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THE CRYSTAL CHEMISTRY OF HEXAVALENT URANIUM: POLYHEDRON GEOMETRIES, BOND-VALENCE PARAMETERS, AND POLYMERIZATION OF POLYHEDRA

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ABSTRACT

The geometry, bond valences, and polymerization of hexavalent uranium polyhedra from 105 well-refined structures are analyzed. The U^{6+} cation is almost always present in crystal structures as part of a nearly linear $(\text{UO}_2)^{2+}$ uranyl ion that is coordinated by four, five or six equatorial anions in an approximately planar arrangement perpendicular to the uranyl ion, giving square, pentagonal and hexagonal bipyramids, respectively. The $\text{U}^{6+}\text{–O}_{Ur}$ bond length (O_{Ur}: uranyl-ion O atom) is independent of the equatorial anions of the polyhedra; averages of all polyhedra that contain uranyl ions are: $^{[6]}\text{U}^{6+}\text{–O}_{Ur} = 1.79(3)$, $^{[7]}\text{U}^{6+}\text{–O}_{Ur} = 1.79(4)$, and $^{[8]}\text{U}^{6+}\text{–O}_{Ur} = 1.78(3)$ Å. Not all $^{[6]}\text{U}^{6+}$ polyhedra contain uranyl ions; there is a continuous series of coordination polyhedra, from square bipyramidal polyhedra with uranyl ions to holosymmetric octahedral geometry. The $^{[7]}\text{U}^{6+}$ and $^{[8]}\text{U}^{6+}$ polyhedra invariably contain a uranyl ion. The equatorial $\text{U}^{6+}\text{–}\phi$ (ϕ: O^{2-}, OH^-) bond-lengths of uranyl polyhedra depend upon coordination number; averages for all polyhedra are $^{[6]}\text{U}^{6+}\text{–}\phi_{\text{eq}} = 2.28(5)$, $^{[7]}\text{U}^{6+}\text{–}\phi_{\text{eq}} = 2.37(9)$, and $^{[8]}\text{U}^{6+}\text{–}\phi_{\text{eq}} = 2.47(12)$ Å. Currently available bond-valence parameters for U^{6+} are unsatisfactory for determining bond-valence sums. Coordination-specific bond-valence parameters have been derived for U^{6+}, together with parameters applicable to all coordination geometries. The parameters give bond-valence sums for U^{6+} of ~6 *vu* and reasonable bond-valences for $\text{U}^{6+}\text{–O}_{Ur}$ bonds. The bond-valence parameters facilitate the recognition of U^{4+}, U^{5+} and U^{6+} cations in refined crystal structures. The crystal-chemical constraints of polyhedral polymerization in uranyl phases are discussed.

Keywords: uranium, uranium mineral, uranyl, polyhedral geometry, bond valence.

SOMMAIRE

La géometrie, les valences de liaison, et le degré de polymérisation des polyèdres contenant l'uranium hexavalent dans 105 structures bien affinées sont ici analysés. Dans les structures cristallines, le cation U^{6+} fait presque toujours partie d'un ion uranyle, $(\text{UO}_2)^{2+}$, quasiment linéaire et coordonné à quatre, cinq ou six anions dans un agencement à peu près planaire perpendiculaire à l'ion uranyle, ce qui mène à des groupes carrés, pentagonaux et en bipyramides hexagonales, respectivement. La longueur de liaison $\text{U}^{6+}\text{–O}_{Ur}$ (O_{Ur}: atome d'oxygène faisant partie de l'ion uranyle) est indépendante de l'agencement des anions équatoriaux des polyèdres; les moyennes de tous les polyèdres qui contiennent l'ion uranyle sont: $^{[6]}\text{U}^{6+}\text{–O}_{Ur} = 1.79(3)$, $^{[7]}\text{U}^{6+}\text{–O}_{Ur} = 1.79(4)$, et $^{[8]}\text{U}^{6+}\text{–O}_{Ur} = 1.78(3)$ Å. Par contre, pas tous les polyèdres contenant $^{[6]}\text{U}^{6+}$ contiennent l'ion uranyle. Il existe une série continue de polyèdres de coordinence, de bipyramide carrée avec ions d'uranyle à octaèdre holosymmétrique. Les polyèdres contenant $^{[7]}\text{U}^{6+}$ et $^{[8]}\text{U}^{6+}$ contiennent sans exception l'ion uranyle. La longueur des liaisons $\text{U}^{6+}\text{–}\phi$ (ϕ: O^{2-}, OH^-) des polyèdres à uranyle dépend de la coordinence. Les moyennes pour tous les polyèdres sont $^{[6]}\text{U}^{6+}\text{–}\phi_{\text{eq}} = 2.28(5)$, $^{[7]}\text{U}^{6+}\text{–}\phi_{\text{eq}} = 2.37(9)$, et $^{[8]}\text{U}^{6+}\text{–}\phi_{\text{eq}} = 2.47(12)$ Å. Les paramètres présentement disponibles pour les valences de liaison impliquant U^{6+} ne sont pas adéquats pour en déterminer la somme. De tels paramètres propres à une coordinence particulière ont été dérivés pour

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l'uranium hexavalent, ainsi que des paramètres applicables à toutes les géométries des polyèdres. Ces paramètres mènent à des sommes des valences de liaison pour U^{6+} d'environ 6 unités et des valeurs raisonnables pour les liaisons U^{6+}–O_{Ur}. Ces nouveaux paramètres facilitent l'identification de U^{4+}, U^{5+} et U^{6+} dans les composés dont la structure a été affinée. Nous évaluons les contraintes cristallochimiques imposées sur la polymérisation des polyèdres des composés à uranyle.

(Traduit par la Rédaction)

Mots-clés: uranium, minéral uranifère, uranyle, géométrie des polyèdres, valence de liaison.

INTRODUCTION

The U^{6+} (uranyl) minerals are major constituents of the oxidized parts of uranium deposits, where they are commonly found as the products of alteration of uraninite (Frondel 1958, Finch *et al.* 1992, Finch & Ewing 1992, Pearcy *et al.* 1994). These minerals have recently received renewed interest because of their significance to the environment. Uranyl minerals are products of the oxidation of radioactive mine-tailings; they impact upon the release of U and Pb into the environment. In addition, uranyl minerals are prominent alteration-induced phases in laboratory experiments on UO_2 as well as spent nuclear fuel subjected to oxidative dissolution (Wadsten 1977, Wang & Katayama 1982, Wronkiewicz *et al.* 1992, Forsyth & Werme 1992, Johnson & Werme 1994, Finn *et al.* 1996, Wronkiewicz *et al.* 1996). Under oxidizing conditions, such as those found at the proposed nuclear-waste repository at Yucca Mountain, Nevada, the UO_2 in spent fuel is unstable, and the rate of alteration in the presence of water is likely to be appreciable (Murphy & Pabalan 1995). Spent fuel contains fission products (*e.g.*, Sr, Cs and I) and transuranic elements (*e.g.*, Np, Pu, Am, Cm) (Oversby 1994). The generally low concentrations of fission products and transuranic elements in spent fuel will generally preclude them from forming discrete phases during alteration (Oversby 1994). The formation of the alteration products of UO_2, mainly U^{6+} phases, will lower the concentration in solution of these radionuclides if they are incorporated into the structures of the alteration products. Laboratory studies have provided evidence for the retention of some radionuclides in the alteration phases of spent nuclear fuel (Finn *et al.* 1996).

There are about 170 minerals known to contain U as a necessary structural constituent. Of these, most contain U^{6+}, the oxidized form of U, although U^{4+} also occurs in several minerals. The crystal structures of 56 U^{6+} minerals and about 120 synthetic U^{6+} phases have been reported. As part of our on-going examination of the structural relations in U^{6+} phases, Burns *et al.* (1996) have proposed a structural hierarchy for U^{6+} minerals and inorganic phases. The structures are organized on the basis of the polymerization of cation polyhedra of higher bond-valence, resulting in sheet, chain, finite cluster, isolated polyhedron, and framework classes. The majority of U^{6+} phases (106) adopt a structure that is based upon infinite sheets of polyhedra that share corners and edges. Burns *et al.* (1996) grouped these sheets according to the topological arrangement of the anions in the sheet.

A detailed understanding of the crystal chemistry and bonding of U^{6+} will aid in evaluating the likelihood of the incorporation of fission products and transuranic elements in low quantities into the structures of U^{6+} phases (Burns *et al.* 1997a). In addition, an appreciation of the underlying controls of bond topology is a necessary step toward understanding the relations between the hierarchy of mineral structures and the paragenesis of the minerals. Despite the wealth of crystal-structure data available, the current state of knowledge of the crystal chemistry and bonding of U^{6+} lags behind that of most of the lighter elements. The coordination polyhedra of many cations important in minerals have been investigated in detail using theoretical approaches (*e.g.*, silicates: Gibbs 1982, Lasaga & Gibbs 1987, 1988, 1990, 1991; borates: Tossell 1986, 1990, Burns 1995; carbonates: Tossell 1986; copper oxysalts: Burns & Hawthorne 1995a,b), but there has been little quantitative theoretical work done on the coordination chemistry of U^{6+}. This is because U^{6+} complexes present serious problems when applying quantum-chemistry methods, owing to the large number of electrons (requiring the use of effective core potentials) and relativistic effects. Despite these difficulties with theoretical approaches, some calculations have been reported for U^{6+} complexes (Tatsumi & Hoffmann 1980, Wadt 1981, van Wezenbeek *et al.* 1991, Pyykkö & Zhao 1991, Pyykkö *et al.* 1994, Craw *et al.* 1995).

BONDING IN U^{6+} POLYHEDRA

The oxidation states of the 5*f* actinide elements are quite variable owing to the screening of the 5*f* electrons from the nucleus. Uranium can occur as U^{4+}, U^{5+} or U^{6+} in crystal structures, with U^{6+} preferred under oxidizing conditions. The U^{6+} cation usually occurs in crystal structures as part of an approximately linear $(U^{6+}O_2)^{2+}$ uranyl ion (Evans 1963). *Ab initio* molecular-orbital calculations (Craw *et al.* 1995) have shown that the U^{6+}–O bonding mechanism in the uranyl ion is primarily by donation of electrons from the *p* orbital of

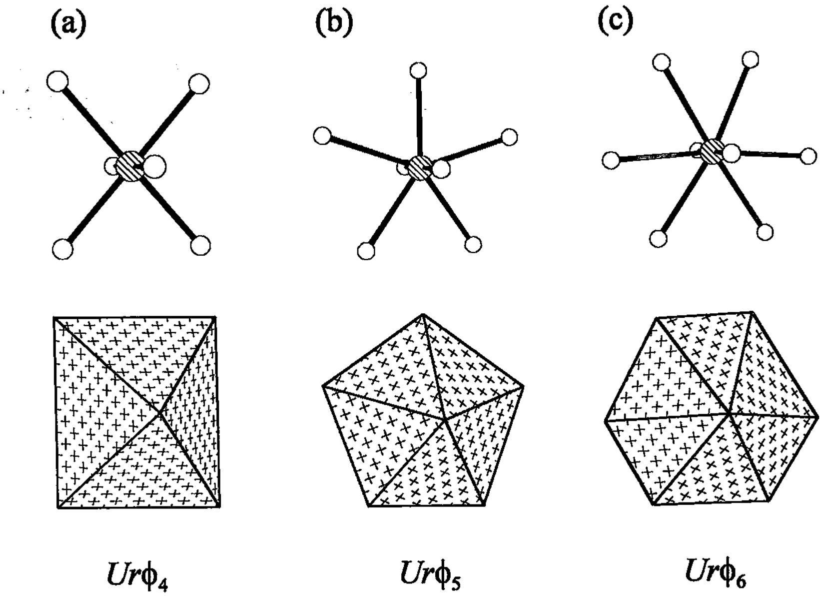

FIG. 1. The three types of $Ur\phi_n$ polyhedra [Ur: $(UO_2)^{2+}$ uranyl ion, ϕ: O^{2-}, OH^-]. U^{6+} cations are shown as circles shaded with parallel lines, and anions are shown as unshaded circles.

the O atom into the empty *d* and *f* orbitals of the U atom. Average U^{6+}–O bond-lengths in the uranyl ion are ~1.8 Å, and thus the bond-valence requirements of the uranyl-ion O atoms (hereafter referred to as O_{Ur}) are largely satisfied without additional bonding.

In crystal structures, the uranyl ion is coordinated by four, five or six anions in an approximately planar arrangement essentially perpendicular to the uranyl ion, giving $Ur\phi_4$ square, $Ur\phi_5$ pentagonal and $Ur\phi_6$ hexagonal bipyramids (Ur: uranyl ion, ϕ: O^{2-},OH^-), respectively (Fig. 1). The uranyl ion has a formal valence of 2+, and thus the typical bond-valences associated with each U^{6+}–ϕ_{eq} (ϕ_{eq}: equatorial ϕ) bond are ~0.5, ~0.4 and ~0.33 valence units (*vu*) for $Ur\phi_4$, $Ur\phi_5$ and $Ur\phi_6$, respectively. As the bond-valence requirements of the equatorial anions are only partly satisfied by the U^{6+}–ϕ_{eq} bond, $Ur\phi_4$, $Ur\phi_5$ and $Ur\phi_6$ polyhedra may polymerize with other $Ur\phi_n$ polyhedra or with other cation polyhedra to form complex structures without violating the valence-sum rule (Brown 1981). Because the equatorial anions are close to being coplanar, and the O_{Ur} bond-valence requirements are largely satisfied without further substantial bonding, $Ur\phi_n$ polyhedra may share equatorial edges and corners, commonly resulting in infinite sheets. In such cases, the uranyl ion is oriented approximately perpendicular to the sheet, and the sheets are most often connected through weaker bonds to interlayer cations and through H bonds.

GEOMETRIES OF U^{6+} POLYHEDRA

EXAFS data

Extended X-ray absorption fine-structure (EXAFS) spectroscopy is a useful technique for determining the speciation of actinide elements in solutions and solids (Nitsche 1995, Reich *et al.* 1996). EXAFS spectra readily provide bond-length information for U polyhedra, although few studies of minerals have been reported. Typical uranyl-ion U^{6+}–O bond-lengths obtained from EXAFS spectra are 1.78 and 1.79 Å (Charpin *et al.* 1985, Moll *et al.* 1994, 1995, Allen *et al.* 1995, 1996). X-ray-diffraction studies have shown that the two uranyl ion U^{6+}–O bond-lengths can differ for a single uranyl ion, but EXAFS techniques do not resolve these two distances. EXAFS is usually not capable of resolving individual equatorial U^{6+}–ϕ bond-lengths, but instead gives an average equatorial U^{6+}–ϕ bond-length that is comparable to the average bond-length obtained from X-ray-diffraction studies (Moll *et al.* 1994).

X-ray-diffraction data

The accurate refinement of crystal structures that contain U^{6+} is more difficult than in the case of most other mineral groups owing to the high absorption of X rays by U. Thus, many of the published U^{6+} structures

TABLE 1. STRUCTURES INCLUDED IN THIS STUDY

Mineral Name	Formula	Ref.	Mineral Name	Formula	Ref.
α-uranophane	$Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$	1	moctezumite	$PbTe[(UO_2)O_3]$	18
andersonite	$Na_2Ca[(UO_2)(CO_3)_3](H_2O)_5$	2	phosphuranylite	$KCa(H_3O)_3(UO_2)[(UO_2)_3(PO_4)_2O_2]_2(H_2O)_8$	19
bayleyite	$Mg_2[(UO_2)(CO_3)_3](H_2O)_{18}$	3	phuralumite	$Al_2((UO_2)_3(PO_4)_2(OH)_2)(OH)_4(H_2O)_{10}$	20
cliffordite	$(UO_2)(Te_3O_7)$	4	phurcalite	$Ca_2[(UO_2)_3(PO_4)_2(OH)_2](OH)_2(H_2O)_4$	21
cuprosklodowskite	$Cu[(UO_2)(SiO_3OH)]_2(H_2O)_6$	5	roubaultite	$[Cu_2(UO_2)_3(CO_3)_2O_2(OH)_2](H_2O)_4$	22
curite	$Pb_3[(UO_2)_8O_8(OH)_6](H_2O)_3$	6	saléeite	$Mg[(UO_2)(PO_4)]_2(H_2O)_{10}$	23
demesmaekerite	$Pb_2Cu_5[(UO_2)(SeO_3)_3]_2(OH)_6(H_2O)_2$	7	schmitterite	$[(UO_2)(TeO_3)]$	24
dewindtite	$Pb_3[H(UO_2)_3O_2(PO_4)_2]_2(H_2O)_{12}$	8	schoepite	$[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$	25
fourmarierite	$Pb[(UO_2)_4O_3(OH)_4](H_2O)_4$	9	schröckingerite	$NaCa_3[(UO)_2(CO_3)_3](SO_4)F(H_2O)_{10}$	26
francevillite	$Ba_{0.96}Pb_{0.04}[(UO_2)_2(V_2O_8)](H_2O)_5$	10	sklodowskite	$Mg[(UO_2)(SiO_3OH)]_2(H_2O)_6$	27
françoisite-(Nd)	$Nd[(UO_2)_3(PO_4)_2O(OH)](H_2O)_6$	11	soddyite	$(UO_2)_2(SiO_4)(H_2O)_2$	28
guilleminite	$Ba[(UO_2)_3(SeO_3)_2O_2](H_2O)_3$	12	swartzite	$CaMg[(UO_2)(CO_3)_3](H_2O)_{12}$	29
johannite	$Cu[(UO_2)_2(SO_4)_2(OH)_2](H_2O)_8$	13	upalite	$Al[(UO_2)_3(PO_4)_2O(OH)](H_2O)_7$	30
kasolite	$Pb[(UO_2)(SiO_4)](H_2O)$	14	vandenbrandeite	$[(UO_2)Cu(OH)_4]$	31
liebigite	$Ca_2[(UO_2)(CO_3)_3](H_2O)_{11}$	15	walpurgite	$Bi_4O_4[(UO_2)(AsO_4)_2](H_2O)_2$	32
metatorbernite	$Cu_{0.92}[(UO_2)(PO_4)]_2(H_2O)_8$	16	zippeite	$K[(UO_2)_2(SO_4)(OH)_3](H_2O)$	33
meta-uranocircite	$Ba[(UO_2)(PO_4)]_2(H_2O)_6$	17			

Compound	Ref.	Compound	Ref.	Compound	Ref.
$Li_2[(UO_2)O_2]$	34	$[Mg(UO_2)(B_2O_5)]$	58	Ca_3UO_6	82
$Ba[(UO_2)O_2]$	35	$K_2[(UO_2)(MoO_4)]$	59	Sr_3UO_6	83
γ-$[(UO_2)(OH)_2]$	36	α-$[(UO_2)(OH)_2]$	60	$K_2Li_4UO_6$	84
$Pb[(UO_2)O_2]$	37	$Cs_2(U_2O_7)(D_2O)_{0.444}$	61	Li_6UO_6	85
$[(UO_2)H(PO_4)](H_2O)_4$	38	α-$Sr[(UO_2)O_2]$	62	γ-UO_3	86
$K[(UO_2)(PO_4)](D_2O)_3$	39	$[(UO_2)(BO_3)O]$	63	UO_3 HP	87
$ND_4[(UO_2)(PO_4)](D_2O)_3$	40	$[(UO_2)TiNb_2O_8]$	64	δ-UO_3	88
$[(UO_2)D(AsO_4)](D_2O)_4$	41	$Na_4[(UO_2)O_3]$	65	Ba_2MgUO_6	89
$Li[(UO_2)(AsO_4)](D_2O)_4$	42	$[(UO_2)(HSeO_3)_2(H_2O)]$	66	$K_9BiU_6O_{24}$	90
$Mg[(UO_2)(SO_4)_2](H_2O)_{11}$	43	$Cu_4[(UO_2)(MoO_4)_2](OH)_6$	67	$Cu(UO_2)O_2$	91
$[(UO_2)(SO_4)_2]H_2(H_2O)_5$	44	$[(UO_2)(H_2PO_4)_2(H_2O)](H_2O)_2$	68	$Mn(UO_2)O_2$	92
$K_2[UO_2(SO_4)_2](H_2O)_2$	45	$Mn[(UO_2)(SO_4)_2(H_2O)](H_2O)_4$	69	$(UO_2)(MoO_4)$	93
$Li[(UO_2)(BO_3)]$	46	$[(UO_2)(SO_4)(H_2O)_2](H_2O)_{1.5}$	70	β-$(UO_2)(SO_4)$	94
$Mg\ [(UO_2)(AsO_4)]_2(H_2O)_4$	47	$[(UO_2)(SO_4)(H_2O)_2](H_2O)_{0.5}$	71	α-$(UO_2)(MoO_4)(H_2O)_2$	95
$K_2[(UO_2)_2O_3]$	48	$[(UO_2)(SO_4)(H_2O)_2]_2(H_2O)_3$	72	$Sr(UO_2)_6(MoO_4)_7(H_2O)_{19}$	96
$[H_2(UO_2)_3O_4]$	49	$[(UO_2)(SeO_4)(H_2O)_2](H_2O)_2$	73	$Ba(UO_2)_3(MoO_4)_4(H_2O)_4$	97
$[(UO_2)(CuO_4)]$	50	$Cs_4[(UO_2)(CO_3)_3](H_2O)_6$	74	$Mg(UO_2)_3(MoO_4)_4(H_2O)_8$	98
$Ni[(UO_2)_2(V_2O_8)](H_2O)_4$	51	$Sr_2[(UO_2)(CO_3)_3](H_2O)_8$	75	$Na_2(UO_2)(P_2O_7)$	99
$Cs_2[(UO_2)_2(V_2O_8)]$	52	$(NH_4)_4[(UO_2)(CO_3)_3]$	76	$(UO_2)_2(GeO_4)(H_2O)_2$	100
$Cs_2[(UO_2)_2(Nb_2O_8)]$	53	$Rb[(UO_2)(NO_3)_3]$	77	$Pb_2(UO_2)(TeO_3)_3$	101
$[Pb_3(UO_2)_{11}O_{14}]$	54	$Rb_2[(UO_2)(NO_3)_4]$	78	$Mg(UO_2)_6(MoO_4)_7(H_2O)_{14}$	102
$K[(UO_2)(CrO_4)(OH)](H_2O)_{1.5}$	55	$[(UO_2)(NO_3)_2](H_2O)_2$	79	$Cs_2U_2O_7$	103
$Cs[(UO_2)(PO_3)_3]$	56	$K_8[(UO_2)_2O_6]$	80	$Ca_3U_2O_7$	104
$(NH_4)_2[(UO_2)(SO_4)_2(H_2O)](H_2O)$	57	Pb_3UO_6	81	$UO_2Se_2O_5$	105

References: 1: Ginderow (1988), (2): Mereiter (1986c), (3): Mayer & Mereiter (1986), (4) Branstaetter (1981b), (5) Rosenzweig & Ryan (1975), (6) Taylor *et al.* (1981), (7) Ginderow & Cesbron (1983), (8): Piret *et al.* (1990), (9): Piret (1985), (10): Mereiter (1986e), (11) Piret *et al.* (1988), (12): Cooper & Hawthorne (1995), (13): Mereiter (1982c), (14): Rosenzweig & Ryan (1977a), (15): Mereiter (1982a), (16): Stergiou *et al.* (1993), (17): Khosrawan-Sazedj (1982a), (18): Swihart *et al.* (1993), (19): Demartin *et al.* (1991), (20): Piret *et al.* (1979), (21): Atencio *et al.* (1991), (22): Ginderow & Cesbron (1985), (23): Miller & Taylor (1986), (24): Meunier & Galy (1973), (25): Finch *et al.* (1996), (26): Mereiter (1986a), (27): Ryan & Rosenzweig (1977), (28): Demartin *et al.* (1992), (29): Mereiter (1986b), (30): Piret & Declercq (1983), (31): Rosenzweig & Ryan (1977b), (32): Mereiter (1982b), (33): Vochten *et al.* (1995), (34): Gebert *et al.* (1978), (35): Reis *et al.* (1976), (36): Siegel *et al.* (1972b), (37): Cremers *et al.* (1986), (38): Morosin (1978), (39): Fitch & Cole (1991), (40): Fitch & Fender (1983), (41): Fitch *et al.* (1983), (42): Fitch *et al.* (1982), (43): Serezhkin *et al.* (1981b), (44): Alcock *et al.* (1982), (45): Niinistö *et al.* (1979), (46): Gasperin (1990), (47): Bachet *et al.* (1991), (48): Saine (1989), (49): Siegel *et al.* (1972a), (50): Dickens *et al.* (1993), (51): Borène & Cesbron (1970), (52): Dickens *et al.* (1992), (53): Gasperin (1987b), (54): Ijdo (1993a), (55): Serezhkina *et al.* (1990), (56): Linde *et al.* (1978), (57): Niinistö *et al.* (1978), (58): Gasperin (1987a), (59): Sadikov *et al.* (1988), (60): Taylor (1971), (61): Mijlhoff *et al.* (1993), (62): Fujino *et al.* (1977), (63): Gasperin (1987c), (64): Chevalier & Gasperin (1969), (65): Wolf & Hoppe (1986), (66): Mistryukov & Michailov (1983), (67): Tali *et al.* (1993), (68): Krogh-Andersen *et al.* (1985), (69): Tabachenko *et al.* (1979), (70): Brandenburg & Loopstra (1973), (71): van der Putten & Loopstra (1974), (72): Zalkin *et al.* (1978), (73): Serezhkin & Trunov (1981a), (74): Mereiter (1988), (75): Mereiter (1986d), (76): Serezhkin *et al.* (1983), (77): Zalkin *et al.* (1989), (78): Kapshukov *et al.* (1971), (79): Taylor & Mueller (1965), (80): Wolf & Hoppe (1986), (81): Sterns *et al.* (1986), (82): van Duivenboden & Ijdo (1986), (83): Ijdo (1993b), (84): Wolf & Hoppe (1987), (85): Wolf & Hoppe (1985), (86): Loopstra *et al.* (1977), (87): Siegel *et al.* (1966), (88): Weller *et al.* (1988), (89): Padel *et al.* (1972), (90): Gasperin *et al.* (1991), (91): Siegel & Hoekstra (1968), (92): Bacmann & Bertaut (1966), (93): Serezhkin *et al.* (1980a), (94): Brandenburg & Loopstra (1978), (95): Serezhkin *et al.* (1980b), (96): Tabachenko *et al.* (1984b), (97): Tabachenko *et al.* (1984a), (98); Tabachenko *et al.* (1983), (99): Linde *et al.* (1984), (100): Legros & Jeannin (1975), (101): Branstätter (1981a), (102): Tabachenko *et al.* (1984b), (103): van Egmond (1976), (104): Holc & Golic (1983), (105): Trombe *et al.* (1985).

are of low precision, and high *R* indices commonly are reported. Owing to the high X-ray scattering efficiency of U, as compared to O, the O atom positions are in many cases imprecisely known, and this problem is especially pronounced in Rietveld refinements using X-ray powder data.

The structures considered here are listed in Table 1. In each structure considered, U^{6+} bonds to O^{2-}, OH^- or H_2O; structures with F or Cl bonded to U^{6+} have been excluded from consideration. Structures containing both U^{4+} and U^{6+} (or possibly U^{5+}) have been omitted because of the possibility of U^{4+}–U^{6+} disorder. Structures refined using X-ray data collected from single crystals, or neutron data collected from powders, have been included where the *R* index is less than 7%. Structures refined using X-ray data collected from powders have been excluded.

General trends

Data have been grouped according to the coordination number of U^{6+}: six, seven or eight, including the O_{Ur} atoms. U^{6+}–ϕ bond-length data for all coordination numbers are presented in Figure 2. There is a completely bimodal distribution of U^{6+}–ϕ bond-lengths in both the $^{[7]}U^{6+}$ and $^{[8]}U^{6+}$ polyhedra; the bimodal distribution for $^{[6]}U^{6+}$ is less pronounced (Fig. 2).

$^{[7]}U^{6+}$ and $^{[8]}U^{6+}$ polyhedra

The U^{6+}–ϕ bond-length distributions in $^{[7]}U^{6+}$ and $^{[8]}U^{6+}$ polyhedra (Fig. 2) are completely bimodal owing to the presence of a uranyl ion in *every* polyhedron. All $^{[7]}U^{6+}$ and $^{[8]}U^{6+}$ polyhedra are $Ur\phi_5$ pentagonal bipyramids and $Ur\phi_6$ hexagonal bipyramids, respectively. In both cases, the population centered around ~1.8 Å corresponds to the U^{6+}–O_{Ur} bonds, and the population centered around ~2.4 Å corresponds to the U^{6+}–ϕ_{eq} bonds. The populations at ~2.4 Å are larger than at ~1.8 Å because there are more U^{6+}–ϕ_{eq} bonds than U^{6+}–O_{Ur} bonds in each polyhedron.

The average $^{[7]}U^{6+}$–O_{Ur} and $^{[7]}U^{6+}$–ϕ_{eq} bond-lengths for all 93 $Ur\phi_5$ polyhedra are 1.79 ($\sigma = 0.04$) and 2.37 ($\sigma = 0.09$) Å, respectively. In 28 $Ur\phi_6$ polyhedra, the average $^{[8]}U^{6+}$–O_{Ur} and $^{[8]}U^{6+}$–ϕ_{eq} bond-lengths are 1.78 ($\sigma = 0.03$) and 2.47 ($\sigma = 0.12$) Å, respectively.

$^{[6]}U^{6+}$ polyhedra

The U^{6+}–ϕ bond-length distribution for polyhedra containing $^{[6]}U^{6+}$ is irregular, and bond lengths range from 1.74 to 2.34 Å (Fig. 2). Unlike $Ur\phi_5$ and $Ur\phi_6$ polyhedra, a $(U^{6+}O_2)^{2+}$ uranyl ion is not evident in some $^{[6]}U^{6+}$ polyhedra. Figure 3 shows the relationship between the average of the pair of shortest *trans* $^{[6]}U^{6+}$–ϕ bond-lengths and the average $^{[6]}U^{6+}$–ϕ bond-length of the remaining four (equatorial) bonds.

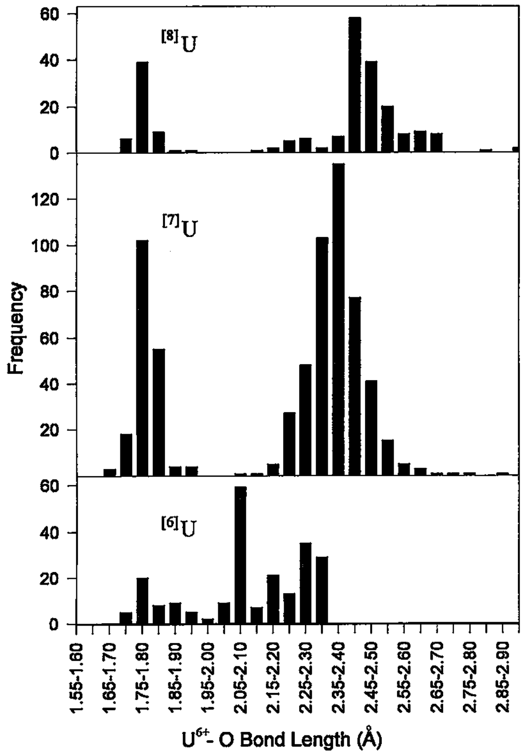

FIG. 2. The distribution of U^{6+}–ϕ bond-lengths in well-refined structures.

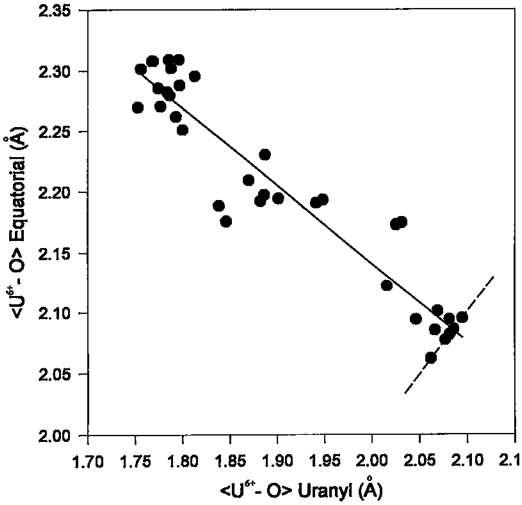

FIG. 3. U^{6+}–ϕ bond-length relations in $^{[6]}U^{6+}$ polyhedra. The average of the two shortest *trans* bond-lengths (in some cases corresponding to bonds in the uranyl ion) *versus* the average of the remaining four equatorial bond-lengths. The solid line is the least-squares-fit line. The broken line represents the trend for holosymmetric octahedra.

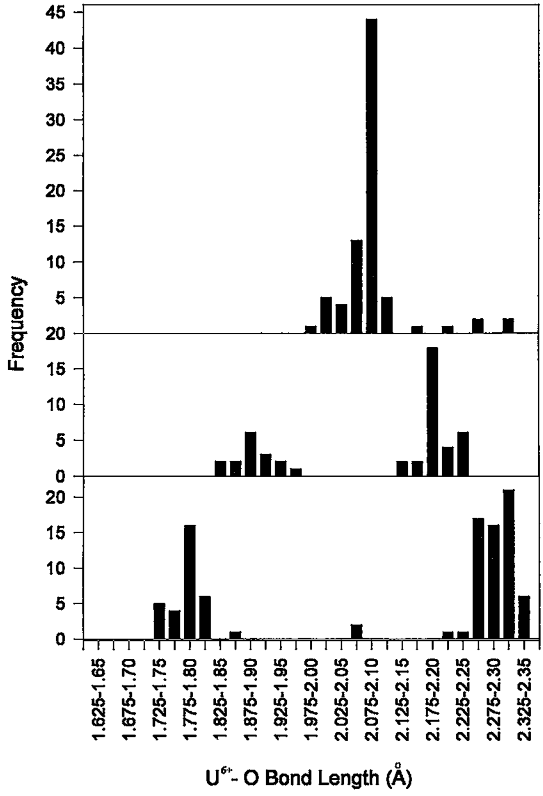

FIG. 4. The distribution of U^{6+}–ϕ bond-lengths for $^{[6]}$U^{6+} polyhedra in well-refined structures. Bottom: square bipyramidal polyhedra that contain a uranyl ion, middle: intermediate geometries, top: approximately octahedral geometries.

Note that where a uranyl ion is present, the average $^{[6]}$U^{6+}–O$_{Ur}$ bond-length corresponds to the shortest average *trans* $^{[6]}$U^{6+}–ϕ bond-length. The data in Figure 3 plot in three clusters; one corresponds to $Ur\phi_4$ polyhedra that contain uranyl ions with a typical U^{6+}–O$_{Ur}$ bond-length of ~1.8 Å, one corresponds to a holosymmetric or approximately holosymmetric octahedral coordination, and the third corresponds to a geometry that is intermediate between the two. The U^{6+}–ϕ bond-length distributions for each of these three groups are shown separately in Figure 4. Considering only the sixteen $^{[6]}$U^{6+} polyhedra that contain typical uranyl ions (*i.e.*, U^{6+}–O_{Ur} ~1.8 Å), the average $^{[6]}$U^{6+}–O$_{Ur}$ and $^{[6]}$U^{6+}–ϕ_{eq} bond-lengths are 1.79 (σ = 0.03) and 2.28 (σ = 0.05) Å, respectively.

The $^{[6]}$U^{6+} polyhedral geometries display a trend from the typical $Ur\phi_4$ square bipyramid to a holosymmetric octahedron (Fig. 3). The ubiquity of the uranyl ion in $^{[7]}$U^{6+} and $^{[8]}$U^{6+} polyhedra (Fig. 2) indicates that a uranyl ion is always energetically favorable in those coordination geometries. The $^{[6]}$U^{6+} polyhedral geometries presented in Figures 3 and 4 were obtained using diffraction techniques; as such, they represent long-range average configurations that may in some cases differ from local site-geometries. Two possible models explain the trend shown in Figure 3: (1) the energetics of a $Ur\phi_4$ square bipyramid and a U$^{6+}\phi_6$ octahedron may be similar, and the pathway between the two coordination geometries may not have a significant energy-barrier, thus permitting the range of polyhedron geometries to exist and be observed by diffraction techniques. (2) A (U^{6+}O$_2$)$^{2+}$ uranyl ion may be locally present in each polyhedron, but either static or dynamic disorder results in the range of polyhedral geometries observed by diffraction techniques.

Pyykkö & Zhao (1991) have reported quasirelativistic *ab initio* calculations for (UO$_6$)$^{6-}$ clusters with $Ur\phi_4$ and octahedral geometries, as well as for geometries intermediate between these two coordination polyhedra. The calculations predict a trend similar to that shown in Figure 3, although the predicted bond-lengths are seriously in error. More significantly, the energy of the cluster was found to vary very little over the range of geometries. Thus, Pyykkö & Zhao (1991) concluded that the range of $^{[6]}$U^{6+}–O$_{Ur}$ bond-lengths may be interpreted as a soft e$_g$ vibration mode of the cubic (UO$_6$)$^{6-}$ cluster.

Where positional disorder is not present, the anisotropic-displacement ellipsoids of anions are typically nearly spherical, or they are elongate subperpendicular to the cation–anion bond, reflecting the relative ease of bond-bending compared to bond-stretching. As the typical $^{[6]}$U^{6+}–O$_{Ur}$ bond-length is ~0.5 Å shorter than

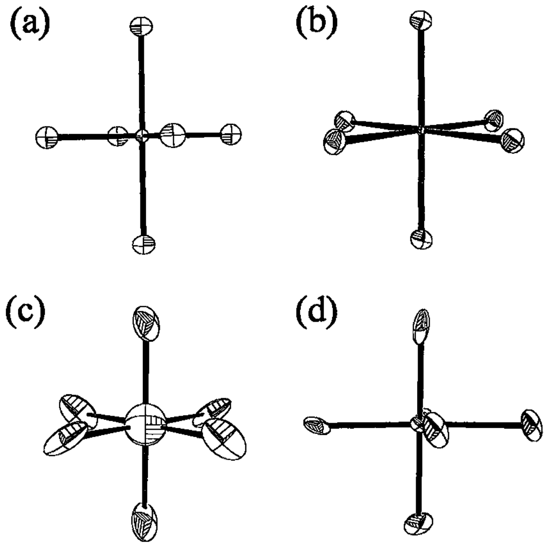

FIG. 5. Anisotropic displacement ellipsoids (50% probability) for U^{6+} polyhedra in: (a) $Na_4[(UO_2)O_3]$, (b) α-Li_6UO_4, (c) $K_2Li_4UO_6$, (d) $K_8[(UO_2)O_6]$.

the typical ${}^{[6]}U^{6+}–\phi_{eq}$ bond-length, disorder in the uranyl ion positions within the polyhedron should result in anion anisotropic-displacement ellipsoids that are elongate subparallel to the $U^{6+}–\phi$ bond. Anisotropic-displacement parameters are available for only a small number of well-refined U^{6+} structures that contain holosymmetric or near-holosymmetric $U^{6+}\phi_6$ octahedra. Consideration of these structures supports both models for the observed ${}^{[6]}U^{6+}$ polyhedron-geometry trends. The structures of $Na_4[(UO_2)O_3]$ (Wolf & Hoppe 1986) and α–Li_6UO_6 (Wolf & Hoppe 1985) both contain holosymmetric $U^{6+}\phi_6$ octahedra; in both cases, the anisotropic-displacement ellipsoids (Figs. 5a, b) of the anions are consistent with absence of significant positional disorder of the anions, and thus are compatible with model (1). In contrast, the anisotropic-displacement ellipsoids of anions for the holosymmetric $U^{6+}\phi_6$ octahedron in the structure of $K_2Li_4UO_6$ (Wolf & Hoppe 1987) and the distorted $U^{6+}\phi_6$ octahedron in the structure of $K_8[(UO_2)O_6]$ (Wolf & Hoppe 1986) show considerable elongation parallel to the cation–anion bonds (Figs. 5c, d), and are therefore compatible with model (2), without contradicting model (1).

Uranyl-ion bond-length

The average $U^{6+}–O_{Ur}$ bond-lengths for $Ur\phi_4$, $Ur\phi_5$ and $Ur\phi_6$ polyhedra, as derived from crystal-structure analysis, are 1.79(3), 1.79(4) and 1.78(3) Å, respectively. Thus, the uranyl-ion bond-lengths are insensitive to the number of anions that coordinate the uranyl ion, in the cases where the coordination anions are O^{2-} and OH^-. The average $U^{6+}–O_{Ur}$ bond lengths obtained from X-ray-diffraction studies are in agreement with the values obtained using EXAFS spectroscopy for various structures (above).

Uranyl-ion linearity

The distributions of $O–U^{6+}–O$ bond-angles in the uranyl ions of $Ur\phi_n$ polyhedra are shown in Figure 6. The uranyl-ion bond-angle is usually linear or close to linear in $Ur\phi_4$ and $Ur\phi_6$ polyhedra, with most bond angles in the range 179 to 180°. In contrast, the uranyl-ion bond-angles in $Ur\phi_5$ polyhedra, although being close to linear, show a strong tendency to be somewhat distorted away from 180°, with the maximum of the distribution in the range 178 to 179°.

A possible explanation of the bond-angle distribution in $Ur\phi_5$ polyhedra involves the positions of the equatorial anions of the polyhedra. In general, the equatorial anions and the U^{6+} cation are close to being coplanar, and the uranyl ion is positioned roughly orthogonal to a plane drawn through the equatorial atoms. However, in many crystal structures, considerations of local bonding apparently require the uranyl ion to be subperpendicular to the plane containing the equatorial anions. In the case of $Ur\phi_4$ and $Ur\phi_6$ polyhedra, the distribution of the equatorial anions is such that the uranyl ion may be subperpendicular to the equatorial plane while maintaining roughly equal repulsion between both O_{Ur} anions and the equatorial anions. However, in the case of $Ur\phi_5$ polyhedra, any tilting of the uranyl ion relative to the normal to the equatorial plane will result in the two O_{Ur} atoms being subjected to different amounts of Coulombic repulsion from the equatorial anions (Fig. 7), thus causing the uranyl-ion bond-angle to depart from 180°.

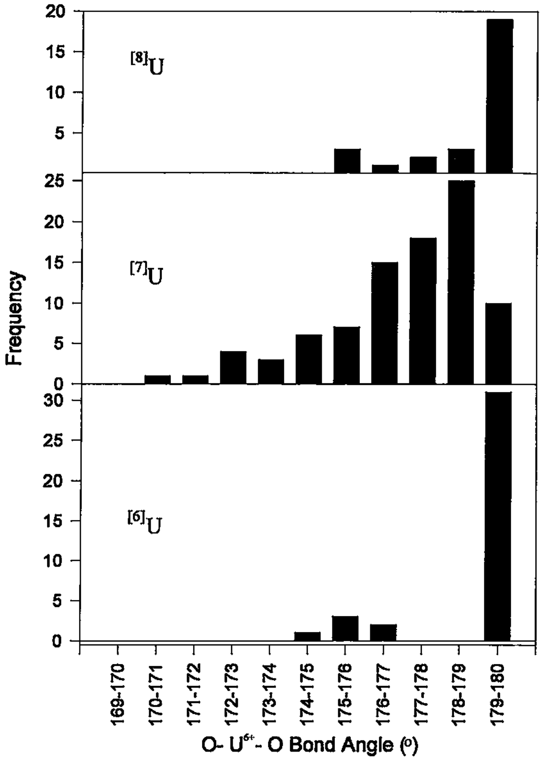

FIG. 6. Bond-angle distributions of the uranyl ion in well-refined structures.

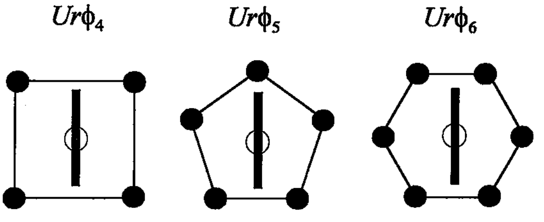

FIG. 7. The distribution of equatorial anions with respect to possible tilting of the uranyl ion in U^{6+} polyhedra.

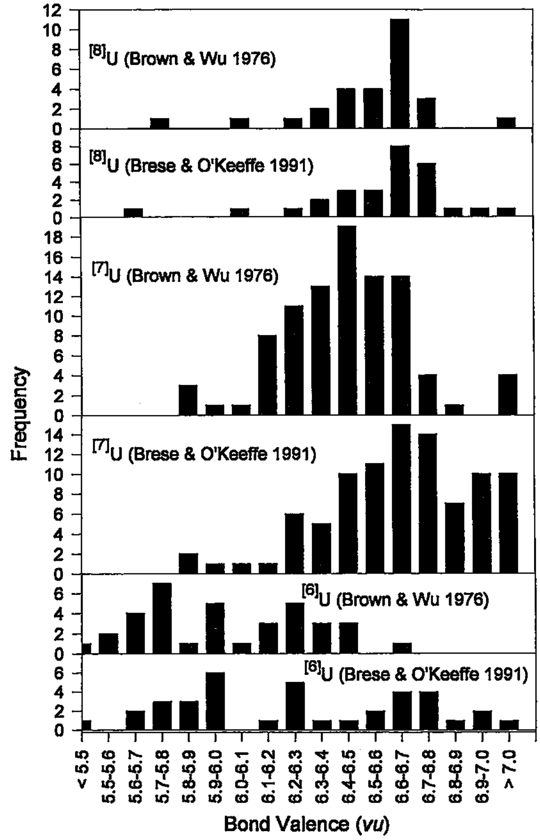

FIG. 8. The distribution of bond-valence sums calculated for the U^{6+} position in well-refined structures using the parameters of Brese & O'Keeffe (1991) and Brown & Wu (1976).

A BOND-VALENCE APPROACH

Hydrous uranyl phases form during the oxidative dissolution of UO_2 and spent fuel in the presence of water (*e.g.*, Wadsten 1977, Wang & Katayama 1982, Wronkiewicz *et al.* 1992, Forsyth & Werme 1992, Johnson & Werme 1994, Finn *et al.* 1996, Wronkiewicz *et al.* 1996) and during the alteration of uraninite (Finch & Ewing 1992). Hydrogen bonding plays a crucial role in the stability of these structures, as in, for example, the structures of schoepite (Finch *et al.* 1996) and ianthinite (Burns *et al.* 1997b), where adjacent sheets of $U\phi_n$ polyhedra are held together only by H bonds. Unfortunately, it is usually impossible to determine the positions of H atoms in uranyl phases based upon X-ray-diffraction experiments.

The bond-valence method (Brown 1981) has proven to be a powerful tool for the prediction and interpretation of bond lengths in solids. Bond-valence sums at both cation and anion positions are regularly used to analyze refined structures and give information on cation oxidation-states, anion identities and H bonding. The strength of this approach is that the bond length is a unique function of bond valence (Brese & O'Keeffe 1991). However, it is not uncommon for apparently well-refined structures that contain U^{6+} to have bond-valence sums at the U^{6+} position that depart significantly from 6 *vu*.

The most recently published bond-valence parameter R_{ij} given for U^{6+} by Brese & O'Keeffe (1991) and Brown & Altermatt (1985) is 2.075 Å (for bonds to oxygen), and the *b* constant is 0.37 Å. However, the bond-valence parameters R_{ij} = 2.059 Å and N = 4.3 given by Brown & Wu (1976) are in common usage. Other bond-valence parameters for U^{6+} are given by Zachariasen (1978). In our study, only reasonably well-refined structures are considered, and thus cation bond-valence sums for $^{[6]}U^{6+}$, $^{[7]}U^{6+}$ and $^{[8]}U^{6+}$ polyhedra should cluster around 6 *vu*. The distributions of bond-valence sums at the U^{6+} positions calculated using the parameters of Brese & O'Keeffe (1991) and Brown & Wu (1976) for the structures of the phases listed in Table 1 are shown in Figure 8. The bond-valence sums are usually significantly different from the expected value of 6 *vu* (Fig. 8). In the case of $^{[7]}U^{6+}$ and $^{[8]}U^{6+}$, the majority of the bond-valence sums calculated with both sets of parameters are significantly greater than 6 *vu*, and the maximum in each distribution corresponds to bond-valence sums in the range 6.4 to 6.7 *vu*, depending on the choice of parameters, although sums greater than 7 *vu* are not uncommon. The average sums of bond valences for $^{[7]}U^{6+}$ and $^{[8]}U^{6+}$ calculated using the parameters of Brese & O'Keeffe (1991) are 6.7 (σ = 0.3) and 6.6 (σ = 0.3) *vu*, respectively. The average sums of bond valence calculated with the parameters of Brown & Wu (1976) for $^{[7]}U^{6+}$ and $^{[8]}U^{6+}$ are 6.4 (σ = 0.3) and 6.5 (σ = 0.2) *vu*, respectively. In most cases, the bond-valence parameters of Brese & O'Keeffe (1991) result in uranyl ion $U^{6+}–O_{Ur}$ bond-valences in excess of 2.0 *vu*, suggesting (erroneously) that O_{Ur} atoms do not participate in any additional bonding. There is a broader range of bond-valence sums for $^{[6]}U^{6+}$ if one uses the parameters of Brese & O'Keeffe (1991) or Brown & Wu (1976), with most falling between 5.6 and 7.0 *vu*. The average bond-valence sum for $^{[6]}U^{6+}$ in structures is 6.3 (σ = 0.4) *vu* when using the parameters of Brese & O'Keeffe (1991), and 6.0 (σ = 0.3) *vu* when using the parameters of Brown & Wu (1976); however, there is no clear trend in either distribution.

Most U^{6+} environments in crystal structures give bond-valence sums that differ significantly from the expected 6 *vu* (Fig. 8) when using the parameters of Brese & O'Keeffe (1991). However, a total of nine $^{[6]}U^{6+}$ cation environments give bond-valence sums in the range 5.8 to 6.0 *vu*. Of these polyhedra, none contain a uranyl ion with $U^{6+}–O_{Ur} \approx 1.8$ Å; rather, most

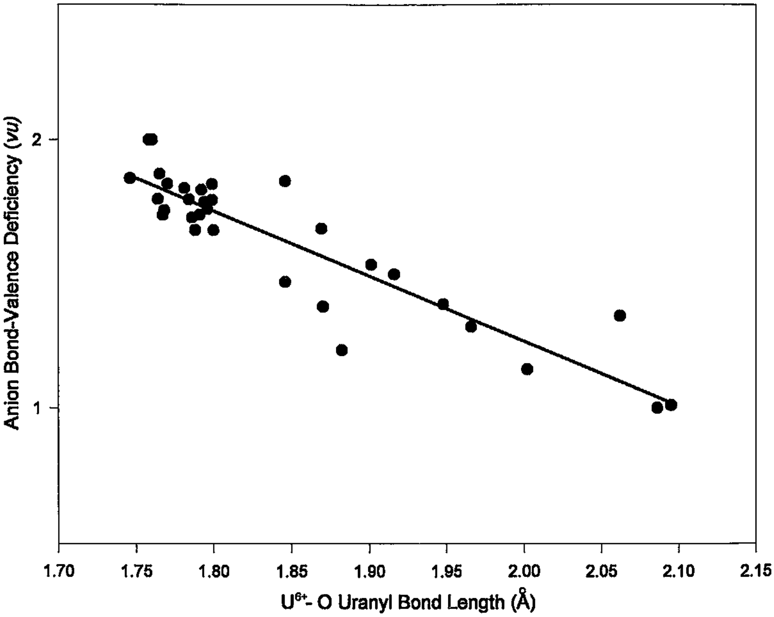

FIG. 9. The U^{6+}–O bond length of the uranyl ion *versus* the bond-valence deficiency of the uranyl-ion O-atom in well-refined anhydrous structures.

are holosymmetric or near-holosymmetric octahedra. Thus, it must be concluded that the bond-valence parameter (2.075 Å) of Brese & O'Keeffe (1991), when used with b = 0.37 Å, is inadequate for U^{6+} structures that contain the uranyl ion, and this parameter should not be used to analyze refined structures, to predict U^{6+}–ϕ bond-lengths, or to interpret H bonding. The use of this bond-valence parameter where a uranyl ion is present will usually result in bond-valence sums that are significantly greater than 6 *vu*, and the bond-valence sums at the anion positions will be incorrect. The parameters of Brown & Wu (1976) result in more reasonable bond-valence sums at the O_{Ur} atoms, although the parameters result in bond-valence sums at the $^{[7]}U^{6+}$ and $^{[8]}U^{6+}$ positions that are usually greater than 6.0 *vu*.

Derivation of bond-valence parameters for U^{6+}

The most serious drawback of the bond-valence parameters for U^{6+} given by Brese & O'Keeffe (1991) is that the bond valences calculated for U^{6+}–O_{Ur} bonds are in many cases 2.0 *vu* or greater. It is common for O_{Ur} anions to be bonded to cations such as K^+ or Na^+, or to accept H bonds (or both), indicating that the bond-valence requirements of O_{Ur} anions are in many instances not met by the U^{6+}–O_{Ur} bond alone. The inability of the bond-valence parameters of Brese & O'Keeffe (1991) to provide appropriate bond valences for U^{6+}–O_{Ur} anions makes interpretation of H bonding difficult in hydrous structures that contain U^{6+}.

It is impossible to fully assess the correct bond-valence requirements of the O_{Ur} bond in hydrous structures, as the O_{Ur} anion in many cases accepts a H bond, but the precise position of the H atom is usually not known. However, H bonding is not a factor in anhydrous structures, and the sum of bond valences at the O_{Ur} position from cations other than U^{6+} may be calculated using the parameters of Brese & O'Keeffe (1991). The variation of the U^{6+}–O_{Ur} bond-length with the bond valence associated with the U^{6+}–O_{Ur} bond (obtained by subtracting the sum of bond valences to O_{Ur} from cations other than U^{6+} from the formal valence of 2.0 *vu*) is shown in Figure 9. The data are reasonably well characterized by a straight line (R^2 = 82%). The equation of the least-squares-fit line indicates that a bond valence of 2.0 *vu* corresponds to a U^{6+}–O bond-length of 1.691 Å.

The expected U–O_{Ur} bond-length where the O_{Ur} atom bonds only to U^{6+} is 1.691 Å, as this corresponds to a bond valence of 2 *vu*. Note that this value cannot be derived using EXAFS spectroscopy of solutions, as the O_{Ur} anion will accept hydrogen bonds from the solvent. This value may be compared to theoretically predicted bond-lengths. Within the Hartree–Fock limit, Pyykkö *et al.* (1994) obtained U–O_{Ur} bond-lengths for

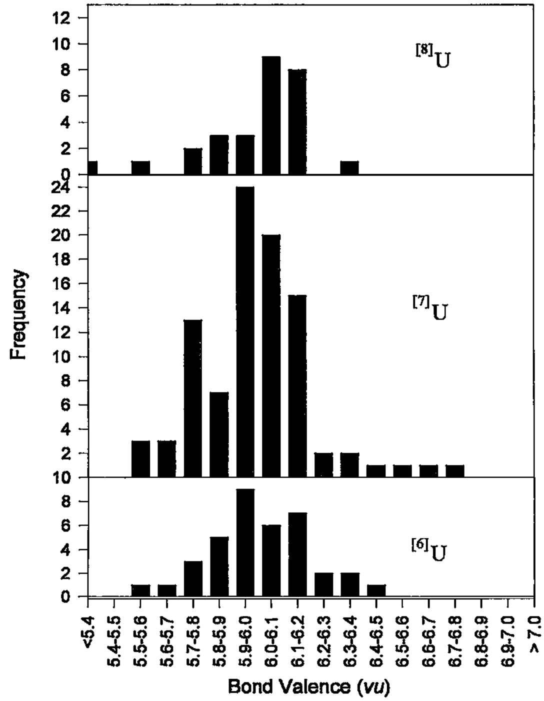

FIG. 10. The distribution of bond-valence sums calculated for the U^{6+} position in well-refined structures using the parameters $^{[6]}U^{6+}$: $R_{ij} = 2.074$ Å, $b = 0.554$ Å; $^{[7]}U^{6+}$: $R_{ij} = 2.045$ Å, $b = 0.510$ Å; $^{[8]}U^{6+}$: $R_{ij} = 2.042$ Å, $b = 0.506$ Å.

the uranyl ion in a vacuum that ranged from 1.66 to 1.72 Å, depending upon the parameterization of the calculation. Van Wezenbeek *et al.* (1991) calculated a bond length of 1.67 Å, obtained using nonrelativistic Hartree–Fock–Slater calculations, with the predicted bond-length expanding to 1.70 Å where relativistic effects are taken into account. Craw *et al.* (1995) obtained a uranyl bond-length of 1.663 Å by using Hartree–Fock calculations. Accounting for correlation of dynamic electrons with approximations gave bond lengths ranging from 1.700 to 1.783 Å.

Bond-valence parameters for U^{6+}–ϕ bonds that will result in a valence of 2.0 *vu* for a U^{6+}–ϕ bond-length of 1.691 Å, and bond-valence sums of 6.0 *vu* at the U^{6+} position have been derived. Such parameters were sought for subsets containing $^{[6]}U^{6+}$, $^{[7]}U^{6+}$ and $^{[8]}U^{6+}$ polyhedra that occur in the well-refined structures listed in Table 1. No suitable value of R_{ij} exists if b is fixed at 0.37, as done by Brese & O'Keeffe (1991). However, variation of both R_{ij} and b provides the desired results. For $^{[6]}U^{6+}$ polyhedra, $R_{ij} = 2.074$ Å, $b = 0.554$ Å; for $^{[7]}U^{6+}$ polyhedra, $R_{ij} = 2.045$ Å, $b = 0.510$ Å; for $^{[8]}U^{6+}$ polyhedra, $R_{ij} = 2.042$ Å, $b = 0.506$ Å. Optimal parameters obtained by fitting to the data for all types of U^{6+} coordination polyhedra are $R_{ij} = 2.051$ Å, $b = 0.519$ Å.

The distribution of bond-valence sums for the U^{6+} positions in well-refined structures (Table 1), calculated using the new parameters for each coordination number, are shown in Figure 10. The range of bond-valence sums for $^{[6]}U^{6+}$, $^{[7]}U^{6+}$ and $^{[8]}U^{6+}$ is much narrower than for those calculated using the parameters of Brese & O'Keeffe (1991) or Brown & Wu (1976) (Fig. 8). Also, the maximum of each distribution is in the range 5.9 to 6.1 *vu*.

The distribution of bond-valence sums for each polyhedron calculated with the parameters $R_{ij} = 2.051$ Å, $b = 0.519$ Å, derived for all U^{6+} coordination geometries, is shown in Figure 11. These parameters perform best for $^{[7]}U^{6+}$, and poorest for $^{[6]}U^{6+}$, where the maximum in the distribution of bond-valence sums is in the range 5.7 to 5.8 *vu*. Optimal results are obtained where the coordination-number-specific parameters are used.

The distribution of bond valence for individual U^{6+}–O_{Ur} bonds in well-refined structures, calculated using the coordination-number-specific parameters, is

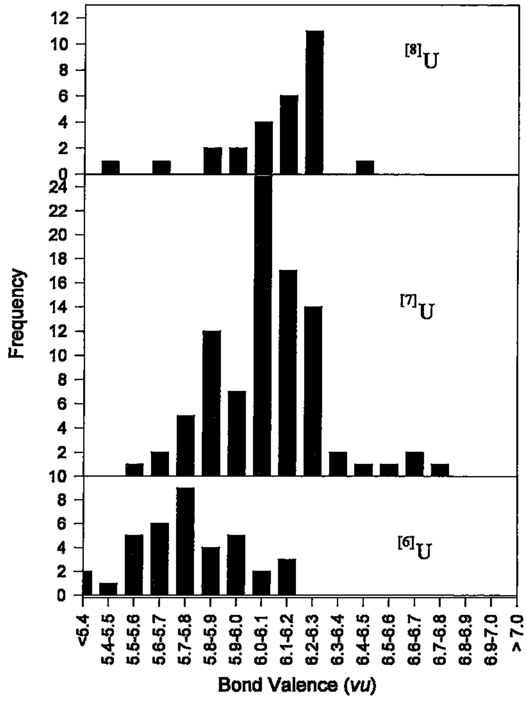

FIG. 11. The distribution of bond-valence sums calculated for the U^{6+} position in well-refined structures using the coordination-independent parameters $R_{ij} = 2.051$ Å, $b = 0.519$ Å.

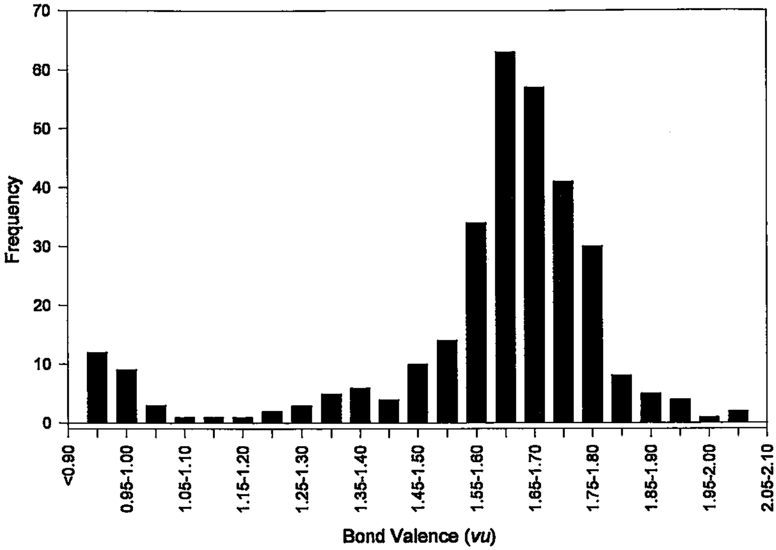

FIG. 12. The distribution of bond-valence sums for U^{6+}–O_{Ur} bonds calculated for well-refined structures using the coordination-specific parameters $^{[6]}U^{6+}$: R_{ij} = 2.074 Å, b = 0.554 Å; $^{[7]}U^{6+}$: R_{ij} = 2.045 Å, b = 0.510 Å; $^{[8]}U^{6+}$: R_{ij} = 2.042 Å, b = 0.506 Å.

TABLE 2. U-O BOND-LENGTHS AND BOND-VALENCE SUMS AT THE URANIUM POSITIONS IN SELECTED STRUCTURES

	U^{5+} in Pentagonal Bipyramidal Coordination								Valence Sum	
	U^{5+}-O (Å)							O-U-O (°)	(*vu*)	Ref.
U_2MoO_8	2.058	2.058	2.113	2.356	2.463	2.733	2.176	178.1	4.92	1
	2.077	2.077	2.319	2.131	2.346	2.146	2.577	164.1	5.12	
$USbO_5$	1.933	2.024	2.505	2.428	2.303	2.135	2.353	173.0	5.23	2
UVO_5	2.050	2.073	2.325	2.206	2.206	2.304	2.304	179.9	5.26	3
$U_5O_{12}Cl$	2.065	2.065	2.246	2.246	2.300	2.300	2.538	178.9	4.95	4
	U^{5+} in Octahedral Coordination									
	U^{5+}-O (Å)									
$NaUO_3$	2.153	2.153	2.151	2.151	2.145	2.145			4.96	5
Ba_2FeUO_6	2.165	2.165	2.165	2.165	2.165	2.165			4.82	6
KUO_3	2.148	2.148	2.148	2.148	2.148	2.148			4.98	7
	U^{4+}, U^{5+} and U^{6+} Polyhedra in Miscellaneous Structures									
	U-O (Å)									
β-U_3O_8	2.080	2.080	2.021	2.287	2.287	2.398	2.398		5.25	8
	1.888	1.888	2.112	2.368	2.368	2.295	2.295		5.96	
	2.087	2.087	2.088	2.088	2.275	2.275			5.03	
α-U_3O_8	2.075	2.075	2.156	2.156	2.257	2.257	2.544		5.27	9
	2.074	2.074	2.178	2.723	2.148	2.130	2.206		5.40	
UNb_2O_7	2.301	2.301	2.312	2.303	2.303	2.303	2.303		4.30	10
UNb_6O_{16}	2.309	2.309	2.277	2.277	2.371	2.371	2.804	2.804	4.06	11
$U(UO_2)(PO_4)_2$	2.219	2.460	2.177	2.171	2.341	2.543	2.318		4.31	12
	1.764	1.767	2.267	2.419	2.362	2.561	2.573		5.91	
UMo_2O_8	2.058	2.058	2.394	2.202	2.324	2.202	2.324		5.17	13

References: (1): Serezhkin *et al.* 1973, (2): Dickens & Stuttard (1992), (3): Dickens *et al.* (1992), (4): Cordfunke *et al.* (1985), (5): Chippindale *et al.* (1989), (6): Grenet *et al.* (1971), (7): Dickens & Powell (1991), (8): Loopstra (1970), (9): Loopstra (1977), (10): Busch & Gruehn (1994), (11): Busch *et al.* (1994), (12): Bénard *et al.* (1994), (13): Cremers *et al.* (1983).

shown in Figure 12. The maximum in the distribution occurs at 1.60 to 1.65 *vu*, indicating that the O_{Ur} atoms usually receive bond-valence contributions in addition to the U^{6+}–O_{Ur} bonds. Only a small number of structures have O_{Ur} anions whose bond-valence requirements are met by the U^{6+}–O_{Ur} bond alone. More commonly, an O_{Ur} atom accepts H bonds or bonds to large monovalent or divalent cations. Note that those U^{6+}–O_{Ur} bonds with valences of ~1.0 *vu* correspond to holosymmetric or near-holosymmetric octahedra, rather than to uranyl ions.

INFERRING THE VALENCE OF URANIUM IN CRYSTAL STRUCTURES

Uranium is only known to occur as U^{4+} and U^{6+} in minerals, although U^{5+} has been reported in about 30 inorganic structures. Furthermore, the recent determination of the crystal structure of ianthinite (Burns *et al.* 1997b) suggests that it may contain U^{5+}. The bond-valence method is often used to determine oxidation states of cations on the basis of bond lengths from refined structures. Although there are parameters available for the calculation of bond valences for U^{4+} and U^{5+} (Brown 1981), it is necessary to first identify the valence of the U cation in order to select the correct set of bond-valence parameters. Here we demonstrate that the new bond-valence parameters R_{ij} = 2.051 Å and b = 0.519 Å, that were derived specifically for U^{6+}, distinguish between U^{4+}, U^{5+} and U^{6+} in well-refined structures.

Coordination geometry and bond-valence sums for U^{5+}

Geometries of polyhedra are presented in Table 2 for seven structures that are reported to contain U^{5+}. The U^{5+} cation occurs either in octahedral coordination, or in a pentagonal bipyramidal coordination that contains a near-linear $(U^{5+}O_2)^{1+}$ ion with a U^{5+}–O bond-length of ~2.05 Å. The latter coordination geometry is similar to the $Ur\phi_5$ polyhedron that is common for U^{6+}, except that the uranyl ion U^{6+}–O bond-length is ~1.8 Å.

The bond-valence parameters R_{ij} = 2.051 Å and b = 0.519 Å give bond-valence sums of ~6 *vu* for U^{6+} in various coordination geometries (Fig. 11). It is informative to calculate the bond-valence sums with these parameters for the U positions in phases containing U^{5+}; these values are given in Table 2. The bond-valence sums for the U^{5+} sites are all close to 5 *vu*, with a range from 4.82 to 5.26 *vu*. This is consistent with the fact that these structures contain U^{5+}, and that the bond-valence parameters are effective in distinguishing U^{5+} and U^{6+}. We will now consider examples to demonstrate further how the bond-valence parameters may be used to distinguish valences of uranium.

Specific examples of valence determination of U in structures

The structure of β–U_3O_8 is considered to contain U^{5+} and U^{6+}, with the formula $U^{5+}{}_2U^{6+}O_8$ (Loopstra 1970). There are three U atoms located in general positions in the space group *Cmcm* (Loopstra 1970); two are coordinated by seven anions in pentagonal-bipyramidal arrangements, and one is in octahedral coordination (Table 2). There are two reasonable possibilities here: either both pentagonal bipyramids contain U^{6+} and the octahedron contains U^{4+}, or one pentagonal bipyramid contains U^{6+} and the other two polyhedra contain U^{5+}. The bond-valence sums at each site are $U(1)$ = 5.25, $U(2)$ = 5.96 and $U(3)$ = 5.03 *vu* (Table 2), consistent with the presence of two U^{5+} and one U^{6+} in the structure of β–U_3O_8.

The structure of α–U_3O_8 is also considered to contain both U^{5+} and U^{6+}, although no uranyl ion is present in the refined structure. There are two U positions in the structure, which crystallizes in the space group *C2mm* (Loopstra 1977). Both sites are coordinated by seven anions in a pentagonal-bipyramidal arrangement, and both polyhedra contain near-linear O–U–O clusters with bond lengths of ~2.07 Å. The absence of a uranyl ion with a U^{6+}–O bond length of ~1.8 Å suggests that neither site contains exclusively U^{6+}. The bond-valence sums for the sites are $U(1)$ = 5.27 and $U(2)$ = 5.40 *vu*, indicating that each site probably contains both U^{5+} and U^{6+}, and as there are twice as many $U(2)$ sites as $U(1)$ sites in the structure, this gives a total U valence of 16.07 *vu*, which is consistent with the formula $U^{5+}{}_2U^{6+}O_8$. However, note that these bond-valence sums are also consistent with U^{4+} – U^{6+} disorder and the formula $U^{4+}U^{6+}{}_2O_8$, as U^{4+} – U^{6+} disorder would result in bond-valence sums of 5.3 *vu* per site in this case.

The structures of UNb_2O_7 (Busch & Gruehn 1994) and UNb_6O_{16} (Busch *et al.* 1994) are each reported to contain U^{4+}, and the U atoms are coordinated by seven and eight O atoms, respectively. The polyhedral bond-lengths are summarized in Table 2, and the bond-valence sums calculated for the uranium sites are 4.30 and 4.06 *vu* for UNb_2O_7 and UNb_6O_{16}, respectively. These results show that the bond-valence parameters also successfully distinguish U^{4+}.

The structure of $U(UO_2)(PO_4)_2$ (Bénard *et al.* 1994) is reported to contain both U^{4+} and U^{6+}, making it one of the relatively few structures known to contain U with both of these valence states. There are two U positions in the structure, which crystallizes in the space group $P\bar{1}$; both are positions coordinated by seven anions in pentagonal-bipyramidal arrangements. Only the $U(2)$ site contains a uranyl ion, which is consistent with the presence of U^{6+} (Table 2). The bond-valence sums calculated for the U sites are $U(1)$

TABLE 3. SUMMARY OF POLYHEDRAL POLYMERIZATION IN URANYL STRUCTURES

	$^{[6]}U^{6+}$	$^{[7]}U^{6+}$	$^{[8]}U^{6+}$		$^{[6]}U^{6+}$	$^{[7]}U^{6+}$	$^{[8]}U^{6+}$
$^{[6]}U^{6+}$	8c,1e	11e	-	$Si^{4+}\phi_4$	-	6e	-
$^{[7]}U^{6+}$	11e	1c,54e	11e	$Cr^{6+}\phi_4$	-	2c	-
$^{[8]}U^{6+}$	-	11e	14e	$Te^{4+}\phi_4$	-	1e	-
$B^{3+}\phi_3$	-	1c,3e	1e	$P^{5+}\phi_4$	9c	3c,1e	9e
$C^{4+}\phi_3$	-	-	2e	$S^{6+}\phi_4$	-	7c	-
$Se^{4+}\phi_3$	-	-	2e	$Nb^{5+}\phi_5$	-	2e	-
$Mo^{6+}\phi_4$	-	1c	-	$V^{5+}\phi_5$	-	6e	-
$As^{5+}\phi_4$	6c	1e	-	$Mo^{6+}\phi_6$	-	2e	-
$Se^{6+}\phi_4$	-	1c	-	$Mo^{6+}\phi_8$	-	-	1e

c = share corners, e = share edges, numbers = number of structures with type of polymerization.

= 4.31 and $U(2)$ = 5.91 *vu*. These values are consistent with $U(1)$ containing U^{4+} and $U(2)$ containing U^{6+}, as reported by Bénard *et al.* (1994).

The structure of UMo_2O_8 is reported to contain U^{4+} and Mo^{6+} (Cremers *et al.* 1983). The structure contains one U position that is coordinated by seven anions in a pentagonal-bipyramidal arrangement (Table 2). There is an approximately linear O–U–O cluster with U–O bond-lengths of 2.06 Å in the polyhedron. The polyhedral geometry is similar to that observed in various polyhedra that contain U^{5+} (Table 2), and the bond-valence sum calculated for the site is 5.17 *vu*. The structure of U_2MoO_8, which is reported to contain U^{5+} (Serezhkin *et al.* 1973), has two similar coordination polyhedra about the U atoms, and bond-valence sums are $U(1)$ = 4.92 and $U(2)$ = 5.12 *vu* (Table 2). Thus, the structure of UMo_2O_8 possibly contains U^{5+}, rather than U^{4+} as reported (Cremers *et al.* 1983), and the chemical composition may be more complicated than that indicated.

The examples provided above demonstrate the efficacy of our revised bond-valence parameters for U^{6+} for determining the valence states of U atoms in refined structures. As such, they should be useful in the analysis of new crystal structures.

CONSTRAINTS ON POLYMERIZATION OF POLYHEDRA IN U^{6+}-BEARING STRUCTURES

Important factors controlling the polymerization of polyhedra in any oxide or oxysalt structure include cation valence, cation coordination number, and the lengths of edges of polyhedra. The rules of Pauling (1960) indicate that cation polyhedra with low coordination number and high valence will tend not to share elements of the polyhedra; in cases where they do, the sharing of corners will be more favorable than the sharing of edges or faces of the polyhedra. In most structures that contain U^{6+}, the U^{6+} cation forms a $(U^{6+}O_2)^{2+}$ uranyl ion. It is common for uranyl polyhedra to share edges with cation polyhedra that contain cations with valences of up to 5+, and also with other uranyl polyhedra, indicating that the uranyl ion behaves more like a divalent cation than a hexavalent cation.

Where the sharing of edges of polyhedra does occur, the degree of mismatch between the ideal length of edges of the polyhedra is an important factor in determining the stability of the structure. Where a uranyl polyhedron shares an edge with another polyhedron of higher bond-valence, the shared edge is always an equatorial edge because the bond-valence requirements of the O_{Ur} anions are largely satisfied by the U^{6+}–O_{Ur} bond (~1.7 *vu*). Assuming that the equatorial anions and the U^{6+} cation are coplanar, and that the bond angles are ideal, estimates of ideal equatorial edge-lengths of polyhedra for $Ur\phi_4$, $Ur\phi_5$ and $Ur\phi_6$ polyhedra are 3.22, 2.79 and 2.47 Å, respectively.

The structural hierarchy of U^{6+} phases presented by Burns *et al.* (1996) includes 106 phases that have structures containing infinite sheets of polyhedra. These structures account for 78% of U minerals for which structures are known, many of which may form owing to the oxidative dissolution of spent nuclear fuel. The nature of the polymerization of polyhedra in each of the 106 structures based upon sheets is summarized in Table 3, where the mode of polymerization is indicated by a letter, and either occurs by the sharing of edges (e) or corners (c) of polyhedra, and the numbers indicate the number of structures that contain each type of polymerization.

The sharing of edges between two $Ur\phi_4$ polyhedra in a sheet only occurs in the structure of $Cs_4[(UO_2)_5O_7]$; the scarcity of $Ur\phi_4$ polyhedra that share edges is presumably due to the Coulombic repulsion of the U^{6+} cations, which are separated by 3.56 Å only in $Cs_4[(UO_2)_5O_7]$. Where $Ur\phi_4$ polyhedra are present in a sheet, it is much more common for the $Ur\phi_4$ polyhedra to share corners only, as in some sheets with the autunite anion-topology (Fig. 4b of Burns *et al.* 1996), or the $Ur\phi_4$ polyhedra share edges with $Ur\phi_5$ polyhedra. In contrast, $Ur\phi_5$ polyhedra usually polymerize with other $Ur\phi_n$ polyhedra in sheets by sharing edges; this includes all of the $Ur\phi_4$, $Ur\phi_5$, and $Ur\phi_6$ polyhedra, although the sharing of edges with other $Ur\phi_5$ polyhedra is most common. Where $Ur\phi_6$ polyhedra are present in a sheet, polymerization occurs by sharing edges with either $Ur\phi_5$ or $Ur\phi_6$ polyhedra, but never by sharing edges with $Ur\phi_4$ polyhedra, presumably owing to the large mismatch of ideal edge-lengths of the polyhedra.

The details of how other polyhedra of higher bond-valence cations polymerize with $Ur\phi_n$ polyhedra are also summarized in Table 3. The mode of polymerization is dependent on both cation charge and polyhedron size, which, in turn, is dependent on cation radius and the number of coordinating anions. In the case of three-coordinated cations in sheets, the triangles usually share an edge with a $Ur\phi_n$ polyhedron. Both $C^{4+}\phi_3$ and $Se^{4+}\phi_3$ share edges with $Ur\phi_6$ polyhedra, whereas $B^{3+}\phi_3$ triangles share edges with both $Ur\phi_5$ and $Ur\phi_6$ polyhedra, or they share only corners with $Ur\phi_5$ polyhedra.

Several four-coordinated cations occur in the sheets of U^{6+} phases (Table 3), and the modes of polymerization are dependent upon cation valence. Where the cation valence is 6+, the tetrahedra share corners only with $Ur\phi_n$ polyhedra; edge sharing with $Ur\phi_n$ polyhedra does not occur, presumably owing to Coulombic repulsion between the tetrahedrally coordinated cation and U^{6+}. The only known exception in a U^{6+} phase is found in the structure of $K_4[(UO_2)(SO_4)_3]$, which contains finite clusters in which $S\phi_4$ tetrahedra share edges with $Ur\phi_5$ polyhedra (Mikhailov *et al.* 1977). Where the cation charge is 5+, the polyhedra share both corners and edges with $Ur\phi_n$ polyhedra. The $As^{5+}\phi_4$ tetrahedron commonly occurs in sheets that are based upon the autunite anion-topology (Fig. 4a of Burns *et al.* 1996), where it shares only corners with $Ur\phi_4$ polyhedra. In the structure of $Mg[(UO_2)(AsO_4)]_2(H_2O)_4$, the $As^{5+}\phi_4$ tetrahedra share edges with $Ur\phi_5$ polyhedra (Bachet *et al.* 1991), and the sheet has the uranophane anion-topology (Burns *et al.* 1996). The $P^{5+}\phi_4$ tetrahedron also occurs in sheets that are based upon the autunite anion-topology, where it shares corners with $Ur\phi_4$ polyhedra. In addition, $P^{5+}\phi_4$ tetrahedra commonly occur in sheets based upon the phosphuranylite anion-topology (Fig. 8a of Burns *et al.* 1996), where the tetrahedra share edges with $Ur\phi_6$ polyhedra.

The As^{5+}–O and P^{5+}–O bond lengths, inferred from sums of effective ionic radii (Shannon 1976), are 1.69 and 1.53 Å, respectively. Assuming ideal bond-angles of these tetrahedra, ideal edge-lengths of $As^{5+}\phi_4$ and $P^{5+}\phi_4$ tetrahedra are 2.76 and 2.50 Å, respectively. Thus, the ideal edge-lengths of $As^{5+}\phi_4$ and $P^{5+}\phi_4$ tetrahedra are best matched to $Ur\phi_5$ and $Ur\phi_6$ polyhedra, respectively. The edge-length of the $As^{5+}\phi_4$ tetrahedron is incompatible with a $Ur\phi_6$ polyhedron, which explains why no structures contain $As^{5+}\phi_4$ tetrahedra in sheets with the phosphuranylite anion-topology. Where the tetrahedron contains a cation with a valence of 4+, the tetrahedron always shares an edge with a $Ur\phi_5$ polyhedron. Most examples involve the $Si^{4+}\phi_4$ tetrahedron, which has an ideal edge-length of 2.64 Å, a fair match for the ideal $Ur\phi_5$ polyhedron. All uranyl silicate sheet structures contain sheets that are based upon the uranophane anion-topology (Fig. 6a of Burns *et al.* 1996), where each $Si\phi_4$ tetrahedron shares an edge with one $Ur\phi_5$ polyhedron and a corner with another.

The only five-coordinated polyhedra that occur in the sheets of U^{6+} phases are $Nb^{5+}\phi_5$ and $V^{5+}\phi_5$ square pyramids. In all cases, the square pyramids share edges with $Ur\phi_5$ polyhedra, and all but one occur in sheets based upon the francevillite anion-topology (Fig. 7b of Burns *et al.* 1996a).

Excluding U^{6+}, polyhedra with cations of higher bond-valence and coordination number greater than five are rare. The only instances are two examples of $Mo^{6+}\phi_6$ octahedra, each of which share edges with $Ur\phi_5$ polyhedra in sheets based upon the iriginite anion-topology (Fig. 7e of Burns *et al.* 1996), and a $Mo^{6+}\phi_8$ hexagonal bipyramid that shares edges with $Ur\phi_6$ polyhedra in the structure of umohoite, $[(UO_2)(MoO_4)](H_2O)_4]$ (Makarov & Anikina 1963) (Fig. 10a of Burns *et al.* 1996).

Considering each of the U^{6+} structures that are based upon infinite sheets, the following observations may be made:

(1) $Ur\phi_4$ polyhedra commonly share corners only with other uranyl polyhedra, and where $Ur\phi_4$ polyhedra share edges with other uranyl polyhedra, it is almost invariably with $Ur\phi_5$ polyhedra.

(2) No structure contains either a $Ur\phi_5$ or a $Ur\phi_6$ polyhedron that shares a corner only with another uranyl polyhedron; where polymerization occurs, it involves the sharing of edges between polyhedra.

(3) $Ur\phi_5$ polyhedra most commonly share edges with other $Ur\phi_5$ polyhedra, although edge-sharing with both $Ur\phi_4$ or $Ur\phi_6$ polyhedra also is common.

(4) $Ur\phi_6$ polyhedra commonly share edges with either $Ur\phi_5$ or $Ur\phi_6$ polyhedra, but never with $Ur\phi_4$ polyhedra.

(5) The most important factor in determining the mode of polymerization between $Ur\phi_n$ polyhedra and other cation polyhedra is cation charge.

(6) Those cation polyhedra (excluding U^{6+} polyhedra) with high-charge cations (6+) and low coordination number (<6) do not commonly share edges with $Ur\phi_n$ polyhedra.

(7) Polyhedra containing pentavalent cations regularly share edges with $Ur\phi_5$ and $Ur\phi_6$ polyhedra, but they also commonly share only corners with $Ur\phi_n$ polyhedra.

(8) Cation polyhedra with lower-charge cations (≤4) almost invariably share edges with $Ur\phi_5$ or $Ur\phi_6$ polyhedra, but never with $Ur\phi_4$ polyhedra.

(9) An important geometrical factor for the polymerization of polyhedra is the edge-length mismatch between the ideal polyhedra, which is mainly due to cation size. Small degrees of mismatch favor edge-sharing, whereas larger degrees of mismatch favor the sharing of corners.

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RECOMMENDED NOMENCLATURE FOR ZEOLITE MINERALS: REPORT OF THE SUBCOMMITTEE ON ZEOLITES OF THE INTERNATIONAL MINERALOGICAL ASSOCIATION, COMMISSION ON NEW MINERALS AND MINERAL NAMES

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