

Reviews

Some Aspects of Structure and Bonding in Binary and Ternary Uranium(VI) Oxides

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Aspects of the structure and bonding in binary and ternary uranium oxides are considered using group theoretical and geometrical ideas. A 13-orbital sd^5f^7 bonding manifold for the uranium atoms is sufficient for regular octahedra having six double bonds, elongated “reverse uranyl” octahedra having four equatorial bonds of average order $2^{1/2}$, and flattened uranyl octahedra or pentagonal bipyramids having two axial triple bonds. This is consistent with the uranium–oxygen bond lengths in ternary uranium oxides (uranates) exhibiting these structures. A key factor in determining structural features of uranates $U_xO_yZ^-$ is the formal negative charge per uranium atom (Z/X). A Z/X ratio of 2 corresponds to the tetraoxouranates $M_2^{II}UO_4$ and $M^{III}UO_4$, which have structures consisting of chains or layers of flattened $UO_2^{a-}O_{4/2}^e$ uranyl octahedra or layers of $UO_2^{a-}O_{6/3}^e$ uranyl hexagonal bipyramids with the interstitial counterions bonded to 3–8 oxygen atoms. Most cation-poor uranates with $Z/X < 2$ have layered structures related to those of UO_3 or U_3O_8 consisting of equatorial planes containing quadrilaterals and/or pentagons, short strong axial uranium–oxygen bonds, and interstitial cations between the layers. Cation-rich uranates with $Z/X > 2$ contain either chains of $UO_4^{a-}O_{2/2}^a$ “reverse uranyl” elongated octahedra (e.g., Ca_2UO_5 or Na_4UO_5) or regular UO_6 octahedra (e.g., Ca_3UO_6 or Li_6UO_6).

Introduction

Binary and ternary uranium–oxygen compounds are of interest from both fundamental and practical points of view. Thus uranium, like its neighboring actinides neptunium, plutonium, and americium, has the unusual property of forming strong covalent bonds in one dimension and weak electrostatic bonds in the other two dimensions. This is exemplified by the numerous uranyl derivatives having short strong “primary” uranium–oxygen multiple covalent bonds in the axial direction coupled with labile electrostatic “secondary” bonds to ligands in the equatorial plane.¹ This directional anisotropy can lead to low-dimensional materials consisting of chains or layers constructed from uranium–oxygen networks. Furthermore, uranium–oxygen compounds are of obvious practical importance in view of the important role of uranium oxides in nuclear reactor fuels. In addition uranium-oxide-based catalysts including U_3O_8 have been shown to be useful for the oxidative destruction of hydrocarbon and chlorine-containing organic pollutants.²

Several years ago,³ the properties of the 12-orbital d^5f^7 manifold from actinide 6d and 5f orbitals were examined for forming the strong covalent bonds in certain types of actinide derivatives such as the actinyl derivatives, AnO_2^{2+} , and the actinocenes (C_6H_8)₂An. Subsequently, Denning⁴ published an extensive review

on the electronic structure and bonding in actinyl ions. Relevant uranium chemistry has been reviewed by Morss⁵ as well as van Egmond.⁶ More recently, Burns, Ewing, and their collaborators have made an extensive survey of the crystal structures of uranium(VI) minerals and related inorganic uranyl phases⁷ including studies of their polyhedron geometries, bond-valence parameters, and polymerization of their fundamental polyhedral building blocks.⁸ Their work led to a novel approach for the description and classification of uranium oxide hydrate sheet anion topologies.⁹

This paper extends the approach of my earlier paper³ to the infinite solid-state structures of uranium–oxygen derivatives with the need to consider the 7s as well as the 6d and 5f orbitals to account for some covalency of all of the uranium–oxygen bonds, thereby leading to a 13-orbital sd^5f^7 manifold. In addition, some relevant geometrical aspects of the considerable variety of binary and ternary uranate structures are discussed. The range of uranate structures considered in this paper includes not only structures containing discrete uranyl units (UO_2^{2+}) treated by Burns, Ewing, and collaborators^{7–9} but also more cation-rich structures with the uranium(VI) atoms in other environments not found in mineral structures. Quaternary and higher structures containing elements other than uranium, oxygen, and an electropositive metal such as an alkali or alkaline earth metal are not considered in this paper.

Table 1. Bonding Possibilities in Uranium–Oxygen Derivatives Using the sd^5f^7 13-Orbital Manifold

	octahedral derivatives				
	regular C_h UO_6	elongated D_{4h} $UO_4^aO_{2/2}^a$	flattened D_{4h} $UO_2^aO_{4/2}^e$	D_{5h} pentagonal bipyramidal $UO_2^aO_5^e$	D_{6h} hexagonal bipyramidal $UO_2^aO_6^e$
orbitals involved in σ -bonding (Γ_σ)	$A_{1g}(s)$ $E_g(x^2 - y^2, z^2)$ $T_{1u}(\phi)$	$2A_{1g}(s, z^2)$ $B_{1g}(x^2 - y^2)$ $A_{2u}(z^3)$ $E_u[x(x^2 - 3y^2, y(3x^2 - y^2)]$	$2A_{1g}(s, z^2)$ $B_{1g}(x^2 - y^2)$ $A_{2u}(z^3)$ $E_u(x(x^2 - 3y^2, y(3x^2 - y^2))$	$2A_{1g}(s, z^2)$ $E_1'(x(x^2 - 3y^2, y(3x^2 - y^2))$ $E_2'(x^2 - y^2, xy)$ $A_2''(z^3)$	$2A_{1g}(s, z^2)$ $E_{2g}(x^2 - y^2, xy)$ $A_{2u}(z^3)$ $B_{1u}[x(x^2 - 3y^2)]$ $E_{1u}(xz^2, yz^2)$ $E_{1g}(xz, yz)$ $E_{1u}(\text{used for } \sigma)$
orbitals involved in π -bonding (Γ_π)	T_{1g} $T_{2g}(xy, xz, yz)$ T_{1u} (used for σ) $T_{2u}(\phi)$	A_{2g} $B_{2g}(xy)$ $E_g(xz, yz)$ $A_{2u}(\text{used for } \sigma)$ $B_{2u}(x^2 - y^2)$ $E_u(xz^2, yz^2)$	$E_g(xz, yz)$ $E_u(xz^2, yz^2)$	$E_1'(xz^2, yz^2)$ $E_1''(xz, yz)$	$E_1'(xz^2, yz^2)$ $E_1''(xz, yz)$
oxygen atoms involved in π -bonding	6(all)	4(equatorial)	2(axial)	2(axial)	2(axial)
average π -bond order per oxygen atom	$6/6 = 1$	$3/4 \pi \parallel$ $3/4 \pi \perp$	$4/2 = 2$	$4/2 = 2$	$2/2 = 1$
total bond order for π -bonded oxygen atoms	2	$2^{1/2}$ $6/4 = 3/2 \pi \text{ (total)}$	3	3	2

Group Theory and Bonding

The group-theoretical treatment of the covalent bonding in uranium–oxygen derivatives supplements the d^5f^7 manifold used in the previous paper² with the 7s orbital, leading to a 13-orbital sd^5f^7 manifold. With the exception of the pentagonal bipyramidal, the uranium coordination polyhedra found in uranium oxide structures, namely, the octahedron and hexagonal bipyramidal, are centrosymmetric. For this reason the 12-orbital sd^5f^6 and 10-orbital sd^4f^5 submanifolds are used in which the number of gerade s and d orbitals equals the number of ungerade f orbitals.^{2,10,11} Table 1 summarizes the uranium orbitals from the sd^5f^7 manifold for the following uranium coordination polyhedra that are available for σ - and π -bonding based on symmetry considerations:

(1) O_h Regular UO_6 Octahedron Found in Some Cation-Rich Uranates Such as Li_6UO_6 and the Perovskite-like Ca_3UO_6 . If the U–O π -bonding in a regular octahedron is distributed equally to all six oxygen atoms, then each uranium–oxygen bond is a double $1\sigma + 1\pi$ bond. This leads to a total of 12 bonds from the central uranium atom to the six oxygen atoms, thereby using a 12-orbital sd^5f^6 submanifold.

(2) D_{4h} Elongated “Reverse Uranyl” $UO_4^aO_{2/2}^a$ Octahedron Found in Ca_2UO_5 and Na_4UO_5 . In the “reverse uranyl” octahedron the two axial U–O bonds are longer than the four equatorial U–O bonds. Distribution of the U–O π -bonding to the shorter equatorial uranium–oxygen bonds leads to an average bond order of $2^{1/2}$ (i.e., $1\sigma + 3/2\pi$) for these bonds. This corresponds again to a total of $(4)(2^{1/2}) + (2)(1) = 12$ bonds from the central uranium atom to the six oxygen atoms and a 12-orbital sd^5f^6 submanifold.

(3) D_{4h} Flattened “Uranyl” $UO_2^aO_{4/2}^e$ Octahedron Found in Tetraoxouranates of the Type $M''UO_4$ and $M_2^I UO_4$. Distribution of the U–O π -bonding to the two axial uranium–oxygen bonds leads to the maximum $\sigma + \pi$ bond order of 3 ($=1\sigma + 2\pi$) and accounts for the relatively short axial uranium–oxygen distances in such derivatives. The central uranium atom forms a total of $(2)(3) + (4)(1) = 10$ bonds, corresponding to a 10-orbital sd^4f^5 manifold.

(4) D_{5h} Pentagonal Bipyramid $UO_2^aO_5^e$. This is the most prevalent coordination polyhedron in uranyl complexes other than those containing small bidentate

ligands such as nitrate and peroxide or π -bonding ligands such as halides.¹² Such pentagonal bipyramidal coordination is rare in infinite solid uranate structures apparently because an equatorial plane cannot be tiled exclusively with regular pentagons (see below). A pentagonal bipyramidally coordinated central uranium atom having triple bonds to the two axial oxygens and single bonds to the five equatorial oxygens uses a total of $(2)(3) + (5)(1) = 11$ orbitals, corresponding to an sd^5f^5 manifold.

(5) D_{6h} Hexagonal Bipyramid $UO_2^aO_6^e$ (or $UO_2^aO_{6/3}^e$) in Uranate Structures Such as $CaUO_4$. Note from Table 1 that appropriate orbitals are not available from an sd^5f^7 manifold to form triple bonds to both axial oxygen atoms and single bonds to all six equatorial oxygen atoms. Thus, the two E_{2u} f $\{xyz, z(x^2 - y^2)\}$ orbitals and the B_{2u} f $\{y(3x^2 - y^2)\}$ orbital^{13,14} are of unsuitable symmetries for σ -bonding or π -bonding to axial ligands, thereby leaving only a 10-orbital manifold available, corresponding to an average axial uranium–oxygen bond order of 2 ($=1\sigma + 1\pi$). In terms of group theory this corresponds to the need for E_{1u} orbital pairs both for equatorial σ -bonding and axial π -bonding but the availability for only one such orbital pair, namely, the f $\{xz^2, yz^2\}$ orbitals, in the sd^5f^7 13-orbital manifold. However, axial uranium–oxygen triple bonding in covalent hexagonal pyramid 2+6-coordinate uranyl derivatives becomes possible by symmetry if the relatively high energy E_{1u} 7p $\{x, y\}$ orbitals become available for π -bonding.

These group theoretical predictions of uranium–oxygen bond orders in uranates are in approximate agreement both with experimentally observed uranium–oxygen bond distances as summarized in Table 2 and quasirelativistic pseudopotential Gaussian 90 computations by Pykkö and Zhao.¹⁵ In this connection the following should be noted:

(1) Uranium–oxygen distances of ≈ 1.7 Å (e.g., uranyl complexes), ≈ 2.1 Å (e.g., Ca_3UO_6 and Li_6UO_6), and ≈ 2.2 Å (e.g., equatorial U–O bonds in uranates with short axial U–O bonds) can be taken as representative of triple, double, and single bonds, respectively.

(2) The lengthening of the short axial uranium–oxygen bond from ≈ 1.7 Å in uranyl complexes to ≈ 1.9 Å in the tetraoxouranates may be viewed as a consequence of the coordination of the axial oxygens to the

Table 2. Some Uranium(VI)–Oxygen Bond Distances

compound	uranium coordination ^a	axial	equatorial	literature reference
(A) Uranyl Complexes				
$\text{UO}_2\text{Cl}_2(\text{Ph}_3\text{PO})_2$	2 + 4	1.76		6
$[\text{UO}_2(\text{O}_2\text{C}_2\text{H}_4\text{CO}_2)\cdot\text{H}_2\text{O}]_n$	2 + 5	1.70		6
$\text{UO}_2(\text{NO}_3)_2(\text{Ph}_3\text{PO})_2$	2 + 6	1.76		6
(B) Tetraoxouranates				
BaUO_4	2 + 4	1.87	2.20, 2.23	15
$\beta\text{-SrUO}_4$	2 + 4	1.89	2.19, 2.21	16
MgUO_4	2 + 4	1.92	2.18	14
PbUO_4	2 + 4	1.85	2.18, 2.20	17
CuUO_4	2 + 4	1.90	2.15, 2.24	20
$\alpha\text{-Na}_2\text{UO}_4$	2 + 4	1.90	2.19	
$\beta\text{-Na}_2\text{UO}_4$	2 + 4	1.91	2.18	22
Li_2UO_4	2 + 4	1.92, 1.97	2.19	23
$\beta\text{-UO}_2(\text{OH})_2$	2 + 4	1.82	2.24, 2.43	25, 26
$\alpha\text{-UO}_2(\text{OH})_2$	2 + 6	1.71	2.46, 2.51	24
$\alpha\text{-SrUO}_4$	2 + 6	2.07	2.30	
CaUO_4	2 + 6	1.96	2.30	18
(C) Cation-Poor Structures				
$\text{K}_2\text{U}_2\text{O}_7$	2 + 6	1.86	1.93–2.34	35
$\text{Na}_2\text{U}_2\text{O}_7$	2 + 6	1.87	2.28	34
$\text{K}_9\text{U}_6\text{O}_{22.5}$	2 + 4	1.69	2.18	42
(D) Cation-Rich Structures				
Sr_2UO_5	U(1): 2 + 4	2.22	2.01	18
Sr_2UO_5	U(2): 2 + 4	1.97	2.12, 2.19	18
Ca_2UO_5	U(1): 2 + 4	2.25	2.01, 2.03	18
Ca_2UO_5	U(2): 2 + 4	1.95	2.13, 2.21	18
$\text{PbO}\cdot\text{Pb}_2\text{UO}_5$	2 + 4	2.17, 2.21	1.99, 2.04, 2.05, 2.06	39, 40
Na_4UO_5	2 + 4	2.32	1.99	38
Li_4UO_5	2 + 4	2.23	1.99	38
Ca_3UO_6	6		2.08	41
$\alpha\text{-Li}_6\text{UO}_6$	6		2.09	43
$\text{K}_2\text{Li}_4\text{UO}_6$	6		2.07	44

^a *a* + *e* in this column means *a* axial atoms and *e* equatorial atoms.

positive counterions of the tetraoxouranates. This requires some of the electron density in the two perpendicular *p* components of the axial uranium–oxygen multiple bonds, thereby reducing the apparent bond order and lengthening the bond.

(3) The ≈ 2.0 Å equatorial uranium–oxygen distances in the elongated octahedral uranates having $\text{UO}_4^{\text{a}}\text{O}_{2/2}^{\text{a}}$ structural units predicted by group theory to correspond to bonds of order $2^{1/2}$ are shorter than the ≈ 2.1 Å uranium–oxygen distances in Ca_3UO_6 and $\alpha\text{-Li}_6\text{UO}_6$ predicted to correspond to double bonds but not as short as the axial bonds in $\text{UO}_2^{\text{a}}\text{O}_{4/2}^{\text{e}}$ and $\text{UO}_2^{\text{a}}\text{O}_{6/3}^{\text{e}}$ units interpreted as triple bonds (before reduction in bond order by oxygen coordination to the positive counterion as noted above).

(4) This group-theoretical approach to uranium–oxygen bond order is not unrelated to classical approaches of Zachariasen¹⁶ and Zachariasen and Penneman¹⁷ using correlations between bond length and bond strength. However, these earlier methods, while of unquestionable pragmatic value, are difficult to relate directly to group theory and properties of atomic and molecular orbitals.

Geometry and Coordination Number

The uranium oxide and uranate structures do not consist of discrete molecules but are infinite in all three dimensions. The uranium–oxygen subnetworks of the uranates may consist of infinite chains (Figure 1) or infinite layers (Figure 2). The infinite layers are of two fundamental types, tetragonal and hexagonal. In an

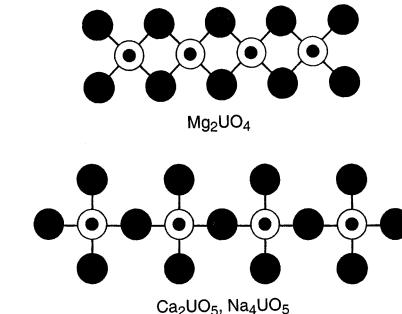


Figure 1. Schematic representations of flattened octahedral $\text{UO}_2^{\text{a}}\text{O}_{4/2}^{\text{c}}$ (e.g., Mg_2UO_4) and elongated octahedral "reverse uranyl" $\text{UO}_4^{\text{a}}\text{O}_{2/2}^{\text{a}}$ (e.g., Ca_2UO_5 and Na_4UO_5) infinite chain structures.

ideal tetragonal layer, the plane is tiled into $\text{UO}_{4/2}$ squares with each square vertex corresponding to an oxygen atom shared by two uranium atoms. Each uranium atom has octahedral coordination after counting the two axial uranyl oxygen atoms. There are empty spaces between the $\text{UO}_{4/2}$ squares that can accommodate the positive counterions (e.g., alkali or alkaline earth metals). In an ideal hexagonal layer, the plane is tiled into $\text{UO}_{6/3}$ hexagons with each hexagon vertex corresponding to an oxygen atom shared by three uranium atoms. Each uranium atom has hexagonal bipyramidal coordination after counting the two axial uranyl oxygen atoms. There are no empty spaces between the $\text{UO}_{6/3}$ hexagons so that the positive counterions must be located between the $\text{UO}_{6/3}$ layers. Frequently, the $\text{UO}_{6/3}$ hexagons in hexagonal layers are buckled with oxygen

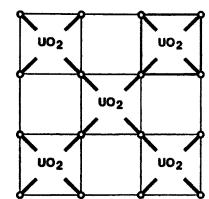
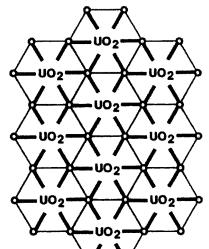
Tetragonal $\text{UO}_2^a\text{O}_{4/2}^4$ Hexagonal $\text{UO}_2^a\text{O}_{6/3}^6$

Figure 2. Schematic representations of tetragonal $\text{UO}_2^a\text{O}_{4/2}^4$ and hexagonal $\text{UO}_2^a\text{O}_{6/3}^6$ infinite layer structures.

atoms alternately above and below the mean plane so that such layers are not strictly planar.

The pentagonal bipyramid is the most prevalent uranium(VI) coordination polyhedron in discrete molecules and ions. However, because regular pentagons cannot exclusively tile a plane, infinite layers cannot simply be constructed from pentagonal bipyramidal uranium atoms. Nevertheless, the hexagonal layers can be converted to layers containing pentagons and triangles by removing $1/6$ of the equatorial oxygen atoms (the right oxygen atom of each pair of doubly circled oxygen atoms in Figure 3). This generates the “arrowhead” chains discussed by Miller, Finch, Burns, and Ewing.⁹ If the initial hexagonal layers are the $\text{UO}_{2/2}^a\text{O}_{6/3}^6$ units of “ideal” $\alpha\text{-UO}_3$, this process of removing $1/6$ of the oxygen atoms corresponds to deoxygenation of $\alpha\text{-UO}_3$ to $\alpha\text{-U}_3\text{O}_8$. In such a process each of the uranium atoms corresponds to the center of a pentagon in Figure 3 so that all of the uranium atoms in $\alpha\text{-U}_3\text{O}_8$ have pentagonal bipyramidal coordination (i.e., $\alpha\text{-U}_3\text{O}_8 = \text{UO}_{2/2}^a\text{O}_{5/3}^6$). A more complicated way of removing $1/6$ of the equatorial oxygen from $\alpha\text{-UO}_3$ by replacing each pair of double circled oxygen atoms by a single oxygen atom equidistant between their locations (Figure 3) leads to a more complicated layer structure consisting of pentagons, rectangles, and triangles having twice the number of pentagons as rectangles. Placing uranium atoms in the centers of the pentagons and rectangles leads to the structure of $\beta\text{-U}_3\text{O}_8$ in which $1/3$ of the uranium atoms have D_{2h} distorted octahedral coordination and the other $2/3$ of the uranium atoms have D_{5h} pentagonal bipyramidal coordination. Such layers containing both pentagons and quadrilaterals (e.g., Figure 3) may be characterized by the ratio p/q , where p is the number of pentagons and q is the number of quadrilaterals. Thus, $p/q = \infty$ and 2, respectively, for the structures of α - and $\beta\text{-U}_3\text{O}_8$ depicted in Figure 3.

An important question in uranate structural chemistry is the relationship between the coordination numbers of the uranium atoms, the positive counterions, and the oxygen atoms. Thus, the sum of the oxygen coordination numbers must equal the sum of the metal

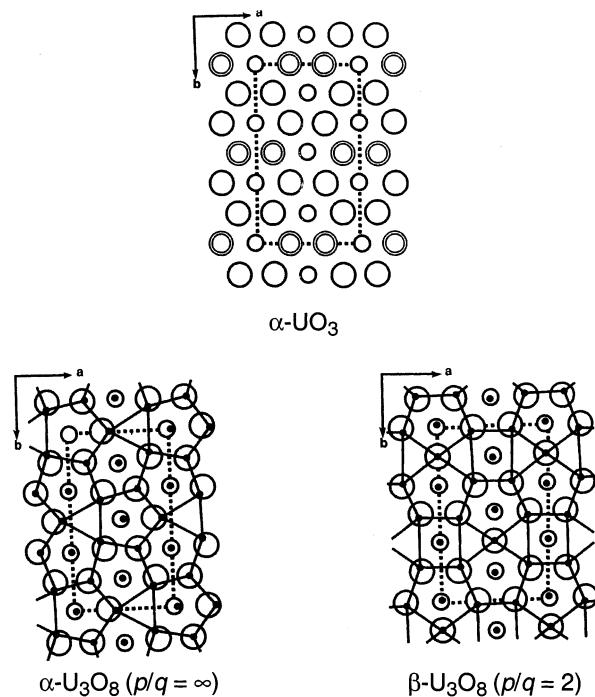


Figure 3. Relation of the hexagonal “ideal” $\alpha\text{-UO}_3$ lattice to the lattices of $\alpha\text{-U}_3\text{O}_8$ in which all of the uranium atoms are pentagonal bipyramidal ($p/q = \infty$) and $\beta\text{-U}_3\text{O}_8$ having both pentagonal bipyramidal and octahedral uranium atoms and a p/q ratio of 2.

coordination numbers of any metal oxide structure. Table 3 illustrates this calculation for the uranium oxide and uranate structures discussed in this paper.

The limitation of oxygen covalent bonding to the four-orbital sp^3 manifold suggests a maximum oxygen coordination number of four using normal two-center U–O and M–O covalent bonds. However, for cation-rich structures containing monovalent cations such as Na_4UO_5 and Li_6UO_6 , four-coordinate oxygen atoms do not provide enough bonds from oxygen to the metal atoms to give the individual metal atoms reasonable coordination numbers. Thus, hypercoordinate oxygen atoms with apparent coordination numbers of five (in Li_6UO_6) or six (in Na_4UO_5) become necessary. Such hypercoordinate oxygen atoms in uranate structures may be regarded as similar to the central octahedrally coordinated μ_6 oxygen atom in $\text{M}_6\text{O}_{19}^{2-}$ ($\text{M} = \text{Mo, W}$) or $\text{M}_6\text{O}_{19}^{8-}$ ($\text{M} = \text{Nb, Ta}$), which may be viewed as an encapsulated O^{2-} ion rather than a covalently bonded oxygen atom.¹⁸

A key factor in determining structural features of uranates $\text{U}_x\text{O}_y^{Z-}$ is the formal negative charge per uranium atom of the uranium–oxygen subnetwork, designated as Z/X . A Z/X ratio of 2 corresponds to the tetraoxouranates $\text{M}_2^{\text{I}}\text{UO}_4$ and $\text{M}^{\text{II}}\text{UO}_4$, which have structures consisting of $\text{UO}_2\text{O}_{4/2}$ chains (Figure 1), $\text{UO}_2\text{O}_{4/2}$ layers (Figure 2), or $\text{UO}_2\text{O}_{6/3}$ layers (Figure 2). In these structures the cations are located in the interstices and bonded to various numbers of oxygen atoms as indicated in Table 3. Cation-poor uranates with Z/X ratios below 2 have structures either derived from layered structures of cation-free uranium oxides (e.g., $\text{Cs}_4\text{U}_5\text{O}_{17}$ or $\text{Cs}_2\text{U}_{15}\text{O}_{46}$) or defect structures derived from other ternary uranium oxides. Cation-rich uranates with Z/X ratios above 2 have either “reverse uranyl” $\text{UO}_4^{\text{a}}\text{O}_{2/2}^{\text{a}}$ chains (Figure 1) or discrete UO_6

Table 3. Balancing the Oxygen and Metal Coordination Numbers in Uranium(VI)–Oxygen Derivatives

compound	numbers of oxygen atoms with coord. numbers:						M–O bonds from oxygen atoms with coord. numbers:						metal coordination number(s)	M–O bonds to metal atoms		
	2	3	4	5	6		2	3	4	5	6	total		M	U	total
$\alpha\text{-UO}_3$	1	2	0	0	0		2	6	0	0	0	8		8	8	
$\beta\text{-UO}_3$	3	0	0	0	0		6	0	0	0	0	6		6	6	
$\alpha\text{-U}_3\text{O}_8$	3	5	0	0	0		6	15	0	0	0	21		21	21	
$\beta\text{-U}_3\text{O}_8$	4	4	0	0	0		8	12	0	0	0	20		20	20	
BaUO_4	0	3	1	0	0		0	9	4	0	0	13	7	7	6	13
MgUO_4	0	4	0	0	0		0	12	0	0	0	12	6	6	6	12
CaUO_4	0	0	4	0	0		0	0	16	0	0	16	8	8	8	16
CuUO_4	2	2	0	0	0		4	6	0	0	0	10	4	4	6	10
Na_2UO_4	0	4	0	0	0		0	12	0	0	0	12	3	6	6	12
Li_2UO_4	1	2	1	0	0		2	6	4	0	0	12	2, 4	6	6	12
Sr_2UO_5	0	0	5	0	0		0	0	20	0	0	20	7	14	6	20
$2(\text{PbO}\cdot\text{Pb}_2\text{UO}_5)$	0	3	9	0	0		0	9	36	0	0	45	5, 6	33	12	45
Na_4UO_5	0	0	0	0	5		0	0	0	30	30	6	24	6	30	
Ca_3UO_6	0	0	6	0	0		0	0	24	0	0	24	6	18	6	24
Li_6UO_6	0	0	0	6	0		0	0	30	0	30	4	24	6	30	

octahedra in which all six U–O bonds have the same lengths.

Tetraoxouranates with $Z\cdot X = 2$

The structures of all tetraoxouranates contain flattened uranium octahedra of the type $\text{UO}_2\text{O}_{4/2}^e$ or uranium hexagonal bipyramids of the type $\text{UO}_2\text{O}_{6/3}^e$. In these structures there are two short axial “primary” uranium–oxygen bonds and four or six long equatorial “secondary” uranium–oxygen bonds shared with a total of two or three uranium atoms, respectively. The short axial uranium–oxygen bonds in tetraoxouranates have lengths of 1.87–1.98 Å (Table 2) and are thus significantly longer than the 1.70–1.76 Å axial uranium–oxygen bonds in discrete uranyl complexes. This considerable lengthening of the axial uranium–oxygen bonds in going from discrete uranyl complexes to tetraoxouranates may be related to the bonding of the uranyl oxygen atoms in tetraoxouranates to the positive counterions in accordance with the ideas of Zachariassen.¹⁶ In addition, the longer axial uranium–oxygen bonds in tetraoxouranates relative to discrete uranyl complexes lead to a number of fundamental chemical differences as summarized by Chaikhorskii.¹⁹

Tetraoxouranates of bivalent metals have the stoichiometry $M^{\text{II}}\text{UO}_4$ and exhibit a variety of structures as follows:

(1) **MgUO₄**:²⁰ $\text{UO}_2\text{O}_{4/2}^e$ chains (Figure 1) with octahedrally coordinated Mg atoms bonded to six oxygen atoms belonging to four different chains.

(2) **BaUO₄**,²¹ $\alpha\text{-SrUO}_4$,²² and **PbUO₄**:²³ Tetragonal $\text{UO}_2\text{O}_{4/2}^e$ layers (Figure 2) with the divalent counterion (Ba, Sr, or Pb) unsymmetrically located in the square interstices so that it is coordinated to seven oxygen atoms in approximate capped trigonal prismatic coordination.

(3) **CaUO₄**²⁴ and **$\beta\text{-SrUO}_4$** :^{25,26} Hexagonal $\text{UO}_2\text{O}_{6/3}^e$ layers (Figure 2) in which the divalent counterion (Ca or Sr), like the uranium atom, is eight-coordinate with puckered hexagonal antiprismatic coordination, being bonded to six uranyl (axial) oxygen atoms and two equatorial oxygen atoms. This structure may be considered to be a distorted version of the fluorite (CaF_2) structure because in CaUO_4 and $\beta\text{-SrUO}_4$ all of the cations (U and Ca or Sr) are eight-coordinate and all of the anions (O) are four-coordinate.

(4) **CuUO₄**:²⁷ Tetragonal $\text{UO}_2\text{O}_{4/2}^e$ units (Figure 2) in which the copper atom is bonded to four oxygen atoms ($\text{Cu}–\text{O} = 1.95\text{--}1.96$ Å) in approximate square planar coordination. There are two much longer (2.59 Å) Cu–O distances to each copper atom (not considered in Table 3), suggestive of the expected extreme Jahn–Teller distortion²⁸ of a Cu_6 octahedron for d^9 Cu(II).

These diverse structures for $M^{\text{II}}\text{UO}_4$ tetraoxouranates noted above are undoubtedly related to the diverse coordination preferences of the divalent counterion, particularly the square planar coordination of d^9 Cu(II), the octahedral coordination of Mg, and the higher coordination numbers (>6) of the heavier alkaline earths and lead.

Tetraoxouranates of univalent metals, such as the alkali metals, have the stoichiometry $M_2\text{UO}_4$. Because there are twice as many positive counterions per UO_4 unit as in the bivalent metal tetraoxouranates $M^{\text{II}}\text{UO}_4$, the counterion coordination numbers in the monovalent metal tetraoxouranates, $M_2\text{UO}_4$, must be considerably lower. In both α - and $\beta\text{-Na}_2\text{UO}_4$ the uranium–oxygen subnetwork consists of $\text{UO}_2\text{O}_{4/2}^e$ layers,^{29,30} which, however, unlike those in BaUO_4 ²¹ are no longer rigorously planar. The sodium counterions may be interpreted as three-coordinate (Na–O distances ranging from 2.33 to 2.46 Å for $\alpha\text{-Na}_2\text{UO}_4$ and from 2.29 to 2.41 Å for $\beta\text{-Na}_2\text{UO}_4$). However, with four longer Na–O distances in $\alpha\text{-Na}_2\text{UO}_4$ (2.51–2.72 Å) and three longer Na–O distances in $\beta\text{-Na}_2\text{UO}_4$ (2.53–2.88 Å), not considered in Table 3, the sodium coordination numbers increase to seven and six, respectively. The Li_2UO_4 structure³¹ is less symmetrical than that of Na_2UO_4 because the two short axial uranium–oxygen distances are different (1.92 and 1.97 Å) and there are two different types of lithium atoms. One type of lithium atom (Li(2) in ref 22) is tetrahedrally coordinated to four oxygen atoms ($\text{Li}–\text{O} = 1.93$ Å) and the other type of lithium atom (Li(1) in ref 22) is linearly bonded to two oxygen atoms ($\text{Li}–\text{O} = 2.06$ Å). However, the linear lithium atom (Li(1)) has four oxygen atoms situated at longer distances (2.21 and 2.29 Å) not considered in Table 3. These additional oxygen atoms increase the coordination of Li(1) to that of an octahedron, which necessarily must involve some type of multicenter bonding because lithium does not have accessible d orbitals for the usual sp^3d^2 octahedral hybridization.²⁰

Table 4. Layered Uranium Oxide Structures Containing Pentagonal Bipyramidal Uranium Atoms

<i>p/q</i>	compound	layer formula and structure ^a	layer O ^a /U	interstitial ions
∞	$\alpha\text{-U}_3\text{O}_8$	$3\text{U}^p\text{O}_{2/2}^a\text{O}_{5/3}^e = \text{U}_3\text{O}_8$	1.67	none
4	$\text{Cs}_2\text{U}_{15}\text{O}_{46}$	$8\text{U}^p\text{O}_{2/2}^a\text{O}_{5/3}^e + 2\text{U}^q\text{O}_{2/2}^a\text{O}_{4/3}^e = \text{U}_{10}\text{O}_{36}^{12-}$	1.60	$2\text{Cs}^+ + 5\text{UO}_2^{2+}$
4	$\text{Cs}_2\text{U}_7\text{O}_{22}$	$4\text{U}^p\text{O}_{2/2}^a\text{O}_{5/3}^e + \text{U}^q\text{O}_{2/2}^a\text{O}_{4/3}^e = \text{U}_5\text{O}_{18}^{6-}$	1.60	$2\text{Cs}^+ + 2\text{UO}_2^{2+}$
2	$\beta\text{-U}_3\text{O}_8$	$2\text{U}^p\text{O}_{2/2}^a\text{O}_{4/3}^e\text{O}_{1/2}^e + \text{U}^q\text{O}_{2/2}^a\text{O}_{4/3}^e = \text{U}_3\text{O}_8$	1.67	none
1	$\text{M}_2\text{U}_2\text{O}_7$	$\text{U}^p\text{O}_{2/2}^a\text{O}_{5/3}^e + \text{U}^q\text{O}_{2/2}^a\text{O}_{4/3}^e = \text{U}_2\text{O}_7^{2-}$	1.50	2M^+
$5/6$	$\text{M}_3\text{U}_{11}\text{O}_{36}$	$2\text{U}^p\text{O}_{2/2}^a\text{O}_{2/3}^e\text{O}_{3/2}^e + 2\text{U}^p\text{O}_{2/2}^a\text{O}_{4/3}^e\text{O}_{1/2}^e + \text{U}^p\text{O}_{2/2}^a\text{O}_{5/3}^e + 2\text{U}^q\text{O}_{2/2}^a\text{O}_{4/3}^e + 2\text{U}^q\text{O}_{2/2}^a\text{O}_{2/2}^e\text{O}_2^e = \text{U}_{11}\text{O}_{36}^{6-}$	1.27	6M^{2+}
$1/4$	$\text{Cs}_4\text{U}_5\text{O}_{17}$	$\text{U}^p\text{O}_{2/2}^a\text{O}_{5/3}^e + 4\text{U}^q\text{O}_{2/2}^a\text{O}_{4/3}^e = \text{U}_5\text{O}_{17}^{4-}$	1.40	4Cs^+

^a U^p = pentagonal bipyramidal uranium atom surrounded by a pentagon of five oxygen atoms in the equatorial plane; U^q = distorted octahedral uranium atom surrounded by a quadrilateral of four oxygen atoms in the equatorial plane.

The hypothetical parent acid of the tetraoxouranates, H_2UO_4 , is known as uranyl hydroxide, $\text{UO}_2(\text{OH})_2$, which exists in three different crystalline forms, the structures of which exemplify the layer structures (Figure 2) found in the tetraoxouranates. The structure³² of orthorhombic $\alpha\text{-UO}_2(\text{OH})_2$ of density 6.73 g/cm³ has hexagonal $\text{UO}_2^a(\text{OH})_{6/3}^e$ layers with $\text{O}^a\cdots\text{H}\cdots\text{O}^e$ hydrogen bonding ($\text{O}(1)\cdots\text{O}(2) = 2.88$ Å), involving uranyl oxygens of one layer and hydroxyl oxygens of another layer and leading to an ≈ 5 Å interlayer separation. The structure^{33,34} of the less dense (5.73 g/cm³) $\beta\text{-UO}_2(\text{OH})_2$ has tetragonal $\text{UO}_2^a(\text{OH})_{4/2}^e$ layers with $\text{O}^a\cdots\text{H}\cdots\text{O}^e$ hydrogen bonding ($\text{O}(1)\cdots\text{O}(2) = 2.88$ Å). The lower density of $\beta\text{-UO}_2^a(\text{OH})_{4/2}^e$ relative to $\alpha\text{-UO}_2^a(\text{OH})_{6/3}^e$ clearly relates to the larger empty spaces in the tetragonal $\text{UO}_2^a(\text{OH})_{4/2}^e$ layer structure relative to the hexagonal $\text{UO}_2^a(\text{OH})_{6/3}^e$ layer structure. The structure³⁵ of monoclinic $\gamma\text{-UO}_2(\text{OH})_2$ of density 5.56 g/cm³ is very similar to that of orthorhombic $\beta\text{-UO}_2(\text{OH})_2$ containing tetragonal $\text{UO}_2^a(\text{OH})_{4/2}^e$ layers and 2.77 Å $\text{O}^a\cdots\text{H}\cdots\text{O}^e$ hydrogen bonds. The structures of β - and $\gamma\text{-UO}_2(\text{OH})_2$ differ only by relatively subtle displacements of the hydrogen atoms.

Cation-Poor Structures with $Z/X < 2$

The ultimate cation-poor structures are the uranium oxides, UO_3 and U_3O_8 . Because no counterions need to be accommodated between the uranium–oxygen layers, the distance between layers is far less than that in layered uranate structures. For this reason the axial oxygen atoms in UO_3 and U_3O_8 are shared between two uranium atoms rather than bonded to a single uranium atom as in the uranates.

Uranium trioxide has two major modifications: $\alpha\text{-UO}_3$ with hexagonal equatorial layers and octacoordinate uranium^{36,37} and cubic $\beta\text{-UO}_3$ with tetragonal equatorial layers and hexacoordinate uranium,³⁸ thereby providing examples of both types of uranium–oxygen layers depicted in Figure 2. Because all oxygen atoms in $\beta\text{-UO}_3$ ($=\text{UO}_{2/2}^a\text{O}_{4/2}^e$) are shared by two equivalent uranium atoms, the symmetry of $\beta\text{-UO}_3$ increases to cubic, leading to the ReO_3 structure.³⁶

Deoxygenation of the ideal $\alpha\text{-UO}_3$ structure in two different ways leads to the structures of both forms of U_3O_8 (Figure 3). In $\alpha\text{-U}_3\text{O}_8$ all of the uranium atoms have pentagonal equatorial planes. In $\beta\text{-U}_3\text{O}_8$ $1/3$ of the uranium atoms have rectangular equatorial planes and the other $2/3$ of the uranium atoms have pentagonal equatorial planes. A more precise neutron and electron diffraction study³⁹ on $\alpha\text{-UO}_3$ suggested a more complicated structure based on $\alpha\text{-U}_3\text{O}_8$ ($=\text{UO}_{2/2}^a\text{O}_{5/3}^e$) with disordered uranium vacancies, leading to the UO_3 stoichiometry rather than an ordered structure with $\text{UO}_{6/3}$ equatorial planes as noted above (e.g., Figure 3).

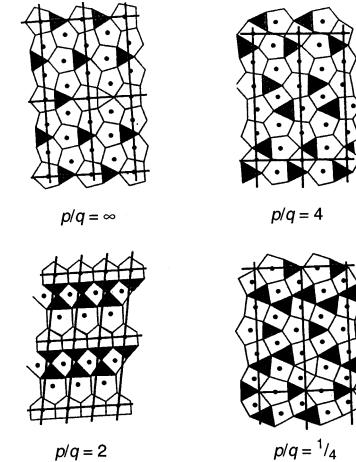
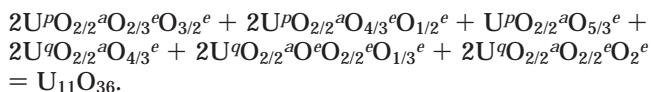


Figure 4. Layers consisting of pentagons and/or quadrilaterals found in uranium oxides and cation-poor uranates with their *p/q* ratios.

Layer structures similar to those in the uranium oxide structures are found in cation-poor alkali metal uranates^{6,40} such as $\text{Cs}_2\text{U}_{15}\text{O}_{46}$, $\text{Cs}_2\text{U}_7\text{O}_{22}$, and $\text{Cs}_4\text{U}_5\text{O}_{17}$ and bivalent metal uranates such as $\text{M}_3\text{U}_{11}\text{O}_{36}$ ($\text{M} = \text{Sr}^{41}$ and Pb^{42}), as summarized in Table 4. Because the spacing between the layers must be large enough to accommodate interlayer alkali metal and sometimes uranyl ions coordinated to appropriate numbers of oxygen atoms, the axial oxygen atoms are now bonded to only a single-layer uranium atom. The equatorial planes in such structures may contain pentagons and/or quadrilaterals of equatorial oxygen atoms (Figure 4) and are characterized by their *p/q* ratios as noted above.

A single-crystal X-ray diffraction study⁴³ on the cation-poor derivative $\text{Li}_2\text{U}_3\text{O}_{10}$ ($Z/X = 2/3$) indicates infinite chains of pentagonal bipyramidal units of the type $\text{UO}_2^a\text{O}^e\text{O}_{4/2}^e$ with infinite chains of uranium octahedra in a diagonal direction with a *p/q* ratio of $1/2$. This leads to overall anionic stoichiometry $\text{U}^q\text{O}_{2/2}^a\text{O}_{4/3}^e + \text{U}^q\text{O}_{1/2}^a\text{O}_{4/3}^e + \text{U}^p\text{O}_{2/2}^a\text{O}_{4/3}^e\text{O}_{1/2}^e = \text{U}_3\text{O}_{10}$ using the designations in Table 4.³³ The equatorial quadrilaterals of the uranium octahedra are not coplanar with the equatorial pentagons of the uranium pentagonal bipyramids because the unique equatorial oxygen of the pentagonal bipyramids is an axial oxygen of an octahedron.

The cation-poor uranates of divalent metals $\text{M}_3\text{U}_{11}\text{O}_{36}$ ($\text{M} = \text{Sr}^{41}$ Pb^{42} $Z/X = 6/11$) exhibit more complicated structures with uranium in both octahedral and pentagonal bipyramidal environments and a *p/q* ratio of $5/6$. There are six different types of uranium atoms in the ratio $2/2/1/2/2/2$ having coordination numbers of $7/7/7/6/6/6$, respectively. The anion stoichiometry arises from



The cation-poor ($Z/X = 1$) alkali metal diuranates $M_2U_2O_7$ exhibit several types of structures. The X-ray powder patterns for $M_2U_2O_7$ ($M = Na$,⁴⁴ K ,⁴⁵ Rb)⁴⁶ were originally interpreted to indicate a $CaUO_4$ -type of structure with $1/4$ of the oxygen atoms missing in the equatorial plane, leading to the $UO_2^aO_{4.5/3}^e = U_2O_7$ stoichiometry of the anion and a theoretical p/q ratio of 1 (Table 4). However, a subsequent single-crystal X-ray diffraction study by Gasperin⁴⁷ on a fortuitously obtained $Na_2U_2O_7$ crystal from a $UO_2/Nb_2O_5/Na_2CO_3$ melt showed that the oxygen vacancies were located in the axial (uranyl) sites rather than the equatorial sites so that the uranium–oxygen network in $Na_2U_2O_7$ is $UO_{1.5}^aO_{6/3}^e = U_2O_7$. A single-crystal X-ray diffraction study on the monoclinic form of potassium diuranate, $K_2U_2O_7$,⁴⁸ indicated a different structure from its sodium analogue with octahedral rather than hexagonal (bi)pyramidal coordination of the uranium. The anion unit is $UO_2^aO_{3/3}^eO_{1/2}^e$ corresponding to U_2O_7 . Similar structures were inferred from X-ray and neutron diffraction powder studies⁴⁹ for both monoclinic forms of $Cs_2U_2O_7$.

Cation-Rich Structures with $Z/X > 2$

The cation-rich uranates $M_2^{II}UO_5$ ($M = Ca, Sr$)²⁴ and M_4UO_5 ($M = Li, Na$)^{50,51} contain infinite chains of elongated $UO_4^eO_{2/2}^a$ “reverse uranyl” octahedra (Figure 1). In the alkaline earth derivatives M_2UO_5 the oxygen atoms are all four-coordinate, leading to seven-coordination for the alkaline earth counterions (Table 3). In the tetragonal alkali metal derivative⁵⁰ M_4UO_5 all metal and oxygen atoms are six-coordinate so that this structure may be derived from the familiar cubic $NaCl$ structure by elongating the uranium octahedron in one direction to give the $UO_4^eO_{2/2}^a$ “reverse uranyl” structural units. The orthorhombic lead uranate of stoichiometry Pb_3UO_6 also contains chains of elongated $UO_4^eO_{2/2}^a$ octahedra^{52,53} and is more accurately represented as $PbO \cdot Pb_2UO_5$. Two of the eight types of oxygen atoms in the structure of $PbO \cdot Pb_2UO_5$ are bonded only to lead atoms. Although the uranium–oxygen subnetwork in $PbO \cdot Pb_2UO_5$ consists of typical $UO_4^eO_{2/2}^a$ chains, the overall structure is very complicated, containing five different types of lead atoms in relative quantities 1/1/1/1/2 having coordination numbers of 5/6/6/6/5, respectively, counting Pb–O distances of 2.91 Å or less as bonding and Pb–O distances 3.14 Å or greater as nonbonding. The oxygen lead ratio in $PbO \cdot Pb_2UO_5$ is 2/1 and the details of the lead–oxygen subnetwork may be summarized as $Pb^{(1)}O_{1/4}^{(3)}O_{2/2}^{(7)}O_{2/3}^{(8)} + Pb^{(2)}O_{1/2}^{(2)}O_{1/4}^{(4)}O_{4/3}^{(6)} + Pb^{(3)}O_{1/2}^{(2)}O_{1/4}^{(4)}O_{2/3}^{(5)}O_{2/3}^{(6)} + Pb^{(4)}O_{1/1}^{(1)}O_{1/4}^{(3)}O_{2/3}^{(5)}O_{2/3}^{(8)} + 2Pb^{(5)}O_{1/4}^{(3)}O_{1/4}^{(4)}O_{1/3}^{(5)}O_{1/3}^{(6)}O_{1/2}^{(7)} = PbO_{23/12} + PbO_{25/12} + PbO_{25/12} + PbO_{31/12} + Pb_2O_{40/12} = Pb_6O_{12}$ in which O(1) and O(7) are bonded to three metal atoms (counting both lead and uranium); O(2), O(3), O(4), O(5), O(6), and O(8) are bonded to four metal atoms (lead in all cases and uranium in the cases of O(2), O(5), O(6), and O(8)); and the atom numbering in the original papers^{52,53} is used.

A cation-rich strontium uranate of stoichiometry $Sr_5U_3O_{14} = SrUO_4 \cdot 2Sr_2UO_5$ ($Z/X = 10/3$) is known containing both regular uranyl and “reverse uranyl”

octahedra in the same structure.⁵⁴ The single regular uranyl uranium atom (U(1) in ref 54) has $U^qO_2^aO_{4/2}^e$ coordination whereas the two “reverse uranyl” uranium atoms (U(2) in ref 54) have $U^qO_2^aO_2^eO_{2/2}^e$ coordination, leading to the observed stoichiometry. The two types of uranium atoms in this structure are readily recognized by the different axial U–O distances.

Cation-rich uranate structures are also known in which the UO_6 octahedra are essentially regular and do not share their oxygen atoms with other uranium atoms. The alkaline earth derivatives Ca_3UO_6 ⁵⁵ and Sr_3UO_6 ⁵⁶ have rhombohedral perovskite structures represented as $M_2(MU)O_6$ ($M = Ca, Sr$) in which all metal atoms are six-coordinate and all oxygen atoms are four-coordinate. A much more complicated perovskite-derived structure is found in the slightly cation-poor ($Z/X = 1.5$) alkali metal uranate of stoichiometry⁵⁷ $K_9U_6O_{22.5}$ derived from a hypothetical $K_{10}U_6O_{24}$ perovskite in which the uranium octahedra are flattened and there are partial occupancies of both potassium and oxygen sites.

Cation-rich alkali metal uranates with $Z/X = 6$ of the general formula $M^I_6UO_6$ are known only when all or a substantial amount of the alkali metal is lithium⁶ apparently because of the necessarily low average coordination number of the alkali metal counterion relative to the oxygen atoms in view of the O/M^I ratio of only 1. A single-crystal X-ray study⁵⁸ of Li_6UO_6 indicates regular octahedral coordination of the uranium (U–O = 2.09 Å), tetrahedral coordination of the lithium (Li–O = 1.94–2.02 Å), and five-coordinate oxygen atoms. A single-crystal study⁵⁹ of $K_2Li_4UO_6$ also indicates regular octahedral uranium coordination (U–O = 2.07 Å) and rather unusual coordination of the alkali metal counterions. Thus, $3/4$ of the lithium atoms have square planar coordination (Li–O = 2.15 Å) and $1/4$ of the lithium atoms have octahedral coordination (Li–O = 2.30 Å) with the rather long Li–O distances indicating fractional bond orders. The coordination polyhedron of the potassium atoms is even harder to define. There is a clearly defined KO_{12} polyhedron with the topology of a cuboctahedron. However, the 12 potassium–oxygen distances forming this distorted cuboctahedron vary so widely (i.e., 3K–O = 2.87 Å, 6K–O = 3.21 Å, 3K–O = 3.65 Å, preserving a C_3 axis) that their bond orders are obscure. It is probably much more realistic to consider ionic formulations $[M^+]_2 [Li_4UO_6^{2-}]$ for these $M_2Li_4UO_6$ ($M^I = K, Rb, Cs$) derivatives in view of the highly ionic character of almost all derivatives of the heavier alkali metals.

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