to a second-sphere ligation shell. The peak in Figure 4, at about 4−5.5 Å, is very broad relative to a simple single-shell peak such as observed for the uranyl ion in perchlorate solution.[17,35,36] Following precedent set by analyses of uranyl chloride solution HEXS PDF patterns as a function of chloride concentration,[35] this feature has been fit with two unresolved Gaussians, centered at 4.5 and 5.1 Å. The Gaussian centered at 4.5 Å integrates to a uranyl correlation to 28(4) electrons, assignable to the oxygens of about three second coordination-sphere waters. The Gaussian at 5.1 Å has an intensity corresponding to 39(4) electrons. In the absence of a series of data with varying bromide concentration, it is not possible to unambiguously assign this peak. On the one hand, it could be due to uranyl correlations with an average of about one outer-sphere bromide ion, as exemplified by second-shell Er chloride solution coordination.[13] On the other hand, it could be the result of a reorientation of some second-sphere waters as they optimize hydrogen bonding, as seen in uranyl chloride solutions.[35] Although published stability constants sometime provide insight into the most likely coordination, in this case the solution is highly concentrated and only the first stability constant has been reported. Resolution of the ambiguity associated with second-sphere uranyl coordination will likely require the acquisition and analysis of a series of uranyl solutions with varying bromide concentrations.

The PDF data in Figure 4a reveal the presence of a uranyl(VI) dibromo complex, a moiety not predicted based on published stability constants, although not a contradictory result considering the very high ionic strength of our stock solution. However, this PDF does not support the existence of higher bromide complexes beyond that of the dibromide complex and certainly does not provide evidence of a dominant concentration of $UO_2Br_4^{2-}$ in solution. Nor does it indicate oligomers of uranium in solution, despite their presence in the solid precipitate.

Structural Discussion. The ability to synthesize higher halogen complexes in the solid state from an aqueous solution that does not contain structural precursors suggests a strong influence of charge compensating cations and metal−solvent interaction strengths toward driving the higher halide coordination in the crystallized solid. Furthermore, in the absence of a countercation in the solution, the ultimate crystalline product obtained from the uranyl bromide solution was a hydrolyzed uranyl dimer that formed upon concentrating the uranium in HBr solution by near total evaporation. The chemical effects of the countercation cannot be quantified in this study, but our observations indicate that there are potentially significant chemical interactions outside the first coordination sphere driving the formation of the tetrabromides or the formation of a uranyl dimer.

Chemical effects in the second-coordination spheres of metal ion complexes and ion-pairing effects have been known to greatly influence the solution chemical behavior of metal ions, complexes, and clusters.[12,13,17,37−39] Ion-pairing in calcium uranyl carbonate has been demonstrated to be responsible for the enhanced solubility of uranium in moderately basic aqueous solutions.[38] More recently, ion-pairing interactions have been demonstrated to play a critical role in tetravalent actinide hydroxide complexes, there too enhancing the solubility of these complexes by several orders of magnitude, thus playing an important role in the environmental chemistry of these elements.[37] Additionally, studies in the solid state and solution state of polyoxometalates of Nb have demonstrated differences in the ion-pairing behavior of different alkali metal cations having marked effects on their solubilities.[39]

Recent calculations on the homoleptic aqua coordination of large metal cations have shown the necessity of explicitly including higher solvation shells in order to accurately model the aquated structure and stoichiometry of such polyvalent metal cations.[40,41] Therefore, it would seem as necessary and appropriate to consider the role of not only outer-sphere solvent interactions in metal complexes but also the chemical role of outer-sphere anions and cations in the formation of metal complexes beyond what is predicted by currently known thermochemical data. Experiments aimed at understanding these interactions within the f-elements are underway in our laboratory.

CONCLUSION

We have reported a series of alkali-metal- and ammonium-containing uranyl tetrabromide salts, $Cs_2UO_2Br_4$, $M_2UO_2Br_4 \cdot 2H_2O$ (M = NH_4, K, Rb). The structures all share a common uranyl tetrabromide dianion, and in the case of the NH_4^+, K^+, and Rb^+ complexes, they are isostructural. Additionally, we have reported the crystal structure and synthesis of a uranyl hydroxo bridged dimer, $(UO_2)_2(OH)_2Br_2(H_2O)_4$, which is isolated from the same uranium stock solution in aqueous hydrobromic acid that was used to prepare the tetrabromide salts. Using HEXS we have investigated uranyl correlations in the stock solution, searching for aqueous precursors to these complexes. The scattering data reveal that the uranyl average inner-sphere coordination number with bromide is about 2, with no evidence for a hydroxo-bridged oligomer of uranium. The results of this study taken together with previous studies within similar chemical systems suggest a significant chemical influence of the counterions in directing both chemistry and structure. Future work is planned in investigating the role of the countercations in these systems as chemical and structure directing agents.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Crystal structure data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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