

## Cation–Cation Interactions between Uranyl Cations in a Polar Open-Framework Uranyl Periodate

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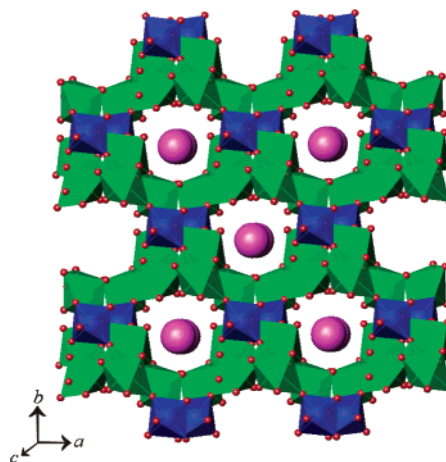
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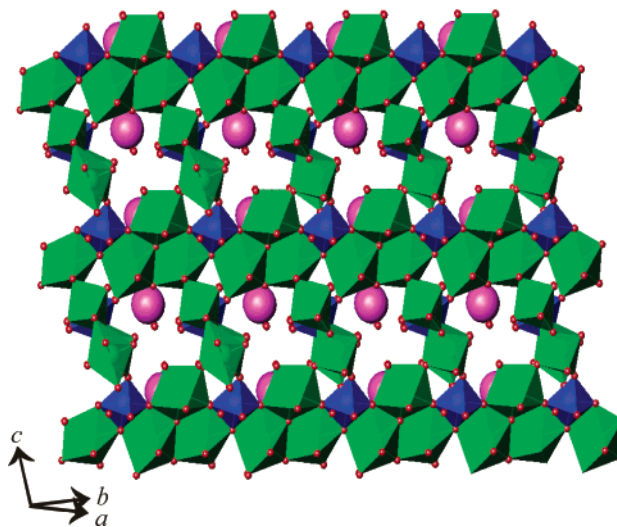
Cation–cation interactions (CCI's) are an integral part of both the solution and the solid-state chemistry of  $AnO_2^+$  ( $An = U, Np, Pu, Am$ ) cations, which contain actinides in +V oxidation state.<sup>1</sup> These interactions occur via coordination of one actinide metal center by the oxo atom of a second actinyl unit and can lead to the formation of dimers, oligomers, one-dimensional chains, two-dimensional sheets, and even three-dimensional networks that do not necessarily require the support of ancillary ligands.<sup>1,2</sup> These interactions are particularly well recognized for  $Np(V)$ ,<sup>3</sup> but have also been identified in  $U(V)$ ,<sup>4</sup>  $Pu(V)$ ,<sup>5</sup> and  $Am(V)$  chemistry.<sup>6</sup> CCI's play a critical role in the inner-sphere electron transfer that leads to the disproportionation of  $U(V)$  into  $U(VI)$  and  $U(IV)$ ,<sup>4</sup> and in interactions in  $Np(V)$  compounds that give rise to Ising-type ferromagnetic and metamagnetic behavior.<sup>7</sup> CCI's are rare in compounds that exclusively contain  $U(VI)$  in the form of uranyl cations (hereafter uranyl refers to the  $UO_2^{2+}$  cation).<sup>8</sup> However, in condensed phases,  $UO_2^{2+}$  cations are known to form interactions with alkali and alkaline earth metal cations.<sup>9</sup>

In an effort to expand solid-state studies on uranyl periodate<sup>10</sup> compounds beyond the single known example of  $K_2[(UO_2)_2(VO)_2(IO_6)_2O] \cdot H_2O$ ,<sup>11</sup> we have explored the hydrothermal reactions of alkali metal carbonates with uranyl nitrate and periodic acid at 185 °C. These reactions result in the formation of  $A[(UO_2)_3(HIO_6)_2(OH)(O)(H_2O)] \cdot 1.5H_2O$  ( $A = Li(1)–Cs(5)$ ) in yields as high as 91%.<sup>12</sup> The primary difficulty in this synthetic procedure is slowing the reduction of the I(VII) to I(V), which results in the formation of  $UO_2(IO_3)_2(H_2O)$ .<sup>13</sup> Compounds **1–5** are isolated as lemon yellow prisms from a colorless mother liquor. The IR vibrational spectra of these compounds show a characteristic  $\delta(OH)$  mode near 1071  $cm^{-1}$ ,<sup>10</sup> as well as strong uranyl symmetric and asymmetric modes.

Single-crystal X-ray diffraction studies on **1–5** reveal that all of the compounds are isostructural and crystallize in the polar monoclinic space group  $Cc$ .<sup>14</sup> The structure of **5**, which will be used to represent all five compounds, results from the assembly of three crystallographically unique uranyl units that are bridged by aquo, hydroxo, oxo, and monoprotonated periodate groups to yield a remarkably complex three-dimensional structure with intersecting channels extending along the  $c$  axis and approximately down 110 and  $\bar{1}\bar{1}0$ , as shown in Figures 1 and 2. Three-dimensional uranyl compounds are uncommon because uranyl polyhedra typically align in a parallel fashion, and, given the terminal nature of the oxo atoms, layered architectures result.<sup>15,16</sup> Alkali metal cations and water molecules fill the channels, which as can be seen in Figure 1 are also polar. The structure is apparently quite rigid, and the channels show almost no measurable size variance with reduction in the size of the alkali metal cations. However, the displacement parameters for the cations smaller than  $Rb^+$  do show considerable enlargement corresponding to rattling within the confines of the channels. This rattling does not result in splitting or disorder of the alkali metal



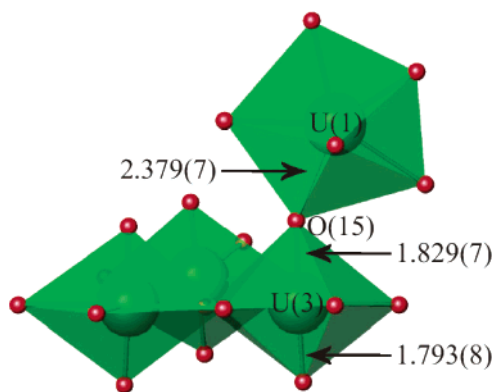
**Figure 1.** A view down the  $c$  axis showing the polar open-framework structures of  $A[(UO_2)_3(HIO_6)(OH)(O)(H_2O)] \cdot 1.5H_2O$  ( $Li(1)–Cs(5)$ ). The major channels running down this axis are filled with alkali metal cations.  $UO_7$  pentagonal bipyramids are shown in green, and  $IO_6$  octahedra are shown in blue.



**Figure 2.** A view of  $A[(UO_2)_3(HIO_6)(OH)(O)(H_2O)] \cdot 1.5H_2O$  ( $Li(1)–Cs(5)$ ) showing the second type of channel that intersects with the channels running down the  $c$  axis to yield an open-framework structure.

cation position. However, in the case of **1**, the  $Li^+$  cation had to be refined isotropically because of the large motion of this cation within the channel.

Each of the three uranyl units in **5** is coordinated by five oxygen atoms in the equatorial plane to yield  $[UO_7]$  pentagonal bipyramids. The uranyl  $U=O$  distances for  $U(1)$  and  $U(2)$  are normal and range from 1.769(8) to 1.781(7) Å. The equatorial  $U–O$  distances are also within normal limits and occur from 2.181(7) to 2.581(6) Å. The shortest  $U–O$  bond length in the equatorial plane is to the



**Figure 3.** An illustration of the cation–cation interaction between the uranyl unit containing U(3) and the uranyl cation containing U(1).

$\mu_3$ -oxide ion. The uranyl unit for U(3) has U=O distances of 1.829(7) and 1.793(8) Å. The former U=O distance does not correspond to a typical terminal uranyl oxo atom, but rather this atom is bridging to a neighboring uranyl unit containing U(1). This bridging distance is within typical limits for donor atoms in the equatorial plane with a distance of 2.379(7) Å, as depicted in Figure 3. This interaction effectively turns uranyl polyhedra perpendicular to one another creating two orthogonal uranium oxide sheets within the structure, which is best viewed in Figure 2, thereby leading to a three-dimensional architecture. Bond-valence sum calculations confirm that these three uranium centers are unambiguously U(VI) with values of 6.06, 6.00, and 6.12 for U(1), U(2), and U(3), respectively.<sup>17–19</sup> This is a rare example of cation–cation interactions between uranyl cations, and it provides a structural link between the CCI's in  $\text{AnO}_2^+$  compounds and those that contain  $\text{UO}_2^{2+}$ .<sup>8</sup>

The question then arises as to what makes U(3) so different from U(1) and U(2) to make the normally terminal uranyl cation form a cation–cation interaction more similar to that expected for an  $\text{AnO}_2^+$  cation instead of  $\text{UO}_2^{2+}$ ? A close look at the individual coordination environments of the uranium centers reveals that U(2) and U(3) are chelated by the  $\text{HIO}_6^{4-}$  anion. This anion also utilizes its oxo atoms to bridge to an additional four uranium centers. The hydrogen periodate anion has five I–O bond distances ranging from 1.830(7) to 1.894(7) Å and a sixth longer I–O(H) bond length of 1.926(8) Å to the nominal hydroxo group. We suggest that, through the chelation of U(3) by the hydrogen periodate anion, significant electron density is transferred from this highly charged anion to the U(3) uranyl cation to make the oxo atoms better Lewis bases than is typically found. We cannot exclude the possibility that this interaction is a consequence of other features of this structure, especially crystal packing forces.

The transfer of charge from the U(3) uranyl unit to an adjacent uranyl cation should result in a strengthening of the interactions with the donor atoms in the equatorial plane, the converse of which is that stronger equatorial bonds result in the formation of CCI's. Unfortunately, the ligand environments for each U center are different, making comparisons difficult. However, the average U–O distance to equatorial atoms surrounding U(3) is 2.322(7) Å, whereas statistically longer U–O distances of 2.377(7) and 2.389(7) Å are observed for U(1) and U(2), respectively. In a recent,

and quite timely, report by Sarsfield and Helliwell, it was shown that uranyl coordination compounds could be rationally prepared that have uranyl oxo atoms of increased Lewis basicity.<sup>20</sup> These oxo atoms are of sufficient basicity to form adducts with  $\text{B}(\text{C}_6\text{F}_5)_3$ . The charge transfer that results from the formation of this adduct also coincides well with the lengthening of the uranyl oxo distances and the shortening of the average bond length in the equatorial plane of this complex.

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**Supporting Information Available:** X-ray crystallographic files for **5** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12)  $\text{Cs}[(\text{UO}_2)_3(\text{HIO}_6)(\text{OH})(\text{O})(\text{H}_2\text{O})] \cdot 1.5\text{H}_2\text{O}$  (**5**): was prepared by loading  $\text{Cs}_2\text{CO}_3$  (173 mg, 0.530 mmol),  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (216 mg, 0.431 mmol),  $\text{H}_3\text{IO}_6$  (116 mg, 0.509 mmol), and 1.5 mL of a Millipore filtered water in a 23 mL PTFE-lined autoclave. The autoclave was heated at 185 °C for 120 h and slow cooled at 5 °C/h to 135 °C where it was held for 12 h. After this, the autoclave was cooled at 5 °C/h to 22 °C. Yellow prisms of **5** were isolated in 91% yield based on uranium (162 mg).
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