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# First Identification and Thermodynamic Characterization of the Ternary U(VI) Species, $UO_2(O_2)(CO_3)_2^{4-}$, in $UO_2-H_2O_2-K_2CO_3$ Solutions

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In alkaline carbonate solutions, hydrogen peroxide can selectively replace one of the carbonate ligands in $UO_2(CO_3)_3^{4-}$ to form the ternary mixed U(VI) peroxo-carbonato species $UO_2(O_2)(CO_3)_2^{4-}$. Orange rectangular plates of $K_4[UO_2(CO_3)_2(O_2)] \cdot H_2O$ were isolated and characterized by single crystal X-ray diffraction studies. Crystallographic data: monoclinic, space group $P2_1/n$, $a = 6.9670(14)$ Å, $b = 9.2158(10)$ Å, $c = 18.052(4)$ Å, $Z = 4$. Spectrophotometric titrations with $H_2O_2$ were performed in 0.5 M $K_2CO_3$, with $UO_2(O_2)(CO_3)_2^{4-}$ concentrations ranging from 0.1 to 0.55 mM. The molar absorptivities ($M^{-1}$ $cm^{-1}$) for $UO_2(CO_3)_3^{4-}$ and $UO_2(O_2)(CO_3)_2^{4-}$ were determined to be 23.3 ± 0.3 at 448.5 nm and 1022.7 ± 19.0 at 347.5 nm, respectively. Stoichiometric analyses coupled with spectroscopic comparisons between solution and solid state indicate that the stable solution species is $UO_2(O_2)(CO_3)_2^{4-}$, which has an apparent formation constant of $\log K' = 4.70 \pm 0.02$ relative to the tris-carbonato complex.

## Introduction

The interaction of hydrogen peroxide with actinides has been of great importance to *f*-element chemistry because of its ability to control the oxidation states and solubilities of uranium and plutonium in acidic and near-neutral solutions.[1,2] Hydrogen peroxide has also been used since the 1950s to dissolve uranium metal and alloys in alkali metal hydroxide solutions.[3] Recently, the actinide−peroxide chemistry in near-neutral aqueous systems has attracted great attention because of the formation of peroxide as a known radiolysis product of water. The ability of peroxide to strongly complex uranium and form insoluble solid phases, such as studtite $[UO_2(O_2)(H_2O)_2](H_2O)_2$,[4,5] is expected to have a significant impact on the migration behavior of actinides in geologic repository sites for nuclear wastes. In sharp contrast to the behavior in acidic media, peroxide significantly increases the solubility of uranium in alkaline solutions compared to that of the well-known uranyl(VI) tris-carbonato complex, $UO_2(CO_3)_3^{4-}$. A fundamental understanding of the solution and solid-state chemistry, including thermodynamic data on solution complexes or solid -phase solubility, of uranium in peroxide-containing carbonate solutions remains unrealized.

The uranium(VI)−peroxide−carbonate system is of inherent complexity because of the formation of mixed-ligand, mono- and polynuclear U(VI) complexes in solution and solid state, as well as the base-catalyzed decomposition of

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peroxide in alkaline media.[6–11] A number of previous studies were conducted in an attempt to understand the behavior of U(VI) in peroxide-containing carbonate solutions. In 1950, Scott reported a significant color change, from a pale yellow to a dark orange, that occurred when peroxide was added to solutions of U(VI)–carbonate.[12] Over the next 35 years, several additional potentiometric and spectrophotometric studies were performed by various investigators, who confirmed the existence of a 1:1 solution complex when peroxide was added to solutions of $UO_2(CO_3)_3^{4-}$.[13–17] While Komarov postulated that the peroxide ligand replaced one of the carbonate ligands to form an anionic complex, $UO_2(OOH)(CO_3)_2^{3-}$,[14,15] the nature of the ternary U(VI) solution complex formed in alkaline solutions remains unclear. Structural information about the solution species can be inferred from single crystal and powder X-ray diffraction studies performed on crystals obtained from U(VI)–peroxide–carbonate solutions. Gurevich and co-workers proposed about a dozen U(VI) peroxo compounds that form under various carbonate and peroxide concentrations without structural evidence.[18] Peroxide was found as a bridging ligand in the one-dimensional structure, $[UO_2(O_2)(H_2O)_2](H_2O)_2$,[19] as well as in two different nanoscale peroxide compounds,[20] while the trisperoxide, $Na_4[UO_2(O_2)_3]\cdot 9H_2O$, displays terminal side-on coordinated peroxide ligands.[21] In the reported molecular structure of the mixed U(VI) peroxo-carbonato complex, $M_4[UO_2(O_2)(CO_3)_2]\cdot nH_2O$ ($M = K$ and $n = 2.5$ or $M = CN_3H_6$ and $n = 2$),[22,23] two carbonato and one peroxo groups are coordinated in the equatorial plane around the U atom. Since this complex exhibits the 1:1 stoichiometry observed by the previous solution studies, it can be assumed that the anion, $UO_2(O_2)(CO_3)_2^{4-}$, could also be present in solution.

We have been engaged in a systematic study to unravel the complex chemistry of uranium in carbonate solutions in the presence of peroxide. In our previous work, dissolution studies of $UO_2$ confirmed the formation of stable U(VI) peroxo-carbonato complexes.[24] These mixed-ligand species greatly increased the solubility of U(VI) and significantly enhanced the dissolution rates of $UO_2$ in carbonate media. We report herein the spectroscopic characterization and thermodynamic stability of the mixed-ligand complex, $UO_2(O_2)(CO_3)_2^{4-}$, in both solution and solid state.

## Experimental Section

Uranyl nitrate, crystallized and purified by precipitation from aqueous solution, was used to prepare a 2.2 M U(VI) stock solution in 3.3 M $HNO_3$. Aliquots were diluted into $K_2CO_3$(aq) solutions to obtain solutions with U(VI) concentrations no greater than 0.55 mM to prevent the formation of polynuclear U(VI) species.[25] The U(VI) concentrations in carbonate solutions were determined by using the molar absorptivity for $UO_2(CO_3)_3^{4-}$ regressed in this work. The $K_2CO_3\cdot 2.5\ H_2O$ (99.9% purity) and technical grade $H_2O_2$ (∼30 wt. %), which was stored at 4 °C, were purchased from Fisher Scientific, Inc. The $H_2O_2$ concentration was periodically verified by titration with $KMnO_4$ in $H_2SO_4$ to account for $H_2O_2$ decomposition.[26] Titrant solutions of $H_2O_2$(aq) were prepared gravimetrically on the day of the experiment, and all solutions were prepared from distilled–deionized water with a specific resistance $\geq 18.0\ M\Omega$ cm.

All titrations were performed with $H_2O_2$ (aq) as the titrant using a Dosimat 775 20 mL automatic burette, manufactured by Metrohm Ltd. Hydrogen peroxide was added to 250 mL of 0.5 M $K_2CO_3$ with varying U(VI) concentrations ($\leq$0.55 mM) at room temperature. Under these concentrations, no complexation changes were observed over the course of the experiments resulting from $H_2O_2$ decomposition. UV–vis spectroscopy (Cary 6000*i*, Varian) with a 1 or 10 cm quartz cuvette was used for solution speciation analysis. Data was taken in double-beam mode with 0.5 nm data spacing, a scan rate of 100 nm/s, full slit height, and a slit width of 0.5 nm. The pH was measured during select experiments with an Accumat glass bodied combination electrode (Ag/AgCl reference) and an Accumat-Research AR25 dual- channel pH–ion meter. The electrode was calibrated before each experiment using pH standards purchased from Fisher Scientific, Inc. The initial pH was measured to be 11.6 ± 0.05. The pH was observed to be nearly constant with increasing peroxide concentration, decreasing by less than 0.05 pH units.

The UV–vis absorbance spectra were deconvoluted by using the pure component spectrum for $UO_2(CO_3)_3^{4-}$ and subtracting the contribution of this species from the raw spectrum. The molar absorptivity of $UO_2(CO_3)_3^{4-}$ was

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determined by preparation of known concentrations of U(VI) in carbonate solutions and measurement of the UV–vis absorption spectrum. These experiments were performed using $Na_2CO_3$ instead of $K_2CO_3$ to evaluate the absorbance at higher uranium concentrations because of the lower solubility of U(VI) in $K_2CO_3$. After subtracting varying fractions of the $UO_2(CO_3)_3{}^{4-}$ spectrum from the raw absorbance spectrum, the residual was assumed to be the pure component spectrum for the second solution species, that is, $UO_2(O_2)(CO_3)_2{}^{4-}$. A least-squares statistical analysis was performed on the molar absorptivity of this species from 300 to 850 nm by simultaneously regressing all data points for each sample within a single experiment. The optimized solution was found by using a Newton search method with a tolerance of 0.05%, a precision of $1 \times 10^{-6}$ and a convergence of $1 \times 10^{-4}$. The optimization was subject to the constraint that the mole fraction for each component ($x_i$) must be $0 \leq x_i \leq 1$. The solution speciation obtained from this optimization routine was subsequently used to calculate the equilibrium constant for the formation of $UO_2(O_2)(CO_3)_2{}^{4-}$.

Single crystals of $K_4[UO_2(CO_3)_2(O_2)]\cdot H_2O$ (**I**) were synthesized by dissolution of 600 mg of $UO_2$ powder in 30 mL of 2 M $K_2CO_3$ and 1.8 mL of 35 wt % $H_2O_2$ at room temperature. The solution was agitated for 60 min, after which it was filtered through a 0.45 $\mu$m polyamide syringe filter. An additional 1.5 mL of 35 wt % $H_2O_2$ was added to the dark red U(VI) solution. Approximately 4 mL of the red solution was transferred to a 20 mL borosilicate scintillation vial and layered with 6 mL of methanol. Within 24 h at room temperature, dark orange rectangular plates formed. Single crystals were isolated and characterized by single-crystal X-ray diffraction using a Bruker D8 diffractometer with APEX II CCD detector. Crystals of **I** were twinned and indexed on a cell identical to $K_4[UO_2(O_2)(CO_3)_2]\cdot 2.5H_2O$ **II**, except for the *c*-axis, which was approximately 3 Å shorter. The presence of additional reflections along the *c*-axis in **I** possibly indicated that **I** was actually a twinned crystal of **II**. Multiple attempts to index **I** on a cell consistent with **II** were unsuccessful. The indexing, subsequent refinement, and packing analysis was convincing that **I** represented a new chemical compound. Additional solid-phase characterization (Raman and diffuse reflectance) was performed with a Nicolet Magna-IR 560 ESD with a Raman accessory and a Cary 5 UV–vis–NIR spectrophotometer with a diffuse reflectance attachment.

Layering of the aqueous solution with methanol was necessary to form crystals of (**I**) or (**II**) because of the high solubility of these mixed peroxo-carbonato complexes in water. While making a homogeneous solution with methanol resulted in the formation of an amorphous precipitate, layering with methanol facilitated the formation of crystals by allowing diffusion-controlled crystallization at the interface. Methanol was selected because it did not appear to catalyze $H_2O_2$ decomposition and could easily be layered on the aqueous sample. Acetonitrile was also used, but it appeared to decompose the $H_2O_2$ before crystals could form, and ethanol and diethyl ether were miscible with the aqueous phase and were not suitable for forming stable layers.

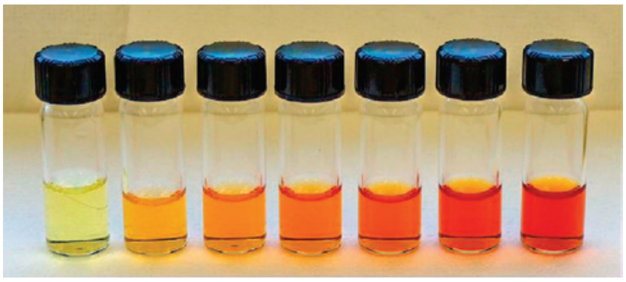

**Figure 1.** When $H_2O_2$ is added to a solution of the U(VI) tris-carbonato complex, $UO_2(CO_3)_3{}^{4-}$, (shown at left), the solution changes color to a deep orange indicating a complexation reaction of the $HO_2{}^-$ ligand with U(VI).

The previously reported synthesis methods for preparing $K_4[UO_2(O_2)(CO_3)_2]\cdot 2.5H_2O$ (**II**) result in mixtures of the desired compound and crystals of $K_4[UO_2(CO_3)_3]$.[23] Pure crystals of **II** were obtained by addition of 80 mmol of U(VI) (in nitric acid) to 1.5 mL of 2 M $K_2CO_3$ in a 4 mL borosilicate scintillation vial. To this solution, 90 mmol of $H_2O_2$ were added, and the solution was stirred until the U completely dissolved. The dark red solution was layered with methanol and allowed to stand for approximately 4 h, until the first yellow $K_4UO_2(CO_3)_3$ crystals began to form. After these crystals begin to precipitate, both phases were filtered independently through 0.45 $\mu$m PTFE syringe filters. Subsequently, orange crystals of pure $K_4[U(CO_3)_2O_2(O_2)]\cdot 2.5\ H_2O$ formed overnight.

## Results and Discussion

The U(VI) tris-carbonato complex, $UO_2(CO_3)_3{}^{4-}$, is well-known as the prevalent solution complex in carbonate solutions.[25,27] The addition of minute amounts of peroxide alter the chemical behavior of U(VI) significantly: The solubility of uranium is increased relative to the ternary salt $M_4UO_2(CO_3)_3$, and the solution speciation is altered, illustrated by the dramatic change of solution color from bright yellow ([U(VI)] > 5 mM) to orange-red shown in Figure 1. The solution speciation is highly dependent on experimental parameters such as pH and carbonate, peroxide, and U(VI) concentrations. As observed in the U(VI) hydrolysis system, increasing U(VI) concentration favors the formation of polynuclear U(VI) species.[25] In this work, we focused on U(VI) concentrations below 0.55 mM to reduce the complexity of this system, and ensure only mononuclear species formation. Under these conditions the following reaction is predominant

$$UO_2(CO_3)_3{}^{4-} + HO_2{}^{-} \leftrightarrow UO_2(O_2)(CO_3)_2{}^{4-} + CO_3{}^{2-} + H^+ \quad (1)$$

**Synthesis and Characterization of $K_4[UO_2(O_2)(CO_3)_2]\cdot nH_2O$ ($n = 1$ and 2.5).** Very few molecular crystal structures are known that could help elucidate the predominant solution species present in U(VI)−peroxide−carbonate solutions. This is in part a result of the bridging nature of the peroxide

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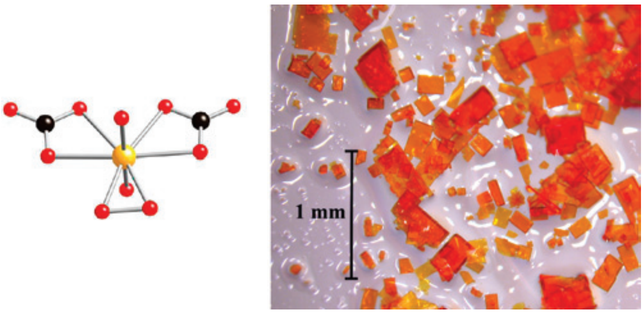

**Figure 2.** (left) Anionic unit, $UO_2(O_2)(CO_3)_2^{4-}$, found in the molecular structure $M_4[UO_2(O_2)(CO_3)_2]\cdot2.5H_2O$ (M = K or $CN_3H_6$) and (right) pictures of the orange rectangular plates of $K_4[UO_2(O_2)(CO_3)_2]\cdot2.5H_2O$.

ligand[28,29] and the ability of U(VI) to form multinuclear complexes,[30] both of which favor the formation of extended two- and three-dimensional arrays. The anion of interest, $UO_2(O_2)(CO_3)_2^{4-}$, shown in Figure 2, has been crystallized in the molecular structures of $M_4[UO_2(O_2)(CO_3)_2]\cdot nH_2O$ (M = K and $n = 2.5$ or M = $CN_3H_6$ and $n = 2$).[22,23] In the present work, we have crystallized a second hydrate, $K_4[UO_2(O_2)(CO_3)_2]\cdot H_2O$ (**I**), exhibiting the same U(VI) coordination as the previously reported 2.5 hydrate, **II**. Complete crystallographic details can be found in the Supporting Information.

Similar to $K_4[UO_2(O_2)(CO_3)_2]\cdot2.5H_2O$, the U atoms in **I** are 8-coordinate, with 6 O atoms in the equatorial plane originating from two carbonate ligands and one peroxide ligand. The [$UO_8$] polyhedra are composed of two trans-O atoms axially ligated to the U metal center, which exhibit an O═U═O bond angle of 175.9(3)°, thus forming a slightly distorted hexagonal bipyramidal coordination geometry. This O═U═O bond angle agrees well with that reported for **II** (175.3(3)°). Similarly, the U═O bond length for the uranyl-O atoms is elongated, with mean U═O bond distances of 1.827(8) and 1.825(8) Å. Four of the O atoms in the [$UO_8$] polyhedra originate from two bidentately coordinated *cis*-carbonate ligands, with little variation in the U−O bond lengths (between 2.429(7) and 2.473(7) Å). These U−O bond lengths compare well with those reported for $K_4UO_2(CO_3)_3$ (mean 2.430(5) Å).[31] It is interesting to note that the terminal O(4) and O(7) atoms of the carbonate ligands bend slightly off the equatorial plane, exhibiting an U−C−O angle of approximately 174°. The U(VI) polyhedra also contain two O atoms from a *side-on*-bound peroxide group with U−O distances of 2.238(7) and 2.255(7) Å. These are more symmetrical than the peroxide ligand in **II** with U−O bonds of (2.240(6) and 2.256(6) Å). Finally, in **I** the O−O bond of 1.469(10) Å is considerably shorter than in **II** (1.496(8) Å) or in other peroxide compounds, such as $(CN_3H_6)_4[UO_2(O_2)(CO_3)_2]\cdot2H_2O$ (1.52 Å),[22] $Na_4[UO_2(O_2)_3]\cdot9H_2O$ (1.51 Å),[21] and $Na_2O_2$ (1.49 Å).[32]

The [$UO_8$] polyhedra of **I** are arranged in rows along both the *a* and *b* axes with the equatorial plane of each polyhedra parallel to one another and orthogonal to the *ac*-plane, shown in Figure 3, which is similar to the more hydrated compound, **II**. The primary difference between **I** and **II** exists in the structure of water molecules between the [$UO_8$] polyhedra. In the higher hydrate (**II**), the water molecules form two-dimensional networks in the *ab*-plane, with each hydrogen-bonded water layer separating a pair of two staggered layers of [$UO_8$] polyhedra. In **I**, the water molecules form rows along the *a*-axis, but are separated by 6.967 Å. Therefore, lacking a network of water in any plane, the structure is stabilized primarily by potassium cations, not by hydrogen bonding. Only one of the four crystallographically distinct K atoms, K1, lies predominantly within the equatorial planes of adjacent [$UO_8$] polyhedra, and it is symmetrically centered between 6 O atoms from three carbonate ligands of three different $[UO_2(O_2)(CO_3)_2]^{4-}$ anionic units. All other K atoms are arranged outside of the equatorial planes of the [$UO_8$] polyhedra.

Additional characterization was performed using Raman spectroscopy. Figure 4 shows the Raman spectra for pure $K_2CO_3$ (s), 30% $H_2O_2$ (aq), $K_4UO_2(CO_3)_3$, and $K_4[UO_2(O_2)(CO_3)_2]\cdot2.5H_2O$. The strongest peaks observed in the Raman spectra are from the symmetric O═U═O stretch, C−O stretch (in $CO_3^{2-}$), and O−O stretch (in peroxide). Raman characterization of $K_4UO_2(CO_3)_3$ has been previously reported, and the spectrum shown in this work closely matches these numbers.[31] The C−O stretch in $K_2CO_3$ occurs at 1060.6 cm$^{-1}$, shifting to 1053.9 and 1052.9 cm$^{-1}$ for $K_4UO_2(CO_3)_3$ and **II**, respectively. The change from a singlet in $K_2CO_3$ to a doublet in both the U(VI) complexes is indicative of bidentate coordination of the $CO_3^{2-}$ ligand to a metal center.[33] The O═U═O stretch occurs at 806.0 cm$^{-1}$ for $K_4UO_2(CO_3)_3$ and at 766.5 cm$^{-1}$ for **II**. Likewise, the O−O stretch also shifts to a lower wavenumber in **II** relative to $H_2O_2$ (aq), moving from 875.5 to 841.7 cm$^{-1}$. The red shift in both the uranyl stretch and the O−O stretch is indicative of a weaker bond and a longer bond distance, which is also consistent with the crystallographic data.[31]

**Spectroscopic Characterization of the Solution Speciation.** It has been well established that in aqueous solutions with carbonate concentrations above 1 mM the tris-carbonato complex, $UO_2(CO_3)_3^{4-}$, is the dominant U(VI) solution species.[25,27] The structural and thermodynamic characteristics of this complex have been studied extensively, and the Nuclear Energy Administration recommends a thermodynamic formation constant of log $K°(298.15\text{ K}) = 21.60 \pm 0.05$ relative to the aquo ion.[25] The molar absorptivity, $\epsilon$ (M$^{-1}$cm$^{-1}$), of the $UO_2(CO_3)_3^{4-}$ ion was calculated from 300 to 850 nm. For quantitative analysis, the sharp peaks between 380 and 480 nm were used. In this study, the initial U(VI) concentration for each $H_2O_2$ titration was determined by

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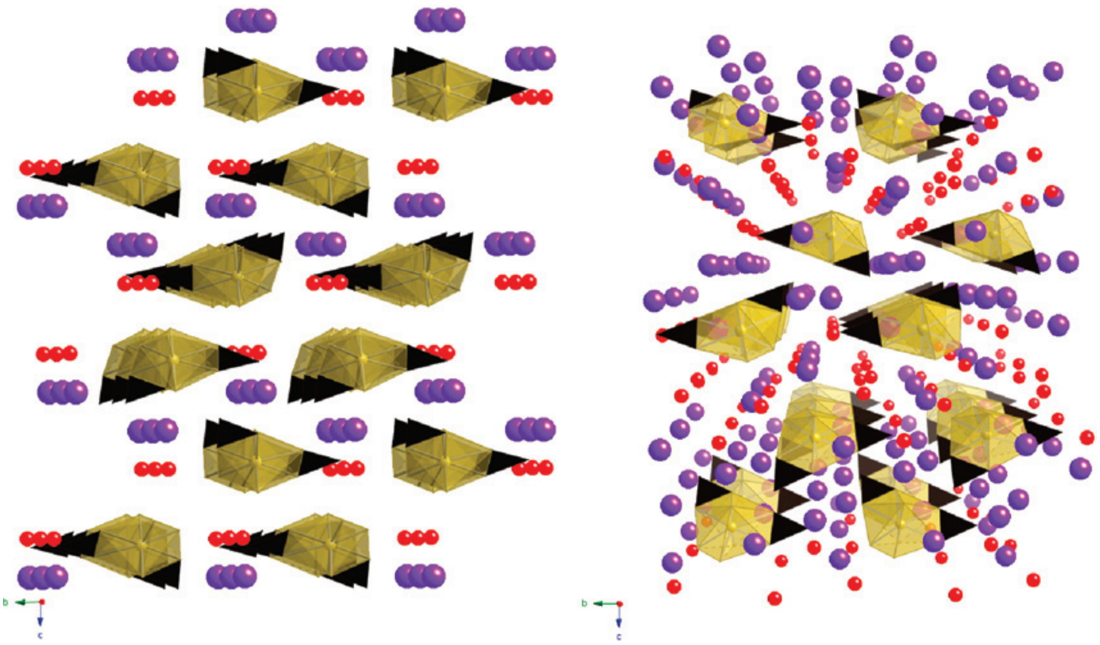

**Figure 3.** Comparison of the packing of the $[UO_2(O_2)(CO_3)_2]^{4-}$ anionic units in $K_4[UO_2(O_2)(CO_3)_2]\cdot H_2O$ (left) and $K_4[UO_2(O_2)(CO_3)_2]\cdot 2.5H_2O$ (right), viewed along the *a*-axis. Purple spheres denote $K^+$ ions, red spheres denote water molecules, yellow polyhedra indicate $[UO_8]$ groups, and black triangles indicates $[CO_3]$ groups.

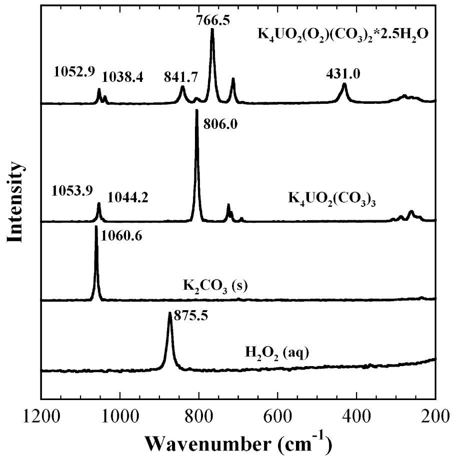

**Figure 4.** Comparison of the measured Raman spectra for $K_4[UO_2(O_2)(CO_3)_2]\cdot 2.5H_2O$, $K_4[UO_2(CO_3)_3]$, $K_2CO_3$, and $H_2O_2$ (aq), showing spectroscopic changes when $H_2O_2$ selectively replaces $CO_3^{2-}$ for U(VI) complexation.

taking a spectrum of the starting U(VI) carbonate solution and calculating the total U(VI) concentration by using $\epsilon(448.5 \text{ nm}) = 26.3 \pm 0.3\ M^{-1}\ cm^{-1}$.

It has already been noted that the addition of small amounts of $H_2O_2$ to a solution of $UO_2(CO_3)_3^{4-}$ results in a dramatic color change from a very pale yellow to a deep gold or light orange indicating a ligand exchange reaction between $UO_2(CO_3)_3^{4-}$ and $H_2O_2$. Figure 5 illustrates a typical spectrophotometric titration of $UO_2(CO_3)_3^{4-}$ (0.21 mM) with $H_2O_2$ in 0.5 M $K_2CO_3$. Clearly, upon addition of peroxide, the total absorbance increases significantly, and the characteristic fingerprint of the $UO_2(CO_3)_3^{4-}$ ion disappears. As the ratio of $H_2O_2$ to U increases the resulting spectrum broadens and becomes a nearly featureless peak (from 300 to 650 nm), containing a distinct peak at around 347.5 nm and a shoulder around 420 nm.

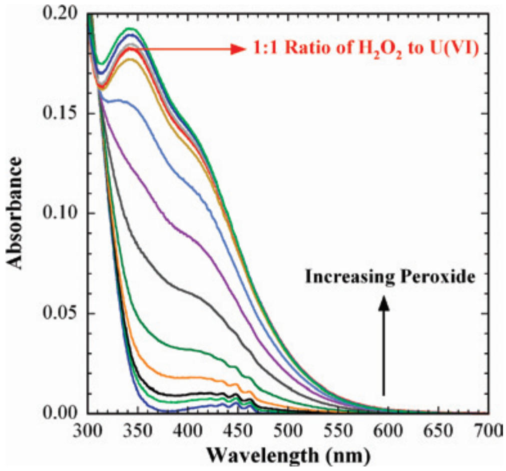

**Figure 5.** Typical spectrophotometric titration illustrating the effect of $H_2O_2$ on the speciation of $UO_2(CO_3)_3^{4-}$ in solution. Titration conditions: 0.21 mM $UO_2(CO_3)_3^{4-}$ in 0.5 M $K_2CO_3$.

The single-component spectra for the second solution species formed, $UO_2(O_2)(CO_3)_2^{4-}$, was calculated by spectral deconvolution. Figure 6 compares the spectroscopic features of both $UO_2(CO_3)_3^{4-}$ and $UO_2(O_2)(CO_3)_2^{4-}$ in solution and solid state, while Table 1 reports selected values of molar absorptivity for the anionic moieties. The molar absorptivity for the mixed peroxy-carbonate species is significantly higher than the values reported for the $UO_2(CO_3)_3^{4-}$ ion with a molar absorptivity of $1022.7 \pm 19.0\ M^{-1}cm^{-1}$ at the maximum absorbance of 347.5 nm. The loss of the fine structure in the absorbance spectrum for the $UO_2(O_2)(CO_3)_2^{4-}$ ion can be explained by the nature of the U−peroxide bond. Charge transfer complexes are typically characterized by a very broad indistinct absorbance with a high molar absorptivity. Additionally, highly symmetric molecules generally have lower molar absorptivities compared to asymmetric molecules. The $UO_2(O_2)(CO_3)_2^{4-}$ ion is clearly less sym-

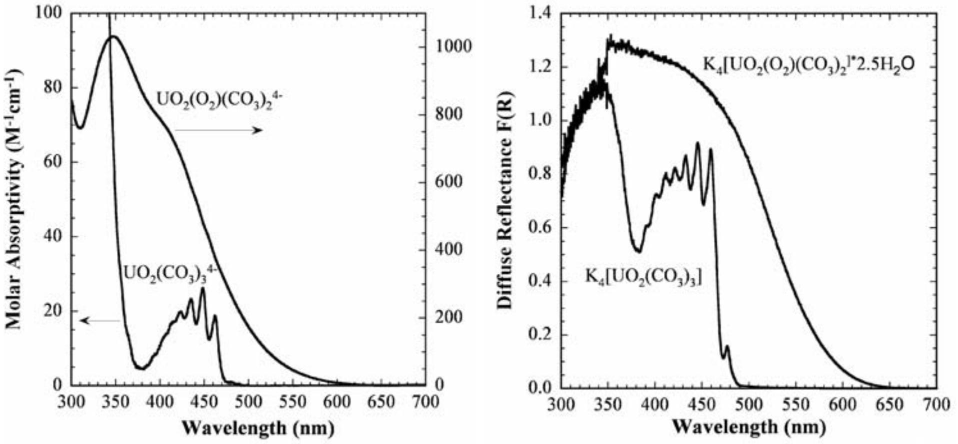

**Figure 6.** Comparison of spectroscopic features of $UO_2(CO_3)_3^{4-}$ and $UO_2(O_2)(CO_3)_2^{4-}$ in solution (left) and solid state (right).

**Table 1.** Selected Molar Absorptivity ($\epsilon$) values for $UO_2(O_2)(CO_3)_2^{4-}$ and $UO_2(CO_3)_3^{4-}$ (Reported Errors Are the Standard Error of the Mean)

| $UO_2(CO_3)_3^{4-}$ | | $UO_2(O_2)(CO_3)_2^{4-}$ | |
|---|---|---|---|
| wavelength (nm) | $\epsilon$ ($M^{-1}$ $cm^{-1}$) | wavelength (nm) | $\epsilon$ ($M^{-1}$ $cm^{-1}$) |
| 424.0 | 19.9 ± 0.2 | 310.5 | 766.6 ± 14.5 |
| 435.0 | 23.3 ± 0.3 | 347.5 | 1022.7 ± 19.0 |
| 448.5 | 26.3 ± 0.2 | 420.0 | 705.5 ± 14.8 |
| 462.0 | 18.8 ± 0.1 | 500.0 | 177.0 ± 4.2 |

metric than the $UO_2(CO_3)_3^{4-}$ ion; therefore, the molar absorptivity for $UO_2(O_2)(CO_3)_2^{4-}$ should be significantly higher. The loss of the fine structure in the electronic absorption spectrum of $UO_2(O_2)(CO_3)_2^{4-}$ is likely caused by the intense ligand-to-metal charge transfer in the electronic structure of the mixed peroxo-carbonato species. A full comparison of the electronic structure of these molecules and interpretation of the vibration and electronic absorption spectra is the topic of a future publication.

The absorption spectrum for the $UO_2(CO_3)_3^{4-}$ ion closely resembles that of the solid state diffuse reflectance spectrum of $K_4[UO_2(CO_3)_3]$, which is characterized by a relatively weak and broad absorption region between 380 and 500 nm with a characteristic fine structure. The similarity of the pure component solution spectra for the new mixed peroxo-carbonato complex to the solid state diffuse reflectance spectrum of $K_4[UO_2(O_2)(CO_3)_2]\cdot 2.5H_2O$ is further corroboration that the U(VI) solution species is $UO_2(O_2)(CO_3)_2^{4-}$. In stark contrast to $K_4[UO_2(CO_3)_3]$, the absorbance spectrum for $K_4[UO_2(O_2)(CO_3)_2]\cdot 2.5H_2O$ shows a single broad featureless peak beginning at 650 nm and increasing in intensity at lower wavelengths, which is consistent with the spectral features of the solution species.

A comparison of the solid Raman spectrum with a solution Raman spectrum for the mixed peroxo-carbonato complex could not be made for two reasons. The concentrations of U used in the UV–vis titrations were below the detection limit of the Raman spectrometer. By increasing the concentration of U, the solution speciation becomes more complicated because of the formation of additional uranium species, and a binary solution no longer exists. Additionally, even at low laser power, the $H_2O_2$ in solution is decomposed by the laser energy, evidenced by the formation of bubbles, causing the solution species to quickly revert back to $UO_2(CO_3)_3^{4-}$. This reversion with peroxide decomposition is evidence for the reversibility of the reaction in eq 1 and indicates a strong dependence on the peroxide concentration.

**Determination of the Formation Constant of $UO_2(O_2)(CO_3)_2^{4-}$(aq).** The apparent isosbestic point at 310 nm indicates the presence of two species in equilibrium. The mole ratio plot in Figure 7 (left) clearly shows that the stoichiometry of $H_2O_2$ to U in the complex is 1:1, which agrees well with reports in the literature.[13–17] Spectrophotometric titrations performed at varying U(VI) concentrations also verified that at $[U(VI)]_{tot} < 0.55$ mM, a monomeric U(VI) carbonato-peroxo solution speciation is formed. The equilibrium constant for the two solution complexes in equilibrium can be defined from eq 1 as

$$K = \frac{[UO_2(O_2)(CO_3)_2^{4-}][CO_3^{2-}][H^+]}{[UO_2(CO_3)_3^{4-}][HO_2^-]} \qquad (2)$$

The 1:1 stoichiometry for the reaction can be confirmed, when eq 2 is rearranged, by the logarithmic concentration ratio of $UO_2(CO_3)_3^{4-}$ and $UO_2(O_2)(CO_3)_2^{4-}$ giving a positive slope of unity, as shown in eq 3.

$$\log\left(\frac{[UO_2(O_2)(CO_3)_2^{4-}]}{[UO_2(CO_3)_3^{4-}]}\right) = \log K + \log[HO_2^-] - \log[CO_3^{2-}] - \log[H^+] \qquad (3)$$

The apparent stability constant, $K'$, for the formed U(VI) complex can then be expressed by the relation

$$\log K' = \log\left(\frac{[UO_2(O_2)(CO_3)_2^{4-}]}{[UO_2(CO_3)_3^{4-}]}\right) - \log[H_2O_2]_{tot} + \log[CO_3^{2-}] \qquad (4)$$

where $[H_2O_2]_{tot}$ is the total free peroxide (e.g., $H_2O_2 + HO_2^- + O_2^{2-}$).

The carbonate concentration was held constant at 0.5 M for all experiments, and the pH changed by less than 0.05 units up to the 1:1 ratio of peroxide to uranium. Only solution spectra below a ratio of 0.75:1 $H_2O_2$ to U were used in the regression analysis to ensure formation of a single mono-

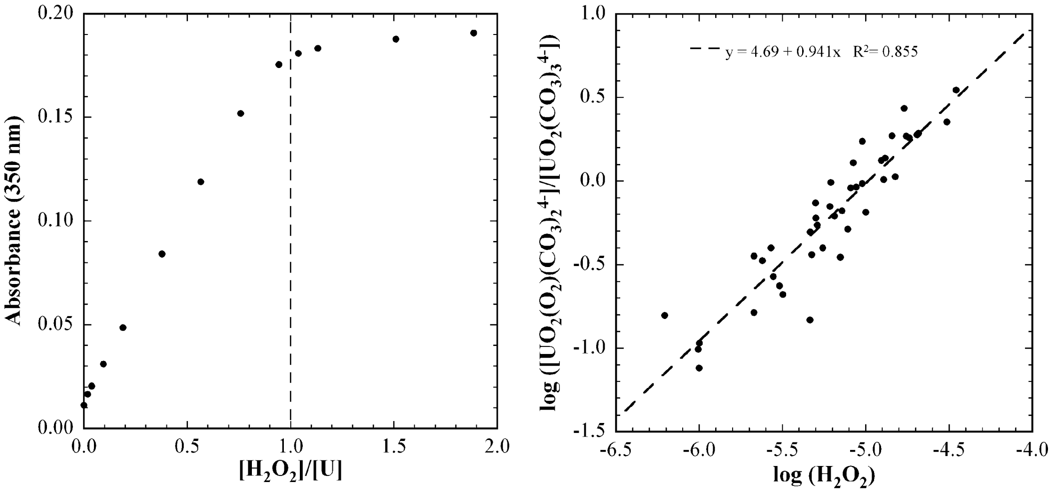

**Figure 7.** Two methods to determine the stoichiometry of the mixed U(VI)−peroxo−carbonato solution species. (Left) mole-ratio plot indicating a 1:1 ratio of $H_2O_2$ to U and (right) summary of the calculation of the equilibrium constant, where the slope also shows a 1:1 stoichiometry.

**Table 2.** Regression Results for the Stability Constant for the Formation of $UO_2(O_2)(CO_3)_2^{4-}$ from $UO_2(CO_3)_3^{4-}$According to eq 1

| | |
|---|---|
| log $K'$ | 4.70 ± 0.02[a] |
| standard deviation | 0.16 |
| no. of data points | 42 |
| [U] (mM) | 0.10–0.55 |
| $[K_2CO_3]$ (M) | 0.5 |
| $T_{av}$ (°C) | 24.4 |

[a] The error is defined as the standard error of the mean.

meric species. On the basis of the raw absorbance and the single-component spectrum of $UO_2(CO_3)_3^{4-}$, the spectrophotometric titrations were deconvoluted to yield the solution species concentrations for both $UO_2(O_2)(CO_3)_2^{4-}$ and $UO_2(CO_3)_3^{4-}$.

A summary of the regression analysis for determining the equilibrium stability constant for the formation of $UO_2(O_2)(CO_3)_2^{4-}$ in 0.5 M $K_2CO_3$ are summarized in Table 2, and Figure 7 illustrates two graphical methods validating the stoichiometry of the solution species $UO_2(O_2)(CO_3)_2^{4-}$. The mole ratio plot indicates a 1:1 stoichiometry of $H_2O_2$ to U but does not exclude the formation of polynuclear species (e.g., a 2:2 stoichiometry). The analysis shown in Figure 7 (right) was performed by varying the total concentration of U up to 0.55 mM. A slope close to unity indicates that the complex being formed has only 1 mol of $H_2O_2$ per mole of U(VI), therefore confirming the solution species as being $UO_2(O_2)(CO_3)_2^{4-}$. The large stability constant (log $K' = 4.70 \pm 0.02$) indicates an unexpectedly high stability of the mixed peroxo-carbonato species over the $UO_2(CO_3)_3^{4-}$ anion. This represents one of the most stable species in inorganic U(VI) solution chemistry, and a similarly strong complex has been observed with tetravalent Pu(IV) in carbonate solutions where peroxide easily replaced carbonate to form the mixed complex, $Pu_2(O_2)_2(CO_3)_6^{8-}$.[34] These complexes are evidence for the exceedingly high affinity of peroxide ions for actinide ions.

## Conclusions

The tris-carbonato complex of U(VI) has long been a focus of investigation because of its high stability over other strong complexing ligands, for example, hydroxide. Minor amounts of peroxide easily displace the carbonate ligands in the inner coordination sphere of $UO_2(CO_3)_3^{4-}$ to form a mixed peroxo-carbonato complex. For the first time, a ternary mixed U(VI) peroxo-carbonato species has been identified and characterized in both solution and solid state. A new hydrate of this complex, $K_4[UO_2(O_2)(CO_3)_2]\cdot H_2O$, exhibiting the same U(VI) coordination as the previously reported higher hydrate has been isolated and characterized by single crystal X-ray diffraction studies. This structure is stabilized by the $K^+$ ion, while $K_4[UO_2(O_2)(CO_3)_2]\cdot 2.5H_2O$ is stabilized by two-dimensional networks of water separating a pair of two staggered layers of $[UO_8]$ polyhedra. The large apparent formation constant for $UO_2(O_2)(CO_3)_2^{4-}$ (log $K' = 4.70 \pm 0.02$) is evidence for the exceedingly high affinity of peroxide ions for actinide ions and illustrates the exceptionally strong complexation power of $HO_2^-$, which is able to out compete $CO_3^{2-}$ for complexation of U(VI) even in concentrated carbonate solutions.

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**Supporting Information Available:** Crystallographic data in CIF format, figure showing the atom-numbering scheme for $UO_2(O_2)(CO_3)_2^{4-}$, and table listing selected geometric parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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