Inorg. Chem. **2007**, *46*, 3657–3662

Inorganic Chemistry
Article

# Expanding the Crystal Chemistry of Uranyl Peroxides: Synthesis and Structures of Di- and Triperoxodioxouranium(VI) Complexes

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Received January 23, 2007

Four compounds containing tri- and diperoxodioxouranium(VI) complexes have been synthesized under ambient conditions and structurally characterized. The crystal structures of $Na_4(UO_2)(O_2)_3(H_2O)_{12}$ (monoclinic, $P2_1/c$, $a = 6.7883(6)$ Å, $b = 16.001(2)$ Å, $c = 16.562(2)$ Å, $\beta = 91.917(2)°$, $V = 1797.9(3)$ Å$^3$, $Z = 4$) and $Ca_2(UO_2)(O_2)_3(H_2O)_9$ (orthorhombic, $Pbcn$, $a = 9.576(3)$ Å, $b = 12.172(3)$ Å, $c = 12.314(2)$ Å, $V = 1435.4(6)$ Å$^3$, $Z = 4$) contain clusters of triperoxodioxouranium(VI). These clusters are bonded through a network of H bonding to $H_2O$ groups and in the Ca compound by bonds to $Ca^{2+}$ cations. In the crystal structure of $Na_2Rb_4(UO_2)_2(O_2)_5(H_2O)_{14}$ (orthorhombic, $Pbcm$, $a = 6.808(2)$ Å, $b = 16.888(6)$ Å, $c = 23.286(8)$ Å, $V = 2677.5(16)$ Å$^3$, $Z = 4$), triperoxodioxouranium(VI) polyhedra share a peroxide edge, forming dimers of polyhedra of composition $(UO_2)_2(O_2)_5^{6-}$. Adjacent dimers are linked through bonding to $Rb^+$ cations and by H bonds to $H_2O$ groups. The crystal structure of $K_6[(UO_2)(O_2)_2(OH)]_2(H_2O)_7$ (orthorhombic, $Pcca$, $a = 15.078(8)$ Å, $b = 6.669(4)$ Å, $c = 23.526(13)$ Å, $V = 2366(2)$ Å$^3$, $Z = 4$) contains diperoxodioxouranium(VI) polyhedra that include two OH groups. These polyhedra share an OH–OH edge, forming dimers of composition $(UO_2)_2(O_2)_4(OH)_2^{6-}$. The dimers are linked by bonds to $K^+$ cations and by H bonding to $H_2O$ groups.

## 1. Introduction

The solution chemistry of the uranium(VI)−peroxide system is important for uranium separation chemistry[1−3] and understanding reactions of water with nuclear waste under geological disposal conditions.[4−10] Despite the importance of uranium(VI)−peroxide complexes under alkaline conditions, relatively little is known about their structures and stabilities. About a dozen uranium(VI)−peroxide compounds were isolated from alkaline solutions by Gurevich and coworkers more than four decades ago, but structures have not been reported for most of these materials.[11−13] Until recently, the only known structure of an inorganic uranium(VI)−peroxide was $Na_4[UO_2(O_2)_3]{\cdot}9H_2O$ with isolated triperoxodioxouranium(VI) clusters.[14] Renewed interest in uranium(VI)−peroxide chemistry under alkaline conditions has provided interesting insights into the complexity of uranium(VI)−peroxide solid-state and solution chemistry. The formation of spherical uranium(VI)−peroxide clusters in alkaline solutions that contain 24, 28, and 32 uranyl polyhedra and their subsequent crystallization have been reported.[15] The mineral studtite, $(UO_2)(O_2)(H_2O)_4$, which forms in nature due to the buildup of peroxide originating from the radiolysis of water,[16] contains one-dimensional chains of uranyl polyhedra with bridging peroxo groups.[17] The newly reported compound $K_4[U(CO_3)_2O_2(O_2)]{\cdot}2.5H_2O$

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10.1021/ic070118h CCC: $37.00

**Table 1.** Crystallographic Data for NaUT, CaUT, NaRbUT, and KUD

| | NaUT | CaUT | NaRbUT | KUD |
|---|---|---|---|---|
| formula | $Na_4(UO_2)(O_2)_3(H_2O)_{12}$ | $Ca_2(UO_2)(O_2)_3(H_2O)_9$ | $Na_2Rb_4(UO_2)_2(O_2)_5(H_2O)_{14}$ | $K_6[(UO_2)(O_2)_2(OH)]_2(H_2O)_7$ |
| mol wt | 674.17 | 608.32 | 1340.11 | 1062.76 |
| space group | $P2_1/c$ | *Pbcn* | *Pbcm* | *Pcca* |
| *a* (Å) | 6.7883(6) | 9.576(3) | 6.808(2) | 15.078(8) |
| *b* (Å) | 16.001(2) | 12.172(3) | 16.888(6) | 6.669(4) |
| *c* (Å) | 16.562(2) | 12.314(2) | 23.286(8) | 23.526(13) |
| $\beta$ (deg) | 91.917(2) | | | |
| *V* (Å$^3$) | 1797.9(3) | 1435.4(6) | 2677(2) | 2366(2) |
| *Z* | 4 | 4 | 4 | 4 |
| $D_{calc}$ (g/cm$^3$) | 2.491 | 2.815 | 3.325 | 2.984 |
| $\mu$ (mm$^{-1}$) | 9.22 | 12.11 | 19.45 | 14.81 |
| R1 | 0.0281 | 0.0397 | 0.0376 | 0.0589 |
| wR2 | 0.0708 | 0.0959 | 0.1065 | 0.1733 |

contains the only example of an inorganic compound with a mixed peroxo−carbonate complex.[18] The first sheet of uranyl peroxide polyhedra has been reported in $Na_5[(UO_2)_3(O_2)_4(OH)_3](H_2O)_{13}$.[19] New insights have also been gained in organometallic uranium(VI)−peroxide complexes.[20]

As part of our ongoing studies of uranium(VI)−peroxide chemistry under alkaline conditions, we have isolated four compounds and characterized their crystal structures. Two of these structures contain isolated triperoxodioxouranium(VI) clusters. The third compound contains triperoxodioxouranium(VI) species that share a peroxide edge, resulting in dimers of polyhedra. The final structure contains a mixed peroxo−hydroxo cluster composed of two uranyl polyhedra that are bridged through a OH−OH edge.

## 2. Experimental Section

**Sample Preparation**. Crystals of $Na_4(UO_2)(O_2)_3(H_2O)_{12}$ (designated NaUT) were synthesized by the combination of 1 mL of 30% $H_2O_2$ in water, 1 mL of 4 M NaOH in water, and 1 mL of 2 M $UO_2(NO_3)_2(H_2O)_6$ in water. The resulting solution stood uncovered for 24 h under ambient conditions, after which time 100 $\mu$L of the solution was placed into a glass vial with 5 $\mu$L of polyethylene glycol hexadecyl ether (Brij-56) added as a precipitation reagent. The vial was stored at room temperature for 2 weeks, after which crystals of NaUT approximately 200 $\mu$m in length were recovered.

Yellow blocky crystals of $Ca_2(UO_2)(O_2)_3(H_2O)_9$ (designated CaUT), up to 1 mm in maximum dimension, were synthesized under ambient conditions by evaporation of a solution containing 1 mL of 0.18 M $UO_2(CH_3COO)_2(H_2O)_2$ in water, 1 mL of 0.18 M $Ca(CH_3COO)_2$ in water, and 1 mL of 30% $H_2O_2$ in water. Upon standing, a pale yellow precipitate formed within minutes. After 30 days, crystals of CaUT were isolated.

Crystals of $Na_2Rb_4(UO_2)_2(O_2)_5(H_2O)_{14}$ (designated NaRbUT) were synthesized by the combination of 1 mL of 30% $H_2O_2$ in water and 4 mL of 3 M RbOH in water. A 2 M solution of $UO_2(NO_3)_2(H_2O)_6$ in water was added to the solution, resulting in a light orange solution that stood uncovered for 24 h. A volume of 100 $\mu$L of the resulting solution was placed in a glass vial with 20 $\mu$L of sodium hydrocarbon sulfonate pyronate (Alkanol 189-S) as a precipitation reagent. The vial was placed in a refrigerator. After 12 days, bright orange needles approximately 300−600 $\mu$m in length were recovered.

Crystals of $K_6[(UO_2)(O_2)_2(OH)]_2(H_2O)_7$ (designated KUD) were synthesized under ambient conditions from a solution created by mixing 1 mL of 8 M KOH in water, 1 mL of 30% $H_2O_2$ in water, and 1 mL of 2 M $UO_2(NO_3)_2(H_2O)_6$ in water. The uranyl nitrate solution was added dropwise with stirring, after which the solution turned red and effervesced. Within 12 days, a dark brown precipitate had formed in the solution. An aliquot of precipitate and solution was pipetted into Infinium oil on a glass slide. Blocky red crystals of KUD crystallized from the solution within minutes.

**X-ray Crystallography**. Crystals suitable for X-ray diffraction were selected using a polarizing stereomicroscope and mounted on Bruker PLATFORM three-circle X-ray diffractometer equipped with a 4K APEX CCD detector and graphite-monochromatized Mo K$\alpha$ radiation with a crystal-to-detector distance of 4.67 cm. For each sample, a sphere of three-dimensional data was collected at 100 K with the crystal contained in a flow of $N_2$.

The Bruker SHELXTL Version 5 system of programs was used for the solution and refinement of each crystal structure. Intensity data was corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. Semiempirical corrections for absorption were applied by modeling each crystal as an ellipsoid. Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from *International Tables for X-Ray Crystallography*, Vol. IV.[21] The structure refinements were straightforward, using the SHELXTL suite of programs.[22] As is typical for uranyl compounds, H atoms were not located in the structures. Crystallographic information is summarized in Table 1, and selected bond lengths are provided in Table 2.

## 3. Results

The crystal structures of NaUT, CaUT, NaRbUT, and KUD each contain uranyl dioxo cations, $UO_2^{2+}$, as fundamental structural units. These uranyl ions are nearly linear and exhibit average bond lengths ranging from 1.828 to 1.88 Å in the structures under study. Each uranyl ion is coordinated by six anions arranged at the equatorial vertices of distorted hexagonal bipyramids that are capped by the $O_{Ur}$ atoms. In the structures of NaUT, CaUT, and NaRbUT, the uranyl ions are coordinated by three peroxide groups, forming $(UO_2)(O_2)_3^{4-}$ polyhedra, as shown in Figure 1. The peroxide O−O bond lengths range from 1.482(4) to 1.53(1) Å in these polyhedra; thus, each polyhedron has three short and three long equatorial edges (Figure 1). In KUD, the two sym-

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**Table 2.** Selected Bond Lengths (Å) for NaUT, CaUT, NaRbUT, and KUD

| NaUT | | CaUT | | NaRbUT | | KUD | |
|---|---|---|---|---|---|---|---|
| U1−O7 | 1.845(2) | U1−O1 | 1.840(6) × 2 | U1−O10 | 1.823(5) | U1−O1 | 1.88(1) × 2 |
| U1−O8 | 1.847(2) | U1−O2 | 2.282(7) × 2 | U1−O1 | 1.833(5) | U1−O3 | 2.29(1) × 2 |
| U1−O1 | 2.296(2) | U1−O3 | 2.299(7) × 2 | U1−O12 | 2.258(5) | U1−O4 | 2.32(2) × 2 |
| U1−O4 | 2.299(2) | U1−O4 | 2.311(6) × 2 | U1−O11 | 2.266(5) | U1−OH7 | 2.41(2) × 2 |
| U1−O2 | 2.302(2) | $\langle U1-O_{Ur}\rangle$ | 1.840 | U1−O4 | 2.290(5) | $\langle U1-O_{Ur}\rangle$ | 1.88 |
| U1−O3 | 2.313(2) | $\langle U1-O_{eq}\rangle$ | 2.297 | U1−O3 | 2.293(5) | $\langle U1-O_{eq}\rangle$ | 2.34 |
| U1−O6 | 2.334(2) | | | U1−O2 | 2.345(2) | | |
| U1−O5 | 2.342(2) | O2−O3 | 1.495(9) | U1−O13 | 2.395(3) | U2−O2 | 1.86(2) × 2 |
| $\langle U1-O_{Ur}\rangle$ | 1.846 | O4−O4 | 1.53(1) | $\langle U1-O_{Ur}\rangle$ | 1.828 | U2−O5 | 2.30(2) × 2 |
| $\langle U1-O_{eq}\rangle$ | 2.314 | | | $\langle U1-O_{eq}\rangle$ | 2.308 | U2−O6 | 2.36(2) × 2 |
| | | | | | | U2−OH7 | 2.42(2) × 2 |
| O1−O4 | 1.482(4) | | | O2−O13 | 1.504(9) | $\langle U2-O_{Ur}\rangle$ | 1.86 |
| O2−O6 | 1.492(3) | | | O3−O4 | 1.483(7) | $\langle U2-O_{eq}\rangle$ | 2.36 |
| O3−O5 | 1.506(3) | | | O11−O12 | 1.502(8) | | |
| | | | | | | O3−O4 | 1.47(2) |
| | | | | | | O5−O6 | 1.52(2) |

metrically distinct uranyl ions are coordinated by two peroxide groups and two hydroxyl groups, forming $(UO_2)(O_2)_2(OH)_2^{4-}$ hexagonal bipyramids (Figure 2).

The uranyl polyhedral geometries in these structures warrant further consideration. The uranyl ion bond lengths range from 1.823(5) to 1.88(1) Å, whereas the average uranyl ion bond length from 35 hexagonal bipyramids in well-refined structures is 1.783 Å, with a standard deviation of 0.030.[23] The average equatorial bond lengths in NaUT, CaUT, and NaRbUT, which contain $(UO_2)(O_2)_3^{4-}$ polyhedra, range from 2.297 to 2.314 Å. In the case of KUD, which contains $(UO_2)(O_2)_2(OH)_2^{4-}$ polyhedra, the average equatorial bond lengths of the two distinct uranyl ions are somewhat longer, at 2.34 and 2.36 Å. In each case, there are four shorter bond lengths corresponding to the peroxide O atoms and two longer bonds to the hydroxyl O atoms (Table 2). The average equatorial bond length for U−O bonds in 35 uranyl hexagonal bipyramids from well-refined structures is 2.460 Å, with a standard deviation of 0.107.[23] Relative to uranyl hexagonal bipyramids lacking peroxide groups, the uranyl ions of the uranyl peroxide polyhedra in the four structures under consideration are significantly elongated, whereas the equatorial bond lengths are shortened by about 0.15 Å. Similar polyhedral geometries have been observed for other uranyl peroxides.[14,15,17,19] Burns[23] found that the equatorial bond-length distribution in uranyl hexagonal bipyramids containing O at the equatorial vertices is asymmetric, with few bond lengths less than 2.4 Å. This asymmetry is attributable to the size constraints of placing six coplanar O atoms about a uranyl ion. In the case of the uranyl peroxide polyhedra, the O−O contacts within the peroxide groups are only ~1.5 Å, making it possible for the O atoms to move closer to the uranyl ion. Relative to uranyl hexagonal bipyramids with no peroxide groups, the electron density within uranyl peroxide polyhedra appears to be shifted from the uranyl ion to bonds within the equatorial plane.

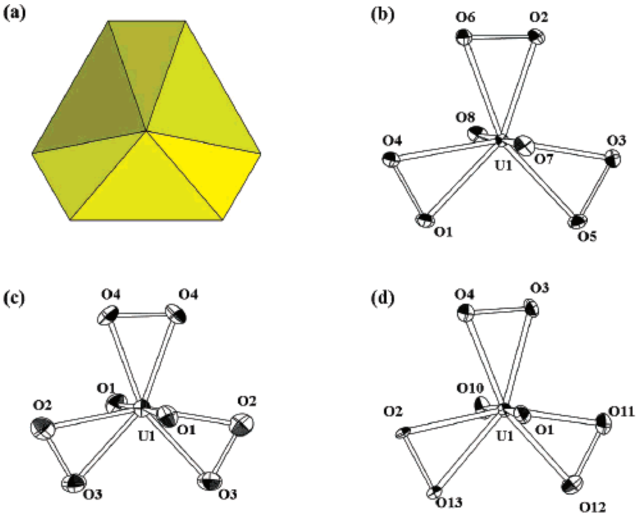

**Figure 1.** $(UO_2)(O_2)_3^{4-}$ polyhedra: (a) polyhedral representation and (b) ellipsoidal representations of NaUT, (c) CaUT, and (d) NaRbUT.

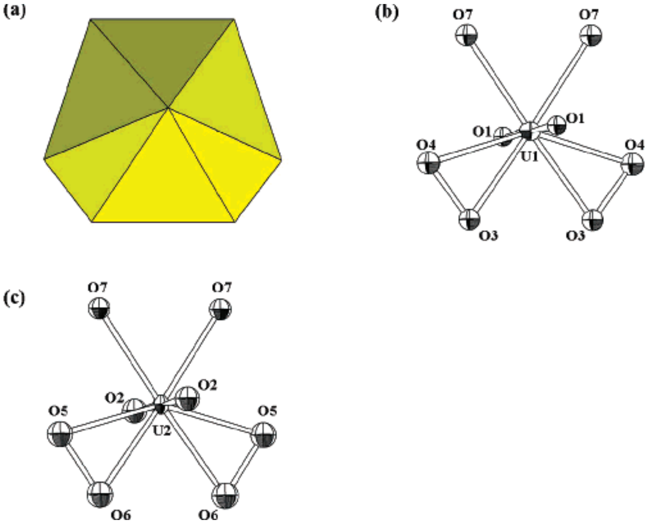

**Figure 2.** $(UO_2)(O_2)_2(OH)_2^{4-}$ polyhedra in the structure of KUD: (a) polyhedral representation, (b) ellipsoidal representation of U1, and (c) ellipsoidal representation of U2.

In the structure of NaUT, the triperoxodioxouranium(VI) polyhedra are isolated from each other and are linked into an extended structure through a H-bonding network (Figure 3). There are four distinct Na sites that are coordinated by five or six $H_2O$ groups with average bond lengths ranging from 2.339 to 2.370 Å. Of the 12 distinct $H_2O$ groups in the structure, 10 are shared between two $Na^+$ cations, and two (O19 and O20) are bonded to only one Na. Remarkably, the Na polyhedra only contain $H_2O$ groups, and all linkages between the Na polyhedra and the triperoxodioxouranium-

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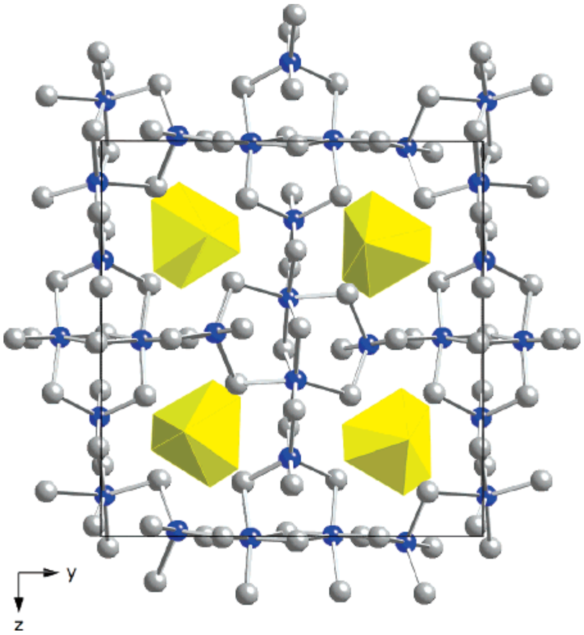

**Figure 3.** Crystal structure of NaUT projected along [100]. Triperoxodioxouranium(VI) polyhedra are yellow, Na atoms are blue spheres, and O atoms of $H_2O$ groups are gray spheres.

(VI) polyhedra are through H bonds. In this regard, all of the vertices of the triperoxodioxouranium(VI) polyhedra probably accept H bonds, as each is formally underbonded in their absence.

The triperoxodioxouranium(VI) polyhedra are isolated from each other in the structure of CaUT (Figure 4). The structure contains a single symmetrically distinct $Ca^{2+}$ cation that is coordinated by nine ligands, with an average bond length of 2.484 Å. Of these nine ligands, four are $H_2O$ groups that are unshared, four are O atoms of peroxide groups within the triperoxodioxouranium(VI) polyhedra, and one is an O atom of the uranyl ion within a triperoxodioxouranium(VI) polyhedron. Each triperoxodioxouranium(VI) polyhedron is linked to four Ca polyhedra, resulting in chains that extend along [001] (Figure 4a). Two of the peroxide edges of the triperoxodioxouranium(VI) polyhedra are shared with two different Ca polyhedra, whereas the third is unshared. The chains of polyhedra are connected only through H bonds, presumably extending between the $H_2O$ groups of one chain and the unshared peroxide edge of a triperoxodioxouranium(VI) polyhedron in an adjacent chain. There is one $H_2O$ group located in an interstitial region of the structure that provides additional linkages through H bonds.

In the structure of NaRbUT, two triperoxodioxouranium(VI) polyhedra share a peroxide edge, resulting in a dimer of polyhedra with composition $(UO_2)_2(O_2)_5^{6-}$ (Figure 5a,b). This is the first structure reported to contain such a dimer as an isolated structural component, although this polyhedral connectivity exists as part of a large cluster containing 28 triperoxodioxouranium(VI) polyhedra.[15] The structure also contains three symmetrically distinct $Rb^+$ cations and a single $Na^+$ cation (Figure 5c,d). The Rb1 cation is bonded to four O atoms of uranyl ions from two different dimers of polyhedra and shares a peroxide edge with one of these dimers, which is also the peroxide edge that is shared between the uranyl polyhedra. Rb1 also bonds to two $H_2O$ groups, with an overall average bond length of 3.016 Å. The Rb2 cation is bonded to two O atoms of uranyl ions from different dimers and also two O atoms of peroxide groups residing in the same two dimers. The Rb2 coordination polyhedron includes four $H_2O$ groups and has an overall average bond length of 3.069 Å. The Rb3 cation bonds to two O atoms of uranyl ions within the same dimer as well as three O atoms of peroxide groups that are also from the same dimer. In this case, each of the three O atoms are from different peroxide groups. The Rb3 polyhedron contains four $H_2O$ groups, and the overall average bond length is 3.065 Å. Finally, the Na1 cation is coordinated by six $H_2O$ groups with an average bond length of 2.362 Å (Figure 5d).

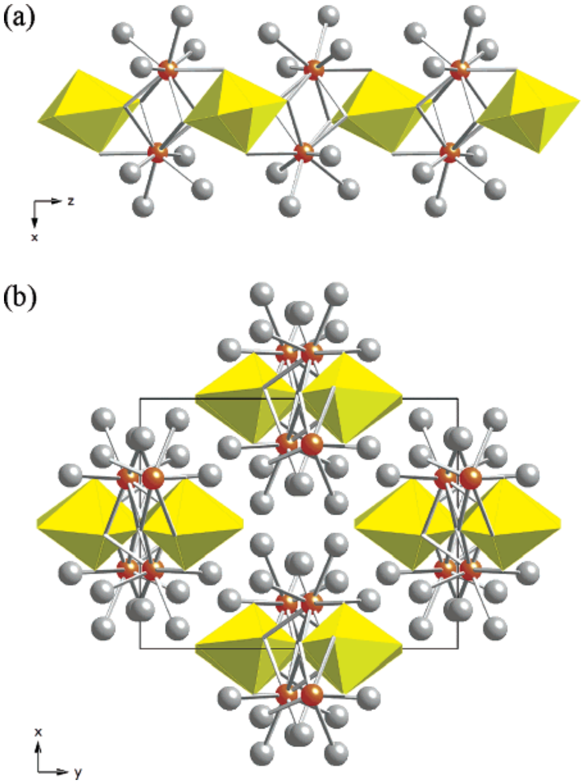

**Figure 4.** Structure of CaUT projected along [100] (a) and [001] (b). Triperoxodioxouranium(VI) polyhedra are yellow, Ca atoms are represented by orange spheres, and O atoms of $H_2O$ groups are represented by gray spheres.

The structure of KUD contains two symmetrically distinct $(UO_2)(O_2)_2(OH)_2^{4-}$ hexagonal bipyramids that share an OH−OH edge, resulting in a dimer of composition $(UO_2)_2(O_2)_4(OH)_2^{6-}$ (Figure 6a,b). This is the first structure that contains dimers of this composition that are isolated as structural units, but similar dimers occur as components of large spherical clusters containing 24 or 32 uranyl polyhedra.[15] The structure contains five distinct K sites (Figure 6c), although the K5 site is only 50% occupied and exhibits disorder in the structure, as indicated by an anomalously large displacement parameter. The K1 cation is coordinated by two O atoms of uranyl ions of two different dimers, by four O atoms of two peroxide groups that occur in two different dimers, and by two $H_2O$ groups. The overall average bond distance to these eight ligands is 2.84 Å. The coordination polyhedron and connectivity of the K2 cation is essentially the same as that

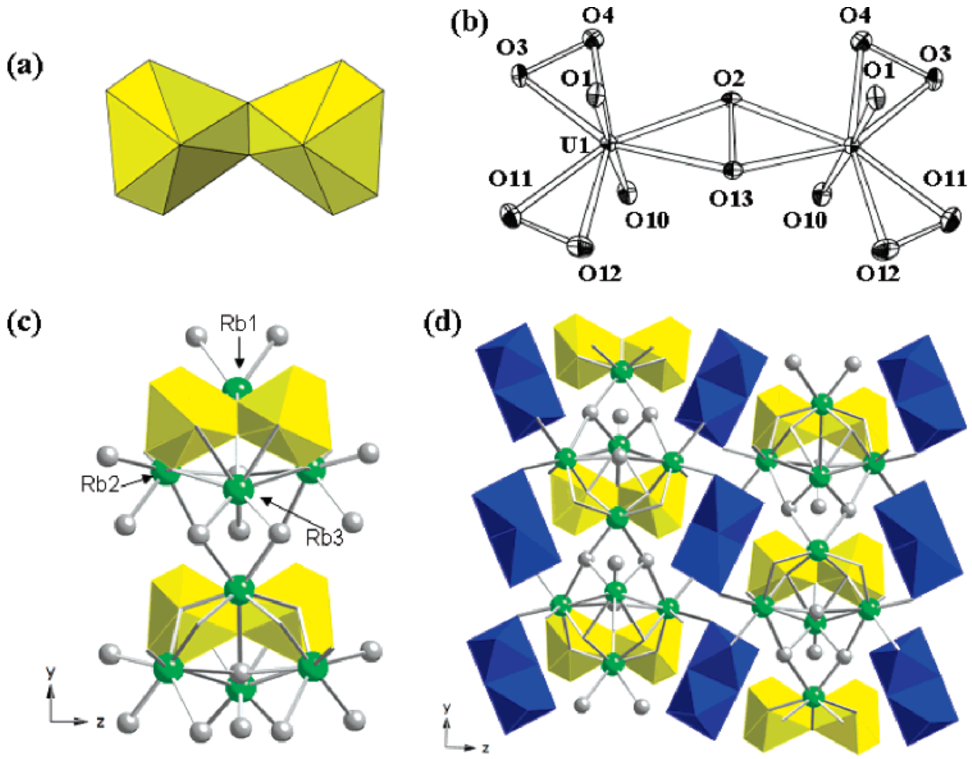

**Figure 5.** Representations of the structure of NaRbUT. (a) Polyhedral representation of the dimer of triperoxidedioxouranium(VI) polyhedra, (b) ellipsoidal representation of the dimer of triperoxidedioxouranium(VI) polyhedra, (c) projection of the structure along [100] showing the connectivity about the $Rb^+$ cations, and (d) projection along [010] showing the overall connectivity. The triperoxidedioxouranium(VI) polyhedra are yellow, Na polyhedra are blue, Rb atoms are shown as green spheres, and O atoms of selected $H_2O$ groups are shown as gray spheres.

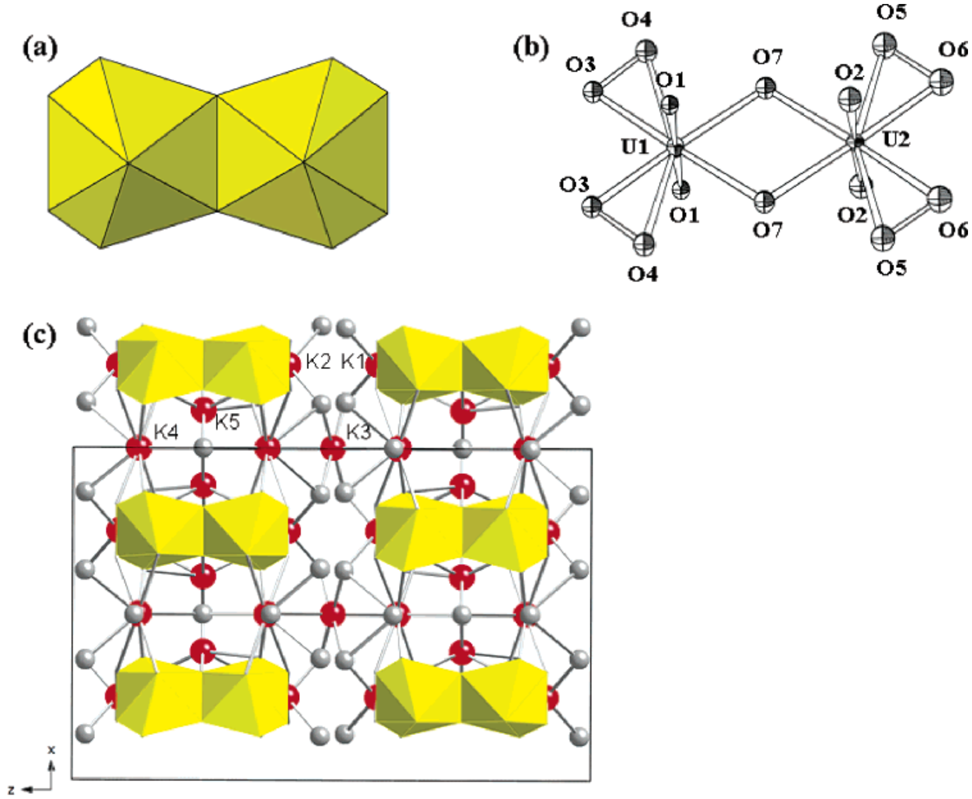

**Figure 6.** Representations of the structure of KUD. (a) Polyhedral representation of $(UO_2)_2(O_2)_4(OH)_2^{6-}$ dimers, (b) ellipsoidal representation of $(UO_2)_2(O_2)_4(OH)_2^{6-}$ dimers, and (c) projection of the crystal structure along [010]. Uranyl polyhedra are shown in yellow, K atoms are represented as red spheres, and O atoms of $H_2O$ groups are represented by gray spheres.

of K1, with an average bond length of 2.87 Å. The K3 cation is coordinated by six $H_2O$ groups with an average bond length of 2.75 Å. The K4 cation resides in a large distorted polyhedron with 10 ligands and an average bond length of

3.03 Å. There are four O atoms that belong to two peroxide groups of two dimers, two O atoms of uranyl ions of the same two adjacent dimers, and four $H_2O$ groups. Finally, the K5 cation is bonded to two O atoms of uranyl ions within the same dimer. It is also linked to one O atom of a hydroxyl group and one O atom of a peroxide group in an adjacent dimer. The polyhedron also includes one $H_2O$ group.

## 4. Discussion

At a time when one might have expected that the crystal chemistry of inorganic uranyl compounds is relatively mature, the introduction of peroxide into uranyl polyhedra is resulting in new structural connectivities. The structures reported in the current contribution contain uranyl peroxide polyhedra and dimers of polyhedra that presumably exist in solutions of uranyl and peroxide under alkaline conditions. These uranyl structural units are the basic building units of extraordinary uranyl peroxide structural topologies that include spherical clusters[15] and porous sheets.[19] It is the substantial shortening of uranyl polyhedral edges that correspond to peroxide groups that appears to result in novel structures. Uranyl peroxide polyhedra show less of a tendency to link into infinite sheets than peroxide-free uranyl polyhedra,[23] which presents interesting opportunities for the directed synthesis of nanostructured uranyl compounds. Although only one neptunyl peroxide structure has been reported,[23] it seems likely that neptunyl and plutonyl peroxides will also exhibit structural complexity and departures from current known structures.

**Acknowledgment.** This research was supported by the National Science Foundation Environmental Molecular Science Institute at the University of Notre Dame (EAR02-21966).

**Supporting Information Available:** Crystallographic data (CIF) for NaUT, CaUT, NaRbUT, and KUD. This material is available free of charge via the Internet at http://pbs.acs.org.

IC070118H