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THE STEREOCHEMISTRY AND CHEMICAL COMPOSITION OF INTERSTITIAL COMPLEXES IN URANYL-OXYSALT MINERALS

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ABSTRACT

The crystal structures and chemical compositions of uranyl-oxysalt minerals (primarily with sheet structural units) are interpreted in terms of the binary representation – bond-valence approach to the structure and chemistry of oxysalts. There is a coherent relation between the average basicity of the structural unit and [CN_{in}], the average number of bonds to oxygen atoms of the structural unit from the interstitial complex and adjacent structural units. This relation allows calculation of the range of Lewis basicity for specific structural units. The Lewis acidity of an interstitial complex is expressed graphically as a function of the amounts and coordination numbers of monovalent, divalent and trivalent interstitial cations and the amount of interstitial transformer (H_2O) groups. The range in Lewis basicity for a specific structural unit may also be expressed graphically, and where there is overlap of the Lewis acidity and Lewis basicity, the valence-matching principle is satisfied, and the details of the possible interstitial complexes can be derived. There are three distinct types of interstitial (H_2O) groups: transformer, non-transformer and inverse-transformer. Inverse-transformer (H_2O) groups accept three bonds from cations, other (H_2O) groups and (OH) groups of the structural unit. Their occurrence is rare and is limited to minerals with low bond-valence distribution factors. Detailed predictions of the number of transformer, non-transformer and inverse-transformer (H_2O) groups in the minerals of the meta-autunite, uranophane, phosphuranylite, carnotite, zippeite and uranyl-hydroxy-hydrate groups (and synthetic analogues) are in good agreement with the observed chemical compositions.

Keywords: H_2O groups, uranyl minerals, bond-valence theory, acidity, basicity, valence-matching principle, structural unit, interstitial complex.

SOMMAIRE

Les structures cristallines et les compositions chimiques des minéraux oxysels uranylés (surtout ceux ayant un module structural en feuillet) sont ici interprétés en termes d'une représentation binaire des compositions et des structures des oxysels, et de leurs valences de liaisons. Il existe une relation cohérente entre la basicité moyenne de l'unité structurale et [CN_{in}], le nombre moyen de liaisons impliquant les atomes d'oxygène de l'unité structurale provenant du complexe interstitiel et des unités structurales adjacentes. Cette relation nous permet de calculer l'intervalle des valeurs de la basicité de Lewis pour certaines unités spécifiques. L'acidité de Lewis d'un complexe interstitiel s'exprime graphiquement en fonction du nombre d'atomes monovalents, bivalents et trivalents, et de leur coordinence, ainsi que du nombre de groupes (H_2O) transformateurs interstitiels. L'intervalle des valeurs de basicité de Lewis pour une unité structurale spécifiée peut aussi être exprimée graphiquement. Là où les distributions des valeurs de basicité et d'acidité de Lewis se chevauchent, le principe de concordance des valences est satisfait, et les détails des complexes interstitiels possibles peuvent être dérivés. Il y a trois types distincts de groupes (H_2O) interstitiels: groupes transformateurs, groupes non-transformateurs, et groupes transformateurs inverses. Ces derniers acceptent trois liaisons de cations, d'autres groupes (H_2O), et des groupes (OH) de l'unité structurale. Leur présence est rare, étant limitée aux minéraux ayant de faibles facteurs de distribution des valences de liaison. Des prédictions détaillées du nombre de groupes (H_2O) transformateurs, non-transformateurs et transformateurs inverses dans les minéraux des groupes méta-autunite, uranophane, phosphuranylite, carnotite, zippéite et uranyl-hydroxy-hydrates (et leurs analogues synthétiques) concordent bien avec les compositions chimiques observées.

(Traduit par la Rédaction)

Mots-clés: groupes H_2O, minéraux uranylés, théorie des valences de liaison, acidité, basicité, principe de la concordance des valences, unité structurale, complexe interstitiel.

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Introduction

The mineralogy and geochemistry of U have assumed considerable practical importance as society has begun to cope with the environmental issues arising from mining and milling of U ores and the disposal of U-based radioactive waste. These issues have led to a major increase in the amount of work done on the structure (Burns 1999a, Burns *et al.* 1996, 1997) and paragenesis (Finch & Murakami 1999) of uranium minerals. Burns & Finch (1999) presented detailed reviews of most aspects of the mineralogy and geochemistry of uranium, particularly with regard to the resulting environmental implications. When dealing with hydroxy-hydrated oxysalt minerals [*e.g.*,althupite, $AlTh[(UO_2)\{(UO_2)_3(PO_4)_2(OH)O\}_2](OH)_3(H_2O)_{15}]$, Piret & Deliens 1987], structural complexity and the difficulty in dealing with (OH) and (H_2O) groups preclude standard theoretical approaches to mineral stability. Moreover, additional issues arise when considering complex minerals: (1) What controls the details of their chemical composition? For example, why are there five (H_2O) groups in uranophane-beta, $^{[8]}Ca(H_2O)_5[(UO_2)(SiO_3OH)]_2$, but only one interstitial (H_2O) group in kasolite, $^{[8]}Pb(H_2O)[(UO_2)(SiO_4)]$, even though both minerals contain cations in [8]-coordination? (2) Such minerals are normally stable over a small range of external conditions (*e.g.*, Eh, pH, T, P) and in many cases are associated with many (*e.g.*, > 20) other complex minerals of similar composition in some parageneses. What factors control their relative stabilities?

The approach developed by Hawthorne (1983, 1985, 1986, 1990, 1994, 1997), Schindler & Hawthorne (2001a, b, c, 2004) and Schindler *et al*. (2000) can address these questions from a structural perspective. In a recent paper, Schindler & Hawthorne (2004) applied these ideas to uranyl-oxide-hydroxy-hydrate minerals. Here, we develop a method to more accurately predict the number and type of interstitial (H_2O) groups, and combine this with previously developed theory to predict the nature of the interstitial complexes in a wide range of uranyl-oxysalt minerals with sheet structural units. Appendix A lists the definitions of various terms pertaining to this general approach to mineral stability.

A Comment on Minerals Versus Synthetic Compounds

It is generally not realized that there is an intrinsic difference between minerals and synthetic compounds: minerals crystallize in a system with a large number of components, whereas synthetic compounds have been grown in chemical systems with a limited number of components. As a consequence, minerals are able to select the most appropriate components when forming, whereas synthetic compounds must make do with what the experimenter has provided them. As a result, synthetic compounds are commonly far more strained than minerals; they generally show much higher deviations from the valence-sum rule of bond-valence theory (Brown 1981, 2002), and they can show very unusual valence states and coordination numbers that are forced on the compounds by the limited chemical elements at their disposal, *e.g.*, $K_2S_2O_7$ (Ståhl *et al.* 2005), $KCoO_2$ (Bernhardt & Hoppe 1994), $K_3[FeO_2]$ and $K_3[NiO_2]$ (Bernhardt & Hoppe 1993). We are trying to understand the factors controlling the chemical composition and stability of minerals, and as far as we are aware, ours is the only work that is attempting to do this from a structural perspective. At the present state of affairs, it is sensible to avoid highly strained structures until we understand more about what is controlling the chemical composition and stability of such complicated phases. Thus we are tending to focus on minerals rather than synthetic compounds at the present time, as we expect some (highly strained) synthetic compounds to deviate from our current findings.

Hydrogen Bonding

Crystal-structure refinement of many uranyl-oxysalt minerals has not resolved the location of the H atoms. Where this is the case, we cannot define transformer and non-transformer (H_2O) groups (Schindler & Hawthorne 2001a, 2004, Hawthorne & Schindler 2007) and calculate the number of bonds from the interstitial complex to the structural unit (Schindler & Hawthorne 2001a, b, c). Hence, we can use only the small number of uranyl-oxysalt minerals for which H-positions are known. Table 1 lists uranyl minerals (1) that form in aqueous solution (*i.e.*, below the critical point of water), (2) that do not contain any disordered cations in their interstices [except for boltwoodite, for which Burns (1998a) presented an ordered model], and (3) for which the hydrogen-bonding schemes could be unequivocally assigned on the basis of local stereochemistry and bond-valence requirements. Appendix B gives two examples of how this was done.

Binary Structural Representation

We can divide any complex structure into two components: (1) the *structural unit*, the strongly bonded part of the structure, and (2) the *interstitial complex*, the assemblage of cations, anions and (H_2O) groups that weakly bind the structural units into a continuous structure (Hawthorne 1983, 1985, 1986, 1990). The constituents of the structure can be considered in a simple additive fashion to produce aggregate sets of properties (*e.g.*, charge, Lewis basicity, Lewis acidity) for the structural unit and the interstitial complex. We may then use the principle of correspondence of Lewis acidity and basicity (Hawthorne & Schindler 2007), a mean-field equivalent of the valence-matching principle (Brown 1981, 2002), to examine the interaction of the

TABLE 1. SELECTED URANYL OXYSALT MINERALS

Mineral	Chemical composition	Interstitial complex[1]	Lewis acidity [*vu*]	$[CN]_{in}$	CDA [*vu*]	Ref.
		Frameworks				
Soddyite	$[(UO_2)_2(SiO_4)(H_2O)_2]$		0.20	0.40	0.08	1
Parsonsite	$[(UO_2)(PO_4)_2{}^{[1+8]}Pb^{2+}{}^{[2+4]}Pb^{2+}]$		0.21	1.20	0.25	2
Moctezumite	$[(UO_2)(TeO_3)_2{}^{[1+6]}Pb^{2+}]$		0.25	0.75	0.19	3
		Sheets				
Meta-ankoleite	$K[(UO_2)(PO_4)](D_2O)_3$	$\{^{[8]}K(D_2O)_0{}^{[5]}(D_2O)_1{}^{[4]}(D_2O)_2\{D_2O\}_0\}^+$	0.14	1.17	0.17	4
Sengierite	$Cu^{2+}{}_2(OH)_2[(UO_2)_2(V_2O_8)](H_2O)_6$	$\{^{[6]}Cu_2(H_2O)_4{}^{[5]}(H_2O)_0(H_2O)_2(H_2O)_0{}^{[5]}(OH)_2\}^{4+}$	0.17	1.00	0.17	5
Boltwoodite	$K[(UO_2)(SiO_3OH)](H_2O)$	$\{^{[7]}K(H_2O)_0{}^{[5]}(H_2O)_1(H_2O)_0(H_2O)_0\}^+$	0.17	1.17	0.20	6
Natroboltwoodite	$Na[(UO_2)(SiO_3OH)](H_2O)$	$\{^{[6]}Na(H_2O)_0{}^{[5]}(H_2O)_1(H_2O)_0(H_2O)_0\}^+$	0.20	1.00	0.20	6
Cuprosklodowskite	$Cu^{2+}[(UO_2)(SiO_3OH)]_2(H_2O)_6$	$\{^{[6]}Cu^{2+}(H_2O)_2{}^{[5]}(H_2O)_0(H_2O)_2(H_2O)_2\}^{2+}$	0.24	0.83	0.20	7
Kasolite	$[(UO_2)(SiO_4)^{[2+6]}Pb^{2+}](H_2O)$	$\{(H_2O)_0{}^{[5]}(H_2O)_0(H_2O)_0(H_2O)_1\}^0$	0.17	1.00	0.17	8
Phurcalite	$Ca_2[(UO_2)_3(PO_4)_2O_2](H_2O)_7$	$\{^{[8]}Ca^{[7]}Ca(H_2O)_3(H_2O)_3(H_2O)_1\}^{4+}$	0.24	1.12	0.25	9
Dumonite	$Pb^{2+}{}_2[(UO_2)_3(PO_4)_2O_2]$	$\{^{[8]}Pb_2(H_2O)_2{}^{[5]}(H_2O)_0(H_2O)_3(H_2O)_0\}^{4+}$	0.22	1.13	0.25	10
Upalite	$^{[6]}Al[(UO_2)_3(PO_4)_2(OH)O](H_2O)_7$	$\{^{[6]}Al(H_2O)_6{}^{[5]}(H_2O)_0(H_2O)_0(H_2O)_1\}^{3+}$	0.23	0.81	0.20	11
Rutherfordine	$[(UO_2)(CO_3)]$	–	0.00	0.00	0.00	12
Johannite	$Cu^{2+}(H_2O)_4[^{[7]}(UO_2)_2(OH)_2(SO_4)_2]$	$\{^{[6]}Cu^{2+}(H_2O)_4(H_2O)_0(H_2O)_4\}^{2+}$	0.20	0.86	0.17	13
Iriginite	$[^{[7]}(UO_2)(^{[6]}MoO_3OH)_2(H_2O)](H_2O)$	$\{(H_2O)_0{}^{[5]}(H_2O)_0(H_2O)_0(H_2O)_1\}^0$	0.20	0.36	0.07	14
Schmitterite	$[^{[7]}(UO_2)(TeO_3)]$		0.00	0.00	0.00	15
Guilleminite	$Ba(H_2O)_3[(UO_2)_3O_2(SeO_3)_2]$	$\{^{[10]}Ba(H_2O)_3{}^{[5]}(H_2O)_0(H_2O)_0(H_2O)_0\}^{2+}$	0.15	0.93	0.14	16
Marthozite	$Cu^{2+}[(UO_2)_3O_2(SeO_3)_2](H_2O)_8$	$\{^{[6]}Cu(H_2O)_4{}^{[5]}(H_2O)_0(H_2O)_0(H_2O)_4\}^{2+}$	0.20	0.71	0.14	17
Vandenbrandeite	$[(UO_2)Cu(OH)_4]$		0.20	0.60	0.13	18
Uranophane	$Ca[(UO_2)SiO_3(OH)]_2(H_2O)_5$	$\{^{[7]}Ca(H_2O)_1{}^{[5]}(H_2O)_0(H_2O)_3(H_2O)_1\}^{2+}$	0.24	0.83	0.20	19
Natrozippeite	$Na_5[(^{[7]}UO_2)_8(SO_4)_4O_6(OH)_3](H_2O)_{12}$	$\{^{[7]}Na_3{}^{[6]}Na_2(H_2O)_0{}^{[5]}(H_2O)_0(H_2O)_{12}(H_2O)_0\}^{5+}$	0.17	0.90	0.14	20
Becquerelite	$Ca[(UO_2)_8O_4(OH)_8](H_2O)_8$	$\{^{[8]}Ca(H_2O)_0{}^{[5]}(H_2O)_0(H_2O)_4(H_2O)_4\}^{2+}$	0.22	0.63	0.145	21
Magnesiozippeite	$Mg^{2+}[(UO_2)_2(SO_4)O_2](H_2O)_{3.5}$	$\{^{[6]}Mg(H_2O)_3{}^{[5]}(H_2O)_0(H_2O)_0(H_2O)_{0.5}\}^{2+}$	0.22	0.90	0.20	20
Zinczippeite	$Zn^{2+}[(UO_2)_2(SO_4)O_2](H_2O)_{3.5}$	$\{^{[6]}Zn(H_2O)_3{}^{[5]}(H_2O)_0(H_2O)_0(H_2O)_{0.5}\}^{2+}$	0.22	0.90	0.20	20
Cobaltzippeite	$Co^{2+}[(UO_2)_2(SO_4)O_2](H_2O)_{3.5}$	$\{^{[6]}Co(H_2O)_3{}^{[5]}(H_2O)_0(H_2O)_0(H_2O)_{0.5}\}^{2+}$	0.22	0.90	0.20	20
Autunite*	$Ca[(UO_2)(PO_4)]_2(H_2O)_{11}$	$\{^{[7]}Ca(H_2O)_3{}^{[5]}(H_2O)_2(H_2O)_2(H_2O)_4\}^{2+}$	0.25	0.66	0.17	22
Torbernite	$Cu^{2+}[(UO_2)_2(PO_4)_2](H_2O)_{12}$	$\{^{[6]}Cu(H_2O)_4{}^{[5]}(H_2O)_0(H_2O)_0(H_2O)_8\}^{2+}$	0.20	0.83	0.17	23
Zeunerite	$Cu^{2+}[(UO_2)_2(AsO_4)_2](H_2O)_{12}$	$\{^{[6]}Cu(H_2O)_4{}^{[5]}(H_2O)_0(H_2O)_0(H_2O)_8\}^{2+}$	0.20	0.83	0.17	23
Metatorbernite	$Cu^{2+}[(UO_2)_2(PO_4)_2](H_2O)_8$	$\{^{[6]}Cu(H_2O)_4{}^{[5]}(H_2O)_0(H_2O)_0(H_2O)_4\}^{2+}$	0.20	0.83	0.17	23
Metazeunerite	$Cu^{2+}[(UO_2)_2(AsO_4)_2](H_2O)_8$	$\{^{[6]}Cu(H_2O)_4{}^{[5]}(H_2O)_0(H_2O)_0(H_2O)_4\}^{2+}$	0.20	0.83	0.17	23
Curite	$Pb^{2+}{}_3(H_2O)_2[(UO_2)_4O_4(OH)_3]_2$	$\{^{[10]}Pb_3(H_2O)_0{}^{[5]}(H_2O)_2(H_2O)_0(H_2O)_0\}^{6+}$	0.21	1.13	0.24	24
Schoepite	$[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$	$\{(H_2O)_0(H_2O)_0(H_2O)_0(H_2O)_{12}\}^0$	0.20	0.40	0.08	25
Roubaultite	$Cu^{2+}[(UO_2)_3(CO_3)_2O_2(OH)_2](H_2O)_4$	$\{^{[6]}Cu_2(H_2O)_4{}^{[5]}(H_2O)_0(H_2O)_0(H_2O)_0\}^{4+}$	0.24	1.13	0.276	26
Agrinierite	$K_2(Ca_{0.65}Sr_{0.35})[(UO_2)_3O_3(OH)_2]_2(H_2O)_5$	$\{^{[9]}Ca^{[7]}K^{[9]}K(H_2O)_1{}^{[5]}(H_2O)_3(H_2O)_1(H_2O)_0\}^{4+}$	0.17	1.22	0.18	27
		Chain				
Ulrichite	$CaCu^{2+}[(UO_2)(PO_4)_2](H_2O)_4$	$\{^{[8]}Ca^{[6]}Cu^{2+}(H_2O)_2{}^{[5]}(H_2O)_0(H_2O)_2(H_2O)_0\}^{4+}$	0.25	1.60	0.40	28
Demesmaekerite	$Pb^{2+}{}_2Cu^{2+}{}_5(OH)_6[(UO_2)(SeO_3)_3]_2(H_2O)_2$	$\{^{[9]}Pb_2{}^{[6]}Cu_5(H_2O)_0{}^{[5]}(H_2O)_0(H_2O)_2(H_2O)_0{}^{[3]}(OH)_6\}^{8+}$	0.235	1.64	0.36	29
Derriksite	$Cu^{2+}{}_4(OH)_6[(UO_2)(SeO_3)_2]$	$\{^{[6]}Cu_4{}^{[3]}(OH)_6\}^{2+}$	0.17	1.50	0.25	30
Walpurgite						
Orthowalpurgite	$[Bi^{3+}{}_4O_4(H_2O)_2(UO_2)(AsO_4)_2]$		0.20	0.25	0.05	31
Deloryite	$Cu^{2+}{}_4(OH)_6[(UO_2)(MoO_4)_2]$	$\{^{[6]}Cu_4{}^{[3]}(OH)_6\}^{2+}$	0.17	1.20	0.20	32
		Cluster				
Bayleyite	$Mg_2[(UO_2)(CO_3)_3](H_2O)_{18}$	$\{^{[6]}Mg_2(H_2O)_{10}{}^{[5]}(H_2O)_0(H_2O)_2(H_2O)_6\}^{4+}$	0.18	2.00	0.36	33
Swartzite	$[^{[6]}Ca^{[6]}Mg[(UO_2)(CO_3)_3](H_2O)_{12}$	$\{^{[8]}Ca^{[6]}Mg(H_2O)_6{}^{[5]}(H_2O)_0(H_2O)_4(H_2O)_0\}^{4+}$	0.18	2.00	0.36	34
Čejkaite	$^{[5.5]}Na_4[(UO_2)(CO_3)_3]$	$\{^{[5.25]}Na_4\}^{4+}$	0.18	2.00	0.36	35
Andersonite	$Na_2Ca[(UO_2)(CO_3)_3](H_2O)_{5.33}$	$\{^{[9]}Na_2{}^{[7]}Ca(H_2O)_0{}^{[5]}(H_2O)_0(H_2O)_5(H_2O)_{0.33}\}^{4+}$	0.21	1.73	0.36	36
Grimselite	$K_3Na[(UO_2)(CO_3)_3](H_2O)$	$\{^{[8]}K_3{}^{[5]}Na(H_2O)_0{}^{[5]}(H_2O)_0(H_2O)_1(H_2O)_0\}^{4+}$	0.14	2.64	0.36	37

[1] Chemical composition of the interstitial complex with the cation $[^{[n]}M^{z+}$, the different types of H_2O groups in the following sequence: (a) transformer (H_2O) group, (b) inverse-transformer[5] (H_2O) group, (c) non-transformer (H_2O) group bonded to *M* cations, and (d) non-transformer (H_2O) not bonded to *M* cations and the number of (OH) groups. * Not stable in dry air.

(1) Demartin *et al.* (1992), (2) Burns (2000), (3) Swihart *et al.* (1993), (4) Cole *et al.* (1993), (5) Piret *et al.* (1980), (6) Burns (1998a), (7) Rosenzweig & Ryan (1975), (8) Rosenzweig & Ryan (1977a), (9) Atencio *et al.* (1991), (10) Piret & Piret-Meunier (1988), (11) Piret & Declercq (1983), (12) Finch *et al.* (1999), (13) Mereiter (1982b), (14) Serezhkin *et al.* (1973), (15) Meunier & Galy (1973), (16) Cooper & Hawthorne (1995), (17) Cooper & Hawthorne (2001), (18) Rosenzweig & Ryan (1977b), (19) Ginderow (1988), (20) Burns et al. (2003), (21) Burns & Li (2002), (22) Locock & Burns (2003c), (23) Locock & Burns (2003d), (24) Li & Burns (2000b), (25) Finch *et al.* (1996); (26) Ginderow & Cesbron (1985), (27) Cahill & Burns (2000), (28) Kolitsch & Giester (2001), (29) Ginderow & Cesbron (1983a), (30) Ginderow & Cesbron (1983b), (31) Mereiter (1982a), (32) Pushcharovsky *et al.* (1996), (33) Mayer & Mereiter (1986), (34) Mereiter (1986a), (35) Ondruš *et al.* (2003), (36) Mereiter (1986e), (37) Li & Burns (2001a).

structural unit with the interstitial complex, and note that it is these weak interstitial bonds that will control the stability of the structure.

Lone-pair-stereoactive interstitial cations

Where present in uranyl oxysalt minerals, interstitial Pb^{2+} commonly has a stereoactive lone-pair of electrons (*e.g.*, Shimoni-Livny *et al.* 1998). Where such cations are not lone-pair stereoactive, they show a distribution of individual bond-lengths similar to that exhibited by spherical cations (*e.g.*, Ca^{2+}, Sr^{2+}) of identical formal valence in the same type of environment. Where lone-pair stereoactive, such cations typically show one to four short bonds to anions arranged on one side of the cation, and several long bonds to anions on the other side of the cation, with room for the lone pair of electrons to project into the space between the long bonds emanating from the central cation. The short bonds are always to O atoms of the structural unit, and are *trans* to the stereoactive lone-pair of electrons; longer bonds can be to O atoms of a structural unit or to interstitial (H_2O) groups (or both). Figure 1 shows the lengths of such bonds in uranyl-oxide and uranyl-oxysalt minerals (data from ICSD 2007). In Figure 1, we have identified the two different types of bonds described above: (1) those with bond valences in the range 0.45 to 0.65 *vu* (mean value = 0.50 *vu*); these bonds are always approximately *trans* to the inferred position of the lone pair of electrons; (2) those with bond valences in the range 0.03 to 0.45 *vu*. Although there is some overlap between the lengths of very short bonds (*trans* to the lone-pair stereoactive electrons) and the shorter of the remaining bonds in Figure 1, *in any particular ($Pb^{2+}\phi_n$) polyhedron* with a stereoactive lone-pair of electrons, there is invariably a distinct gap between these two types of bonds.

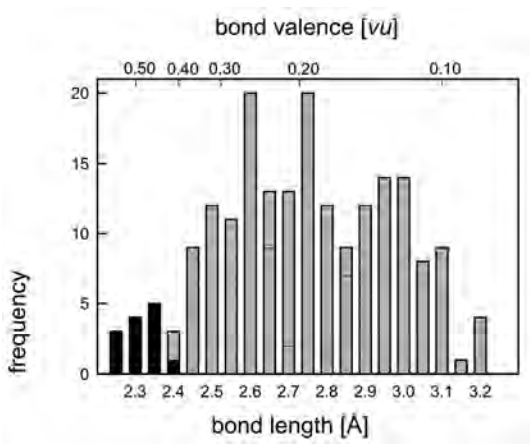

FIG. 1. Frequency of PbB(O,{OH},{H_2O}) bond lengths in uranyl-oxide and uranyl-oxysalt minerals. Type (1) bonds (short, bond valence ≥0.45 *vu*, always *trans* to a stereoactive lone-pair of electrons) are shown in black. Type (2) bonds (long, bond valence ≤0.45 *vu*, usually not *trans* to a stereoactive lone-pair of electrons), with a cut-off value of ~0.03 *vu*, are shown in pale grey.

According to our initial arguments (Hawthorne 1983, 1985, 1994, 1997, Schindler & Hawthorne 2001a), the short strong Pb^{2+}–O bonds should be considered as part of the structural unit. The question then arises as to how we treat the weak bonds involving these lone-pair-stereoactive cations. By analogy with the H atom, which shows a strong O–H bond involved in the structural unit and a weak hydrogen bond emanating from the structural unit, we consider strong $Pb2^{+}$–ϕ bonds (ϕ = O, OH, H_2O) (and other lone-pair-stereoactive cations) as belonging to the structural unit, and weak Pb^{2+}–ϕ bonds are treated in the same way as hydrogen bonds.

The Lewis Basicity of the Structural Unit

The general formula of a uranyl-oxysalt structural unit may be written as $[(UO_2)_k\, O_l\, (OH)_m\, (TO_x)_n]$, with T = Si, P, As^{5+}, Se^{4+}, Te^{4+}, Mo^{6+}, S^{6+}. The average bond-valence in these polyhedra is higher than 0.45 *vu*. This average bond-valence in cation coordination-polyhedra is used as a criterion to distinguish coordination polyhedra that belong to the structural unit or to the interstitial complex (Hawthorne 1983, 1985), and the crystal-chemical classification of Burns (1999a) is basically in accord with this criterion.

The Lewis basicity of the structural unit is defined as *the effective charge on the structural unit divided by the number of bonds to the structural unit* (Schindler & Hawthorne 2001a). To do this calculation, we need to know (1) the effective charge on the structural unit, and (2) the number of bonds required by the structural unit from the interstitial complex and adjacent structural units.

The effective charge on the structural unit

We obviously cannot use the formal charge of the structural unit, or structures with formally neutral structural units could not exist (there would be nothing linking them together). In almost all cases, neutral structural units are linked by hydrogen bonds from the (OH) groups of one structural unit to anions of the adjacent structural unit. From a bonding perspective, we can regard the hydrogen bonds as transferring charge from one structural unit to the next, imparting a polar character to the unit, which acts as a cation on the hydroxyl side and as an anion on the side of the acceptor anion. Thus we have to factor such transfer of charge into the calculation of the charge of the structural unit. Such transfer of charge can only involve cations that show very asymmetric coordination (primarily H, with some lone-pair-stereoactive cations such as Pb^{2+}).

Consider hydrogen bonds that link to anions of the interstitial complex. Where such linkage occurs, there is an overall transfer of charge from the structural unit to the interstitial complex. Hence we define the *effective charge* of the structural unit as *the formal charge of the structural unit as modified by the hydrogen bonds to the interstitial complex*, taking the average bond-valence of a hydrogen bond as *h vu*. Let there be *t* hydrogen bonds emanating from the structural unit, and let *s* of these hydrogen bonds link to the interstitial complex. In this case, the charge of *s* hydrogen bonds is transferred to the interstitial complex; the effective charge of the interstitial complex becomes $(Z + hs)^+$, and the effective charge of the structural unit is $(Z + hs)^-$. At first sight, the fact that the effective charge is a function of *s* seems a problem, as we frequently do not know *s*. However, we always know *t* (the number of hydrogen bonds emanating from the structural unit), and Schindler & Hawthorne (2001a) showed (see their Appendix I) that we can set $s = t$ without adversely affecting the operation of the principle of correspondence of Lewis acidity–basicity (*i.e.*, we may set the effective charge equal to the modified charge, as both the Lewis acidity of the interstitial complex and the Lewis basicity of the structural unit are affected in a similar manner). Thus we calculate the effective charge of a structural unit as the formal charge minus the number of hydrogen bonds emanating from the structural unit multiplied by the strength of those hydrogen bonds, h *vu*, where h is usually set equal to 0.20 *vu* (Brown 1981, 2002). For example, consider the structural unit in becquerelite, $[(UO_2)_3O_2(OH)_3]^-$. The formal charge of the structural unit is 1^-, and there are three hydrogen bonds emanating from the structural unit; hence the effective charge is $(1 + 0.2 \times 3)^- = 1.6^-$.

The number of bonds needed by the structural unit

To calculate this value, we need to be able to predict details of anion coordination in a structural unit; we will consider how to do this next.

The charge deficiency per anion (*CDA*): Schindler *et al.* (2000) introduced a quantity that they designated as *average basicity*, defined as *the average bond-valence per O atom contributed by the interstitial species and adjacent structural units*. This is an extremely important quantity, as it correlates strongly with the average O-coordination number of the structural unit, and hence plays a crucial role in the predictive aspects of our approach. However, the name "average basicity" is inappropriate as it implies that each atom of oxygen of the structural unit receives on average only one bond from the interstitial complex and adjacent structural units; this is not the case, and the name was not meant to imply this restriction. As indicated by its definition, this quantity is the average bond-valence per atom of oxygen required by the structural unit to satisfy the principle of correspondence of Lewis acidity and Lewis basicity, and Hawthorne & Schindler (2007) renamed this quantity the charge deficiency per anion, or CDA. As we will see, the CDA of a structural unit is extremely important, as it correlates strongly with the numbers of bonds to those structural units from the interstitial complex and adjacent structural units, and it is these correlations that play a major role in *a priori* prediction of structural features.

Calculation of CDA: CDA is a simple quantity to calculate. It is the formal charge of the structural unit modified by any charge transferred by the *t* hydrogen bonds that emanate from the structural unit: $(Z + ht)^-$, divided by the number of O atoms in the structural unit.

As an example, consider the structural unit in becquerelite, $[(UO_2)_3O_2(OH)_3]^-$. The effective charge is $(1 + 0.2 \times 3)^-$ and the number of O atoms in the structural unit is $2 \times 3 + 2 + 1 \times 3 = 11$; the resulting CDA = 1.6 / 11 = 0.145 *vu*. As we will see next, there is a close relation between the CDA of a structural unit and the average O-coordination number. Note that in becquerelite itself, the structural unit has a multiplicity of 2 in the unit formula: *i.e.*, $[(UO_2)_3O_2(OH)_3]^-_2 = [(UO_2)_6O_4(OH)_6]^{2-}$. However, the CDA and the Lewis basicity are not affected by this in that these quantities have the multiplicity in both the numerator and the denominator of their expressions, and hence it cancels out in the calculation of these properties. Note, however, that one must be careful with this issue when considering the numbers of bonds between the structural unit and the interstitial complex for interstitial cations of differing charge.

CDA and O-coordination number: There is a correlation between the CDA and the average O-coordination number in borate minerals (Schindler & Hawthorne 2001a, b). This is an extremely important relation, as it allows us to predict the range in average O-coordination number for a specific structural unit, and in turn, this allows us to calculate the range in Lewis basicity of that structural unit. However, Schindler *et al.* (2006) showed that sulfate minerals containing octahedrally coordinated divalent and trivalent cations behave somewhat differently from borate minerals. Structural units involving M^{2+} cations have higher average O-coordination numbers than structural units involving M^{3+} cations, as one would expect from the valence-sum rule (Brown 1981, Hawthorne 1994, 1997). We may consider this situation in more detail by factoring the average O-coordination number into two terms: $[CN] = [CN_{su}] + [_{Cnin}]$, where $[CN_{su}]$ is the number of bonds per anion received from cations of the structural unit, and $[CN_{in}]$ is the number of bonds per anion received from the interstitial complex and adjacent structural units.

CDA versus [CN_{in}] for uranyl-oxysalt minerals

Figure 2a shows the correlation between CDA and $[CN_{in}]$ for the uranyl minerals with sheet-, frame-

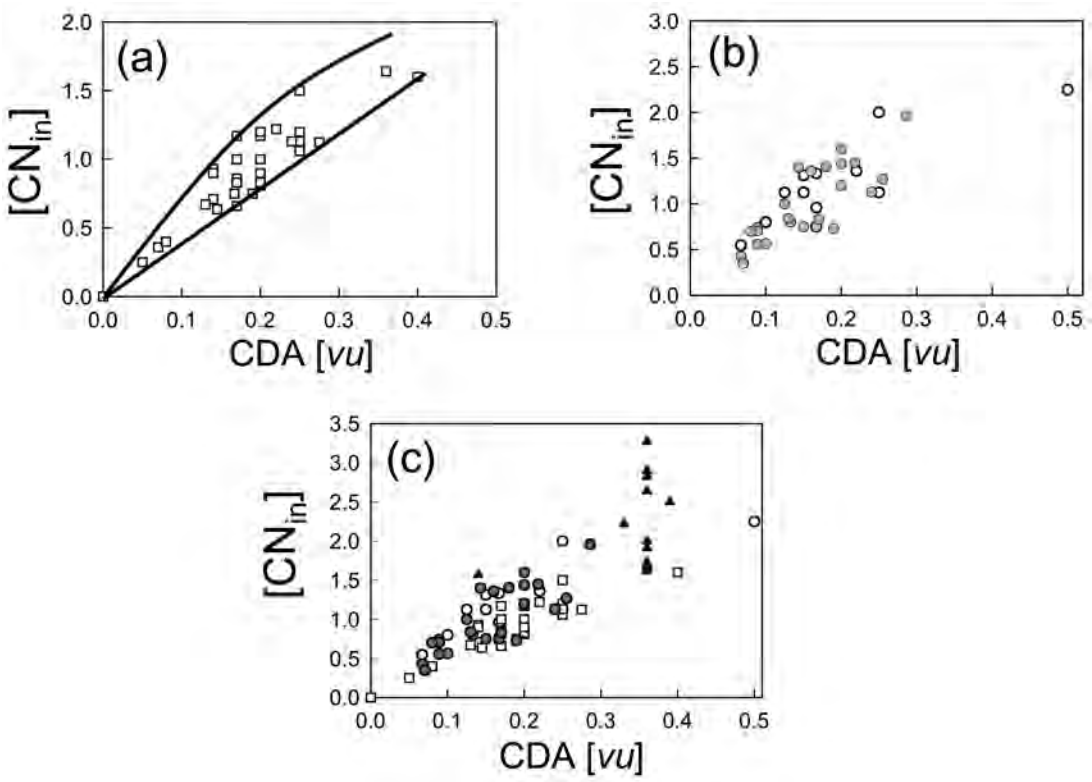

FIG. 2. The variation of $[CN_{in}]$ as a function of the CDA of structural units in (a) uranyl-oxysalt minerals without cluster structural units, (b) in synthetic compounds without cluster structural units, and (c) in minerals and selected synthetic compounds, including those with cluster structural units. The data for minerals are indicated with squares, data for anhydrous synthetic compounds are indicated with circles, data for hydrous synthetic compounds are indicated with black circles, and data for minerals and synthetic compounds with cluster structural units are indicated with black triangles.

work- and chain-structural-units of Table 1. In order to establish the envelope for data at a higher value of CDA, we carefully inspected interstitial hydrogen-bonding in minerals with structural units of higher CDA. For example, a structural unit with such a high CDA occurs in ulrichite, $CaCu^{2+}(H_2O)_4[(UO_2)(PO_4)_2]$ (Birch *et al.* 1988, Kolitsch & Giester 2001), in which the structural unit $[(UO_2)(PO_4)_2]^{4-}$ has a CDA of 0.40 *vu* (Table 1). The interstitial complex in ulrichite is $\{^{[8]}Ca^{[6]}Cu^{2+}(H_2O)_2(H_2O)_2\}^{4+}$, and $[CN_{in}]$ is 1.60. This value matches the proposed lower envelope of the data points at higher CDA (Fig. 2a). It is apparent from Figure 2 that $[CN_{in}]$ is the salient parameter when trying to establish a relation between the number of bonds per anion needed by the structural unit and CDA. If we wish to have any predictive power, we need to be able to derive the CDA value *a priori*, without recourse to a known structure. The relation between CDA and $[CN_{in}]$ shown in Figure 2a allows such a prediction.

There is an even more important issue associated with Figure 2a. As well as predicting details of the number of bonds required by O atoms in a given structural unit, this relation also predicts the *range* of possible numbers of bonds to O atoms in a given structural unit. This range in numbers of bonds to the O atoms of the structural unit reflects the range in pH over which the mineral is stable. Indeed, *it is by varying the numbers of such bonds to the structural unit that the structural unit maintains its stability as the pH of its environment changes*. Furthermore, the relations shown in Figure 2a allow calculation of the range in the number of bonds needed by a specific structural unit. For a specific value of CDA, we derive the minimum and maximum mean interstitial coordination-numbers. Thus the number of bonds needed by the structural unit is in the range $([CN_{in}]^{min} - [CN_{in}]^{max}) \times$ the number of anions in the structural unit.

CDA versus [CN_{in}] for synthetic uranyl-oxysalt compounds

Figure 2b shows the variation in CDA of structural units as a function of [CN_{in}] values for selected synthetic uranyl-oxide compounds (not considering synthetic compounds with cluster structural-units) where the determined structure is in agreement with the criteria listed above. Table 2 lists the corresponding synthetic uranyl-oxide compounds. Figure 2c shows the correlation between the CDA of structural units and the corresponding [CN_{in}] values for minerals and

TABLE 2. SELECTED SYNTHETIC URANYL-OXYSALT COMPOUNDS

Formula	$[CN]_{in}$	CDA	H_2O total	Structural Unit	Ref.
$^{[9.5]}Cs[(UO_2)(HSeO_3)(SeO_3)]$	1.31	0.15	0.0	Sheet	1
$^{[8]}K[(UO_2)(Te_2O_5)(OH)]$	1.13	0.15	0.0	Sheet	2
$^{[8]}K[(UO_2)(HSeO_3)(SeO_3)]$	1.13	0.15	0.0	Sheet	1
$^{[9]}Ba(H_2O)_2[(UO_2)_3(MoO_4)_4(H_2O)](H_2O)$	0.57	0.10	3.0	Framework	3
$^{[8]}Pb(H_2O)[(UO_2)_2(IO_3)_2O_2]$	0.75	0.17	1.0	Chain	4
$^{[10]}Pb_2(H_2O)[(UO_2)_{19}UO_{12}(OH)_6(H_2O)_2]$	0.75	0.15	0.5	Framework	5
$^{[9]}Pb[(UO_2)O_2]$	2.25	0.50	0.0	Sheet	6
$^{[4.5]}Ag_2[(UO_2)(SeO_3)_2]$	1.13	0.25	0.0	Sheet	1
$^{[5.8]}Ag_4[(UO_2)_4(IO_3)_2(IO_4)_2O_2]$	0.96	0.17	0.0	Chains	7
$^{[9.5]}Cs_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$	0.55	0.07	0.0	Framework	8
$^{[8]}Cs_2(H_2O)[(UO_2)(MoO_4)_2]$	1.60	0.20	0.5	Sheet	9
$^{[9]}Cs_2[(UO_2)_2(MoO_4)_3]$	1.13	0.13	0.0	Sheet	10
$^{[8]}Tl_2[(UO_2)(TeO_3)_2]$	2.00	0.25	0.0	Sheet	2
$^{[7]}Tl_3(H_2O)[(UO_2)_2(Te_2O_5(OH))(Te_2O_6)](H_2O)$	1.44	0.20	0.67	Sheet	2
$^{[8]}Tl[(UO_2)(HSeO_3)(SeO_3)]$	1.13	0.15	0.0	Sheet	1
$^{[8]}Tl[(UO_2)_3(IO_3)_4O_2]$	0.80	0.10	0.0	Chain	4
$^{[8]}K_2[(UO_2)(MoO_4)(IO_3)_2]$	1.33	0.17	0.0	Sheet	11
$^{[8]}K[(UO_2)_3(IO_3)_4O_2]$	0.80	0.10	0.0	Chain	12
$^{[8]}Sr[(H_2O)[(UO_2)_2(IO_3)_2O_2]$	0.75	0.17	1.0	Chain	4
$^{[8]}Rb_2[(UO_2)(MoO_4)_2](H_2O)$	1.60	0.20	0.5	Sheet	13
$^{[8]}Rb[(UO_2)_3(IO_3)_4O_2]$	0.80	0.10	0.0	Chain	4
$^{[7]}K(H_2O)[(UO_2)(SO_4)_2(H_2O)]$	1.45	0.22	0.5	Sheet	14
$^{[8]}K_2(H_2O)_4[(UO_2)_2(C_2O_4)_3]$	1.00	0.13	2.0	Sheet	15
$^{[5.67]}Na^{[7.6]}Tl(H_2O)_3[(UO_2)(MoO_4)_3]_2$	1.96	0.29	0.38	Sheet	16
$^{[6]}Na(H_2O)_4[(UO_2)(MoO_4)_2]$	1.20	0.20	2.0	Sheet	16
$^{[7]}Ca(H_2O)[(UO_2)_4O_3(OH)_4](H_2O)$	0.73	0.19	2.0	Sheet	17
$^{[10]}Sr_{1.25}(H_2O)_3[(UO_2)_3O_{3.5}(OH)_{1.5}]$	1.27	0.26	2.36	Sheet	18
$^{[7]}Na(H_2O)[(UO_2)_4O_2(OH)_5](H_2O)$	0.80	0.13	2.0	Sheet	19
$^{[6.5]}Na_2[(UO_2)_3O_3(OH)_2]$	1.36	0.22	0.0	Sheet	20
$^{[8.6]}K_5(H_2O)[(UO_2)_{10}O_8(OH)_9]$	1.41	0.18	0.2	Sheet	21
$^{[8]}Cs_2(H_2O)_3[(UO_2)_{12}O_7(OH)_{13}]$	0.84	0.13	1.0	Sheet	22
$^{[10]}Sr_3(H_2O)_2[(UO_2)_4O_4(OH)_3]_2$	1.13	0.24	0.0	Sheet	23
$^{[7]}Rb_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$	0.43	0.07	0.0	Framework	24
$^{[9]}Cs(H_2O)[(UO_2)(H_2O)(UO_2)_4(PO_4)_4]$	0.74	0.09	1.0	Framework	25
$^{[8.5]}Rb(H_2O)[(UO_2)(H_2O)(UO_2)_4(PO_4)_4]$	0.70	0.09	1.0	Framework	25
$^{[6.5]}K(H_2O)[(UO_2)(H_2O)(UO_2)_4(PO_4)_4]$	0.56	0.09	1.0	Framework	25
$^{[7]}K_2(H_2O)[(UO_2)(MoO_4)_2]$	1.40	0.14	0.5	Sheet	26
$^{[5.5]}Cs_2(H_2O)[(UO_2)(H_2O)(UO_2)_4(AsO_4)_4]$	0.70	0.08	0.5	Framework	27
$[(UO_2)(H_2O)_3(UO_2)_2(AsO_4)_2](H_2O)$	0.35	0.07	--	Framework	28
$[(UO_2)(H_2O)_3(UO_2)_2(PO_4)_2](H_2O)$	0.35	0.07	--	Framework	29
$^{[9]}Ba[(UO_2)_2(IO_3)_2O_2](H_2O)$	0.83	0.17	1.0	Chain	12
$^{[6.5]}Na_{10}[(UO_2)(SO_4)_6]$	2.50	0.39	0.0	Cluster	30
$^{[8]}Sr^{[6]}Mg(H_2O)_{10}[(UO_2)(CO_3)_3](H_2O)_2$	1.64	0.36	6.0	Cluster	31
$^{[8.5]}Cs_4[(UO_2)(CO_3)_3](H_2O)_6$	2.82	0.36	0.75	Cluster	32
$^{[9]}Tl_4[(UO_2)(CO_3)_3]$	3.27	0.36	0.0	Cluster	33
$^{[5.25]}Na_4[(UO_2)(CO_3)_3]$	1.91	0.36	0.0	Cluster	34
$^{[11]}Rb_2[(UO_2)(NO_3)_4]$	1.57	0.14	0.0	Cluster	35
$^{[8]}K_4[(UO_2)(CO_3)_3]$	2.90	0.36	0.0	Cluster	36
$^{[6.7]}Na_6(H_2O)_2[(UO_2)(SO_4)_4]$	2.22	0.33	0.33	Cluster	37

(1) Almond & Albrecht-Schmitt (2002a), (2) Almond & Albrecht-Schmitt (2002b), (3) Tabachenko *et al.* (1984), (4) Bean & Albrecht-Schmitt (2001), (5) Li & Burns (2000a), (6) Cremers *et al.* (1986), (7) Bean *et al.* (2001a), (8) Krivovichev & Burns (2001), (9) Rastsvetaeva *et al.* (1999), (10) Krivovichev *et al.* (2002a), (11) Sykora *et al.* (2002), (12) Bean *et al.* (2001b), (13) Khrustalev *et al.* (2000), (14) Niinisto *et al.* (1979), (15) Jayadevan *et al.* (1975), (16) Krivovichev & Burns (2003), (17) Glatz *et al.* (2002), (18) Burns & Li (2002), (19) Burns & Deely (2002), (20) Li & Burns (2001b), (21) Burns & Hill (2000a), (22) Hill & Burns (1999), (23) Burns & Hill (2000b), (24) Krivovichev & Burns (2002), (25) Locock & Burns (2002a), (26) Krivovichev *et al.* (2002b), (27) Locock & Burns (2003a), (28) Locock & Burns (2003b), (29) Locock & Burns (2002b), (30) Burns & Hayden (2002), (31) Mereiter (1986a), (32) Mereiter (1986b), (33) Mereiter (1986c), (34) Cisarová *et al.* (2001), (35) Irish *et al.* (1985), (36) Anderson *et al.* (1980), (37) Hayden & Burns (2002).

synthetic phases, including data of minerals with cluster structural-units. It is apparent that some [CN_{in}] values in phases with cluster structural-units are much higher than in phases with chain, sheet and framework structural units. These data are for minerals with $(CO_3)^{2-}$ groups (green triangles) and are not in accord with the general trend; the reason for this is not clear.

It is further apparent that the [CN_{in}] values for synthetic phases are, on average, somewhat higher than for minerals. Many selected synthetic compounds contain interstitial monovalent cations such as Rb, Cs and Tl^+ (Table 2), whereas many selected minerals contain interstitial monovalent cations such as K and Na (Table 1). The cations Rb, Cs and Tl^+ commonly have higher coordination-numbers than K and Na, accounting for the higher [CN_{in}] values for the corresponding synthetic compounds. Note that the coordination numbers given in the tables do not always correspond to the values given by the original authors of the corresponding papers on the structure. The criteria that we used to derive coordination numbers are discussed in detail by Schindler & Hawthorne (2001b).

Calculation of Lewis basicity of the structural unit

Consider becquerelite, $^{[7]}Ca\ (H_2O)_4\ [(UO_2)_3\ O_2\ (OH)_3]_2\ (H_2O)_4$. The effective charge of the structural unit is $[3 \times 2 - 2 \times 2 - 3 \times 1 - h \times 3] \times 2 = 3.2^-$. The CDA of the structural unit is thus 3.2 / [$\times$ 3 + 2 + 3] $\times$ 2 = 3.2 / 221 = 0.145 *vu*. From Figure 2, the corresponding range in the number of bonds per anion for this structural unit is [0.58] to [1.05]. Thus the minimum and maximum possible numbers of bonds from the interstitial complex to the structural unit are 0.58 $\times$ 22 = 13 and 1.05 $\times$ 22 = 23.1, respectively. This results in a range in Lewis basicity of 3.2 / 23.1 to 3.2 / 13 = 0.14 – 0.25 *vu*.

The Lewis Acidity of Interstitial Complexes

A general formula for an interstitial complex can be written as follows:

$$[^{[m]}M^{+}{}_{a}\ ^{[n]}M^{2+}{}_{b}\ ^{[l]}M^{3+}{}_{c}\ (H_2O)_d\ (H_2O)_e\ (H_2O)_f\ ^{[q]}(OH)_g\ (H_2O)_r]^{(a\ +\ 2b\ +\ 3c\ -\ f)+}$$

where *M* is any type of interstitial cation, *d*, *e* and *f* denote the numbers of transformer, non-transformer and inverse transformer (H_2O) groups, and *r* denotes the number of interstitial (H_2O) groups not bonded to interstitial cations.

The Lewis acidity of the interstitial complex is defined as *its effective charge divided by the number of bonds from the interstitial complex to the structural unit* (Schindler & Hawthorne 2001a). The effective charge of the interstitial complex can be simply derived from the formula given above: it is the formal charge, $a + 2b + 3c - g$, as modified by the hydrogen bonds emanating from the structural unit, $h \times s$, where *h* is the strength of a hydrogen bond. In order to know *s*, the number of hydrogen bonds emanating from the structural unit, we need to know the structural unit to be considered. At first sight, this requirement seems unnecessary, as one might expect that the effective charge should be affected only by the number of hydrogen bonds incident to the interstitial complex. However, this view fails to consider the effect of polarity of the structural unit. Hawthorne & Schindler (2007) explained this in detail for lizardite, $[Mg_3Si_4O_{10}(OH)_4]^0$, where four hydrogen bonds emanate from the structural unit to bond to an adjacent structural unit. The charge transferred to the adjacent structural unit must be considered in the calculation of the effective charge of the structural unit and the (virtual) interstitial complex or the charge of each is neutral and nothing would hold the layers together. The formal charge of the (virtual) interstitial complex in lizardite is the formal charge, 0.0, as modified by the charge transferred by the hydrogen bonds emanating form the structural unit, 0.20 $\times$ 4 = 0.80 *vu*. Thus the number of hydrogen bonds emanating from the structural unit affects the effective charge of the interstitial complex and must be considered in calculating the Lewis acidity of an interstitial complex. The number of bonds from the interstitial complex to the structural unit may be counted from the above formula as the number of bonds emanating from the cations, $m \times a + n \times b + l \times c$, plus the number of bonds resulting from the transformer action of H_2O, *d*, minus the number of bonds accepted by (OH) groups in the interstitial complex, $g \times [q - 1]$, plus the number of hydrogen bonds emanating from the structural unit, *s*.

Example: Consider the interstitial complex $\{^{[7]}Ca_2\ (H_2O)_7\ (H_2O)_3\}^{4+}$ interacting with a structural unit with three constituent (OH) groups. The interstitial complex has seven transformer (H_2O) groups, three non-transformer (H_2O) group bonded to Ca, no (OH) groups, and no (H_2O) groups not bonded to any cation. The effective charge of the interstitial complex is 4 (the formal charge of the interstitial cations) + 3 $\times$ 0.20 (the charge transferred by the three hydrogen bonds from the structural unit) = 4.6^+. The number of bonds from the interstitial complex to the structural unit is 7 $\times$ 2 (from Ca) + 7 [from transformer (H_2O) groups] + 3 (hydrogen bonds to the interstitial complex) = 24. Thus the Lewis acidity of the interstitial complex is 4.6 / 24 = 0.192 *vu*.

Graphical representation of Lewis acidity in interstitial complexes

The various contributions to the Lewis acidity (*LA*) described above may be combined into a single expression:

$$LA = (a + 2b + 3c - g + h \times s) / (m \times a + n \times b + l \times c + d - g \times [q - 1])$$

Using this expression, we may represent the variation in Lewis acidity of an interstitial complex graphically with a little simplification (Fig. 3). Consider an interstitial complex with a single type of cation with a single coordination number, *e.g.*, $[^{[m]}M^{+}(H_2O)_d(H_2O)_e(H_2O)_f(H_2O)_r]^{a+}$; the Lewis acidity is $(1 + h \times s) / (m + d)$. As *h, s and m* are known [*i.e.*, fixed for this one example: $h = 0.2$, $s = 0$, $m = 8$ (for example)], *LA* is a simple function of *d*, the number of transformer (H_2O) groups ($d = 0$, $LA = 1/8 = 0.125$; $d = 2$, $LA = 1 / (8 + 2) = 0.100$, *etc.*); see the single curve labeled $^{[8]}M^{+}$ in Figure 3. The calculation may be repeated for different values of *m* ([5], [6] and [8] in Fig. 3) to produce a family of curves for monovalent cations, and similar families of curves for divalent and trivalent cations. The complete set of curves in Figure 3 shows the variation of Lewis acidity of a generalized interstitial complex $[^{[m]}M^{+}{}_a{}^{[n]}M^{2+}{}_b{}^{[l]}M^{3+}{}_c(H_2O)_d(H_2O)_e(H_2O)_f{}^{[q]}(OH)_g(H_2O)_r]^{(a + 2b + 3c - f)+}$ as a function of cation valence, cation-coordination number, and the number of transformer (H_2O) groups. Where more than one cation species is present, we may use the weighted arithmetic average of the salient characteristics (charge and coordination number) of these cations in the calculation of Figure 3. Second, in cases where $(OH)^{-}$ is present, we can sum the charges of the cation(s) and the $(OH)^{-}$, and treat the complex as if it contained a cation of the resulting net charge [*i.e.*, $M^{3+} + (OH)^{-} / M^{2+}$].

The Lewis acidity of the interstitial complex decreases as the number of transformer (H_2O) groups increases, as the cation-coordination numbers increase, and as the cation charge decreases. We may also plot the range in Lewis basicity of a specific structural unit on a graph that shows the variation in Lewis acidity of cation complexes (*i.e.*, Fig. 3). Where the properties of the structural unit and the interstitial complexes intersect, their Lewis acidity and basicity correspond, and structures of those specific compositions may be stable. Where the properties of the structural unit and interstitial complexes do not overlap, their Lewis acidity and basicity do not correspond, and structures of those compositions are not stable.

Factors Controlling the Number of Transformer and Total Number of (H_2O) Groups

Hawthorne (1992) described the different roles of (H_2O) groups in crystal structures, and drew a strong distinction between (H_2O) as part of the structural unit and (H_2O) as an interstitial species. In particular, Hawthorne (1992) described the role of (H_2O) as a bond-valence transformer in minerals, and Schindler & Hawthorne (2001a) developed these ideas further. In the interstitial complex, (H_2O) groups have two distinct roles: (1) as transformer (coordination of O is [3]) or inverse-transformer (coordination of O is [5]) (H_2O) groups that affect the Lewis acidity of the interstitial complex; (2) as non-transformer (coordination number of O is [4]) (H_2O) groups whose role is to propagate

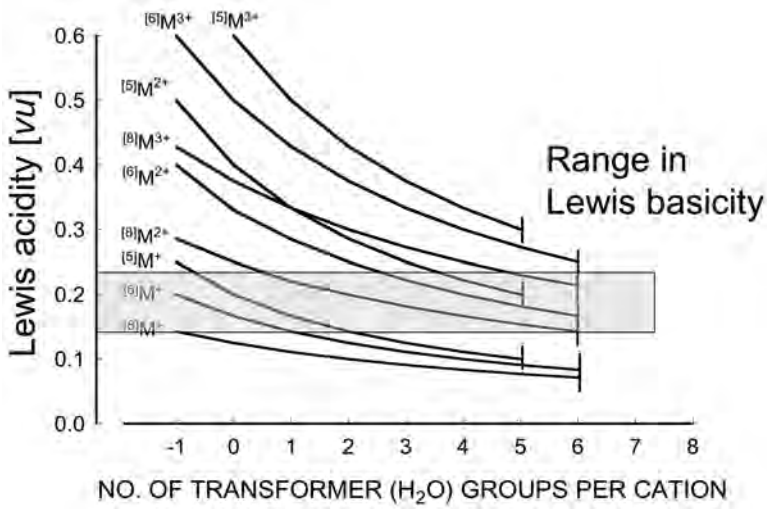

FIG. 3. The variation in Lewis acidity with the number of transformer (H_2O) groups for different interstitial-cation charges and coordination numbers for a general interstitial complex; the range in Lewis basicity of the structural unit of becquerelite, $[(UO_2)_3O_2(OH)_3]$, is marked in grey; where the lines of variable Lewis acidity overlap the range of Lewis basicity of the structural unit, the valence-matching principle is satisfied.

bonds from cations to anions that are too distant to bond directly to the cation. Of course, transformer and inverse-transformer (H_2O) groups also propagate bonds in the same way as non-transformer (H_2O) groups, but they have the additional transformer role. In order to examine the factors affecting the amounts of these types of interstitial (H_2O) groups in uranyl-oxysalt minerals, we will consider the sheet structural unit: $[(UO_2)_8O_8(T^{5+}O_4)_2]^{6-}$, the cluster structural unit $[(UO_2)_3(TO_4)_4]^{6-}$, and the different coordination environments around an interstitial (H_2O) group.

The structural unit $[(UO_2)_8O_8(T^{5+}O_4)_2]^{6-}$ and transformer (H_2O) groups

The CDA of this structural unit is 6 / 32 = 0.188 *vu*. Using this value, we may derive the range in the number of bonds from interstitial cations, $[CN_{in}]$, from Figure 2a: 0.73–1.27. Thus on average, each anion of the structural unit accepts 0.73 to 1.27 bonds from the interstitial complex. The Lewis basicity of a structural unit is defined as the effective charge divided by the number of additional bonds required. As there is a range in the number of bonds required (*i.e.,* 0.73 to 1.27 per anion), the structural unit exhibits a range in Lewis basicity: 6 / 32 × 0.732 to 6 / 32 × 1.27 = 0.14–0.24 *vu*. The valence-matching principle requires that the Lewis acidity of a possible interstitial complex, $\{^{[m]}M^{+}{}_{a}\,^{[n]}M^{2+}{}_{b}\,^{[l]}M^{3+}{}_{c}\,(H_2O)_d\,(H_2O)_e\,(H_2O)_f\,^{[q]}(OH)_g\}^{(a+2b+3c-g)}$ (*d*, *e*, *f* are transformer, non-transformer and inverse-transformer H_2O groups, respectively), must closely match this range. Thus the number of bonds emanating from the interstitial complex, $a \times m + b \times n + c \times l + d - f - g \times (q - 1)$, must be in the range (32 × 0.73) – (32 × 1.27) = 23–41.

Consider the interstitial complex $\{^{[6]}M^{+}{}_{6}(H_2O)_a\}^{6+}$, where *a* is the sum of the different types of (H_2O) groups in the structural unit. The number of bonds emanating from the six octahedrally coordinated monovalent cations, 6 × 6 = 36, is within the range of bonds required by the structural unit, 23–40. Each transformer (H_2O) group increases the number of bonds to the structural unit by one. Hence, the interstitial complex $\{^{[6]}M^{+}{}_{6}(H_2O)_a\}^{6+}$ can occur with the structural unit $[(UO_2)_8O_8(T^{5+}O_4)_2]^{6-}$ where the interstitial cations bond to 0–5 transformer (H_2O) groups.

Consider next the interstitial complex $\{^{[6]}M^{2+}{}_{3}(H_2O)_b\}^{6+}$. The number of bonds emanating from the three divalent cations, 3 × 6 = 18, is outside the range of bonds needed by the structural unit, 23–41. Hence, the interstitial cations must bond to transformer (H_2O) groups in order to bring the number of bonds to the structural unit within the range of that required by the structural unit, 23–41. As each transformer (H_2O) group increases the number of bonds to the structural unit by one, this interstitial complex must bond to a minimum of 23 – 18 = 5 transformer (H_2O) groups. If all ligands to interstitial $^{[6]}M^{2+}$ cations are (H_2O) groups, this results in 18 × 2 = 36 bonds to the structural unit, still within the range of 23–41 needed by the structural unit.

Consider next the interstitial complex $\{^{[6]}M^{3+}{}_{2}(H_2O)_c\}^{6+}$. The number of bonds emanating from the complex is 2 × 6 = 12, well below the number of bonds required by the structural unit, 23–41. The minimum number of transformer (H_2O) groups required is 23 – 12 = 11, *i.e.*, one less than the total number of ligands to the interstitial cations. Thus the interstitial cations bond directly to 12 transformer (H_2O) groups. Additional transformer (H_2O) groups, not bonded directly to the cations, may also occur, increasing the number of bonds to the structural unit (and decreasing the Lewis acidity of the interstitial complex), up to a maximum value of 41 – 24 = 17. Thus the general form of this interstitial complex for this structural unit may be written as $\{^{[6]}M^{3+}{}_{2}\,(H_2O)_{12}\,(H_2O)_N\}$ where $0 \le N \le 17$.

The structural unit $[(UO_2)_8O_8\,T^{5+}O_4)_2]^{6-}$ and non-transformer (H_2O) groups

Consider again the interstitial complex $\{^{[6]}M^{+}{}_{6}(H_2O)_a\}^{6+}$. In addition to the required transformer (H_2O) groups, (H_2O) groups not bonded to interstitial cations may occur as (usually) non-transformer (H_2O) groups [which do not change the number of bonds from the interstitial cations to the structural unit]. These (H_2O) groups distribute the bond-valence from the interstitial cations to all potential bond-valence acceptors of the structural unit. Within the interstitial complex, the relatively large number of cations ensures that the distance between these cations will be relatively small (shown diagrammatically in Fig. 4a), and hence the number of non-transformer (H_2O) groups around an interstitial cation will be small because the ensuing closeness of the (H_2O) groups promotes hydrogen bonding among adjacent (H_2O) groups.

Consider next the interstitial complex $\{^{[8]}M^{2+}{}_{3}(H_2O)_b\}^{6+}$. A uniform distribution of the three interstitial cations (Fig. 4b) results in greater space between these divalent cations than is the case for six monovalent cations (Fig. 4a). Hence in order to distribute the bond valence from these cations to all bond-valence acceptors in the uranyl sheet, there must be more (H_2O) groups than is the case for monovalent cations in the structural unit.

Consider next the interstitial complex $\{^{[6]}M^{3+}{}_{2}(H_2O)_c\}^{6+}$. A uniform distribution of the cations between the sheets (Fig. 4c) results in greater space between cations than in the case of three divalent or six monovalent cations (Figs. 4a, b). Hence, more additional non-transformer (H_2O) groups must occur around an interstitial cation, distributing bond-valence from transformer (H_2O) groups to the eventual acceptor anions.

Distribution of interstitial cations around the cluster structural-unit $[(UO_2)_3(TO_4)_4]^{6-}$

Consider an interstitial complex $\{^{[6]}M^{3+}{}_2(H_2O)_c\}^{6+}$ between the clusters of a $[(UO_2)_3(TO_4)_4]^{6-}$ structural unit (Fig. 4d). It is apparent that the geometry of the cluster structural unit results in a different distribution of bond-valence acceptors than the geometry of a sheet structural unit. The number and distribution of bond-valence acceptors in a cluster vary with the size of the cluster, *i.e.*, the number of polymerized cation-polyhedra in the cluster. Furthermore, clusters have a higher degree of freedom than sheets with regard to possible distances between structural units. The number of interstitial (H_2O) groups thus depends on (1) the distance between the structural units, and (2) the number and distribution of bond-valence acceptors in the structural units. As both factors vary more in minerals with cluster structural units than with sheet structural units, prediction of the number of (H_2O) groups for structures with cluster structural units will be far more difficult than for structures with sheet structural units.

Coordination of an interstitial (H_2O) group

Consider an interstitial transformer (H_2O) group. The (H_2O) group is [3]-coordinated, and the O atom normally accepts one bond from an interstitial cation; alternatively, it could accept one hydrogen bond from an (OH) or (H_2O) group (Fig. 5a). However, the latter case has not been observed yet in oxysalt minerals (Schindler & Hawthorne 2001b, 2004). As discussed above, a transformer (H_2O) group bonded to an interstitial cation may occur in the interstitial complex $\{^{[8]}M^{2+}{}_3(H_2O)_b\}^{6+}$ (Fig. 4b) and must occur in the interstitial complex $\{^{[6]}M^{3+}{}_2(H_2O)_c\}^{6+}$.

Figure 5b shows six possible coordinations of a non-transformer (H_2O) group. The (H_2O) group is [4]-coordinated, and the O atom can accept two bonds either from two cations (1) or two hydrogen atoms of (OH) (6) or H_2O groups (5), or one bond from a cation and one bond from a hydrogen atom of an (OH) (2) or H_2O (3) group, or one hydrogen bond from an (OH) group and one hydrogen bond from an (H_2O) group (4). Coordination (1) requires a short distance between the interstitial cations and small bond-valences of the *M*–(H_2O) bonds. If the average bond-valence of the *M*–(H_2O) bond is, for example, 0.50 *vu*, the O atom of the (H_2O) group accepts 1.00 *vu* and could only accept 0.50 *vu* from each O–H bond. This O–H bond-valence is unusually small and would occur only for a symmetrical hydrogen bond (*e.g.*, Burns & Hawthorne 1994). Hence, coordinations (1) and (3) are most likely to occur in interstitial complexes of the type $\{^{[6]}M^{+}{}_6(H_2O)_a\}^{6+}$ and $\{^{[8]}M^{2+}{}_3(H_2O)_b\}^{6+}$ (Figs. 4a, b), whereas coordination (5) can occur in all three types of interstitial complexes $[\{^{[6]}M^{+}{}_6(H_2O)_a\}^{6+}$, $\{^{[8]}M^{2+}{}_3(H_2O)_b\}^{6+}$ and $\{^{[6]}M^{3+}{}_2(H_2O)_c\}^{6+}]$. Coordinations (2), (4) and (6) require that the structural unit contain (OH) groups. Coordination (2) will more probably occur in $\{^{[6]}M^{+}{}_6(H_2O)_a\}^{6+}$ and $\{^{[8]}M^{2+}{}_3(H_2O)_b\}^{6+}$ complexes rather than in $\{^{[6]}M^{3+}{}_2(H_2O)_c\}^{6+}$, whereas coordination environments (4) and (6) can occur in all three types of interstitial complex.

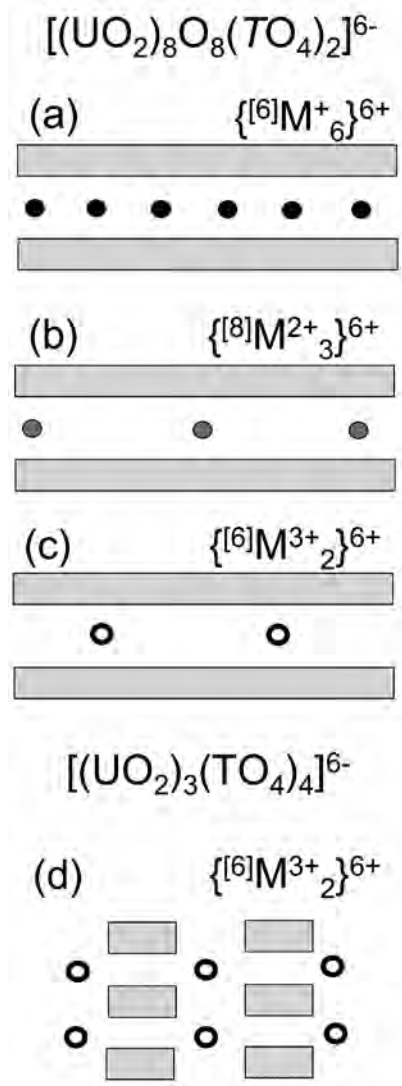

FIG. 4. Schematic of a $[(UO_2)_8O_8(TO_4)_2]^{6-}$ sheet structural unit (grey rectangles) containing (a) six monovalent cations $\{^{[6]}M^{+}{}_6\}^{6+}$, (b) three divalent cations $\{^{[8]}M^{2+}{}_3\}^{6+}$, and (c) two trivalent cations $\{^{[6]}M^{3+}{}_2\}^{6+}$ in the interlayers; (d) sketch of cluster structural units with the composition $[(UO_2)_3(TO_4)_4]^{6-}$ and with two trivalent cations in the interlayer; mono-, di- and trivalent cations are black, grey and white spheres, respectively.

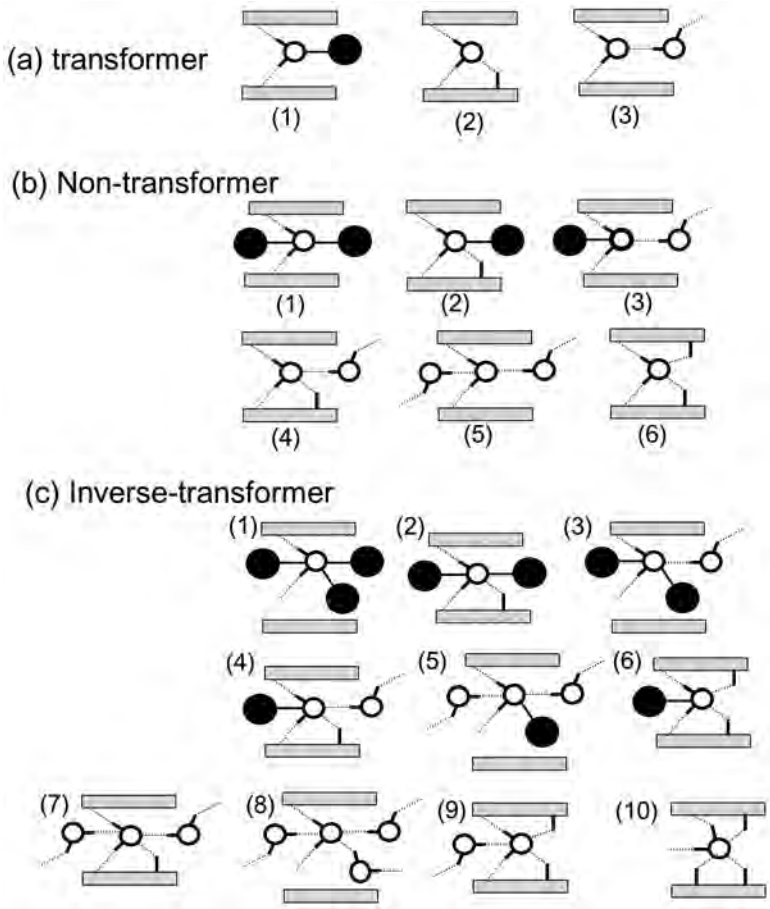

FIG. 5. Possible coordinations of (H_2O) groups (circle) by cations (black circle), other (H_2O) groups or (OH) groups of the structural unit (grey rectangle; hydrogen bonds are dashed lines); (a) transformer (H_2O), $^{[3]}O$; (b) non-transformer (H_2O) groups, $^{[4]}O$; (c) inverse-transformer (H_2O) groups, $^{[5]}O$.

Closer inspection of coordinations (1)–(6) indicates that the numbers of (H_2O) groups required decrease with the number of bonds accepted from interstitial cations and H atoms from (OH) groups belonging to the structural unit. The total number of bonds emanating from (H_2O) groups correlates with the total number of (H_2O) groups. Thus, coordinations (1), (2) and (6) [which involve one (H_2O) group] result in a lower number of hydrogen bonds emanating from (H_2O) groups than coordinations (3), (4) and (5) [which involve more than one (H_2O) group]. Hence, coordinations (2) and (6) may dominate where there is a small number of bond-valence acceptors around an (OH) group [where the (OH) group and the bond-valence acceptors both occur in the structural unit].

Schindler & Hawthorne (2004) showed that in the case of uranyl-oxide-hydroxy-hydrate minerals, less-polymerized sheet structural units contain fewer interstitial (H_2O) groups per interstitial cation than the more highly polymerized sheet structural units. They argued that the density of bond-valence acceptors is lower in the less-polymerized sheet structural units and therefore, fewer (H_2O) groups are required in the interstitial complex. Following the above argument, coordination (6) (Fig. 5b) should occur more often between less-polymerized structural units, whereas coordination (5) should occur more often between more highly polymerized structural units. This aspect will be discussed in more detail below.

Figure 5c shows ten possible coordinations for an inverse-transformer (H_2O) group, in which the O atom is [5]-coordinated. This (H_2O) group rarely occurs in interstitial complexes, but where it does, its O atoms generally accept bonds emanating from three intersti-

tial cations (1) or two interstitial cations and a H atom [(2), (3)]. Coordinations (4) to (10) have not yet been observed (Schindler & Hawthorne 2001b), but are topologically possible.

Summary of factors affecting the amount of interstitial (H_2O)

The number of (H_2O) groups in an interstitial complex depends on the following factors:

(1) The number of bonds required by the structural unit (Lewis basicity) and the number of bonds emanating from the interstitial complex (Lewis acidity); these numbers determine the number of transformer and inverse-transformer (H_2O) groups.

(2) The number, size and distribution of the interstitial cations; these factors determine the distance between the interstitial cations and the bond-valence acceptors.

(3) The number and distribution of the bond-valence acceptors and the sizes of the polyhedra in the structural unit; these factors also control the distance between interstitial cations and bond-valence acceptors.

(4) The number of hydrogen bonds emanating from the structural unit; their number control the number of non-transformer (H_2O) groups.

Note that these factors are not mutually independent as

(5) The number of bond-valence acceptors and the number of bonds required by the structural unit correlate with the number of anions in the structural unit.

(6) The size and number of interstitial cations and the number of (OH) groups in the structural unit correlate with the sum of the bonds emanating from the interstitial cations and (OH) groups.

The size of the polyhedra and the distribution of the bond-valence acceptors in a structural unit depend on the chemical composition and degree of polymerization (*i.e.* chains, sheets, frameworks) of the structural unit. If one considers only structural units of similar composition and degree of polymerization, the number of (H_2O) groups around one interstitial cation should depend principally on the number of anions in the structural unit and on the number of bonds emanating from the interstitial cations and (OH) groups of the structural unit. Hence for minerals with similar structural units, the number of (H_2O) groups per interstitial cation should be dependent primarily on the number of bonds emanating from the interstitial cations and (OH) groups of the structural unit and the number of anions in the structural unit.

Example I: meta-ankoleite versus metatorbernite

Figure 6a shows the structural unit in minerals and synthetic phases of the autunite and meta-autunite groups. Figures 6b, c show the interstitial complexes in synthetic deuterated meta-ankoleite, $[^{[8]}K(D_2O)_1[(UO_2)(PO_4)](D_2O)_2$, Cole *et al.* 1993], and metatorbernite, $[^{[6]}Cu^{2+}(H_2O)_4[(UO_2)(PO_4)]_2(H_2O)_4$, Locock & Burns 2003d]. Both minerals have the same structural unit, but the bonding in their interstitial complexes is very different. Synthetic deuterated meta-ankoleite contains two large cations per formula unit: [8]-coordinated K^+ bonding to five (D_2O) groups and three O atoms of the structural unit. One (D_2O) group accepts a hydrogen bond and a bond from K^+, and another (D_2O) group accepts two bonds from two K^+ cations. Both (D_2O) groups are non-transformer groups (indicated in Fig. 6c), because the average bond-valence from two accepted bonds is similar to the average bond-valence from the two emanating hydrogen bonds (see above). The third (D_2O) group (indicated in Fig. 6c) accepts two bonds from K^+ and one hydrogen bond, and hence is an inverse bond-valence transformer.

There are six atoms of O in the structural unit (per formula unit). The bond valence of the eight bonds emanating from K^+ must be transferred to those anions on both sides of the interstitial complex. However, the number of bonds from K^+ exceeds the number of anions per formula unit, and therefore only a few (H_2O) groups per interstitial cation are required to transfer the bond valence to the anions. If we do not consider the inverse bond-valence transformer (H_2O) group, there are only two H_2O groups per interstitial cation that can transfer the bond valence to anions of the structural unit.

The bonding in the interstitial complex is completely different in the structure of metatorbernite, $^{[6]}Cu(H_2O)_4[(UO_2)(PO_4)]_2(H_2O)_4$. Here, the small Cu^{2+} cation is in [6]-coordination and bonds to four (H_2O) groups and two anions of the structural unit (Fig. 6c). These four (H_2O) groups do not accept any other bonds and are therefore bond-valence transformers. There are an additional four interstitial (H_2O) groups that do not bond to Cu^{2+}. Each of these (H_2O) groups accepts two hydrogen bonds and denotes two hydrogen bonds. Hence, these (H_2O) groups are non-transformer (H_2O) groups. Ten out of twelve anions in the structural unit accept bonds from cations and (H_2O) groups in the interstitial complex. Considering the Jahn–Teller distortion of the Cu^{2+} polyhedra, the four equatorial bonds have an average bond-valence of ~0.415 *vu*, and the two apical bonds, an average bond-valence of 0.17 *vu*. Two apical bonds point directly toward two anions of adjacent structural units. This leaves 10 anions of the structural unit as potential bond-valence acceptors involving the equatorial Cu^{2+}–O bonds. Hence, transformer (H_2O) groups occur as equatorial ligands, and additional non-transformer (H_2O) groups occur between the interstitial cations in order to distribute the bond valence to the remaining eight anions in the structural unit.

Example II: fourmarierite versus becquerelite

Fourmarierite, $^{[8]}Pb(H_2O)_4[(UO_2)_4O_3(OH)_4]$, and becquerelite, $^{[7]}Ca(H_2O)_8[(UO_2)_6O_4(OH)_6]$, have inter-

stitial cations with similar coordination-numbers and structural units with a similar number of (OH) groups. However, becquerelite has eight interstitial (H_2O) groups, whereas fourmarierite has only four. Using the factors above, we can now examine why becquerelite has twice the number of interstitial (H_2O) groups as fourmarierite.

In fourmarierite, eight bonds emanate from the interstitial cations, and there are four (OH) groups and 15 anions in total in the structural unit. Hence, the ratio of anions to bonds from cations and (OH) groups is 15 / 12 = 1.25. Schindler & Hawthorne (2004) showed that fourmarierite has a less highly polymerized sheet structural unit than becquerelite (*i.e.*, a lower density of anions in the structural unit). Inspection of the arrangement of (H_2O) groups in the interstitial complex of fourmarierite (Li & Burns 2000c) indicates that the interstitial complex contains one transformer (H_2O), which bonds to one Pb^{2+} (type 1, Fig. 5a). There are three different types of non-transformer (H_2O) groups: one bonds to two Pb^{2+} (type 1, Fig. 5b), one bonds to one Pb and accepts a hydrogen bond from an (H_2O) group (type 3, Fig. 5b), and one accepts two hydrogen bonds from (OH) groups (type 6, Fig. 5b).

In becquerelite, the ratio of anions to bonds from cations and (OH) groups is 22 / 13 = 1.69. It has a more highly polymerized sheet structural unit than fourmarierite (*i.e.*, a higher density of anions in the structural unit). Inspection of the arrangement of the interstitial complex in becquerelite (Burns & Li 2002) indicates that all (H_2O) groups are of the non-transformer type. There are three different types of non-transformer (H_2O) groups: (1) one (H_2O) group bonds to one Ca and accepts a hydrogen bond from an (OH) group (type 2); (2) three (H_2O) groups bond to Ca and accept a hydrogen bond from a (H_2O) group (type 3); (3) four (H_2O) groups accept one hydrogen bond from an (OH) group and one from a (H_2O) group (type 4). Note that the types of non-transformer H_2O groups given in brackets refer to Figure 5.

We can now summarize the factors that affect the number of (H_2O) groups in each mineral:

(1) the ratio of the number of anions in the structural unit and the number of bonds involving interstitial cations plus the number of (OH) groups in the structural unit;

(2) the degree of polymerization in the structural unit;

(3) the coordination of the interstitial non-transformer (H_2O) groups; in fourmarierite, they occur in coordinations (1), (3) and (6) (Fig. 5b), whereas in becquerelite, they occur in coordinations (2), (3) and (4).

The Bond-Valence Distribution Factor, *D*

As discussed above, the ratio between the number of anions in the structural unit and the number of bonds emanating from interstitial cations and (OH) groups of the structural unit dictate the number and types of (H_2O) groups in the interstitial complex. This ratio is designated the *bond-valence distribution factor*, *D*, because it controls the number of (H_2O) groups (in the interstitial complex), which distribute bond-valence to the anions of the structural unit. It is defined as follows:

$$D = (N^{A:SU}) / [(N^{B:IC}) + (N^{(OH):SU})] \quad (1)$$

where $N^{A:SU}$ is the number of anions (*A*) in the structural unit (*SU*), $N^{B:IC}$ is the number of bonds (*B*) emanating from the interstitial complex (*IC*), and $N^{(OH):SU}$ is the number of (OH) groups in the structural unit.

Important factors controlling the number of bonds emanating from an interstitial complex are (1) the number of $(OH)^-$ groups bonded to interstitial cations, and (2) the number of inverse-transformer (H_2O) groups. Both groups reduce the number of bonds emanating from the interstitial cations, and therefore both groups affect the number of interstitial (H_2O) groups. For each bond removed by the action of an (OH) group or inverse bond-valence transformer (H_2O) group, an additional (H_2O) group (transformer or non-transformer) may be required to distribute the bond valence to the anions of the structural unit. In order to compare the number of transformer (or total number of) (H_2O) groups of interstitial complexes [with or without $(OH)^-$ or inverse-transformer (H_2O) groups], we divide the interstitial complex in two parts: (1) interstitial $(OH)^-$ and (H_2O) groups, and (2) interstitial cations. Next, we calculate the number of bonds removed by the effect of $(OH)^-$ groups and inverse-transformer (H_2O) groups and subtract this number from the number of transformer (or total number of) (H_2O) groups. The result is subsequently divided by the number of cations in the interstitial complex and given either as "the total number of (H_2O) groups per cation" or "transformer (H_2O) groups per cation".

Number of (H_2O) per cation = {interstitial (H_2O) groups – (t –1) $^{[t]}$OH groups – inverse transformer (H_2O) groups} / the number of interstitial cations (2)

Transformer (H_2O) groups per cation = {transformer (H_2O) groups – (t–1) $^{[t]}$OH groups – inverse transformer (H_2O) groups} / the number of interstitial cations (3)

We wish to emphasize here that the parameter *D*, the coordination number of the $(OH)^-$ groups, and the degree of polymerization of the structural unit all can be determined without knowledge of the hydrogen-bonding arrangement. The number of inverse-transformer (H_2O) groups can be determined only if the hydrogen-bonding scheme is known. However, these groups are rare and were ignored for those minerals in which the hydrogen-bonding scheme could be not unequivocally determined (see below).

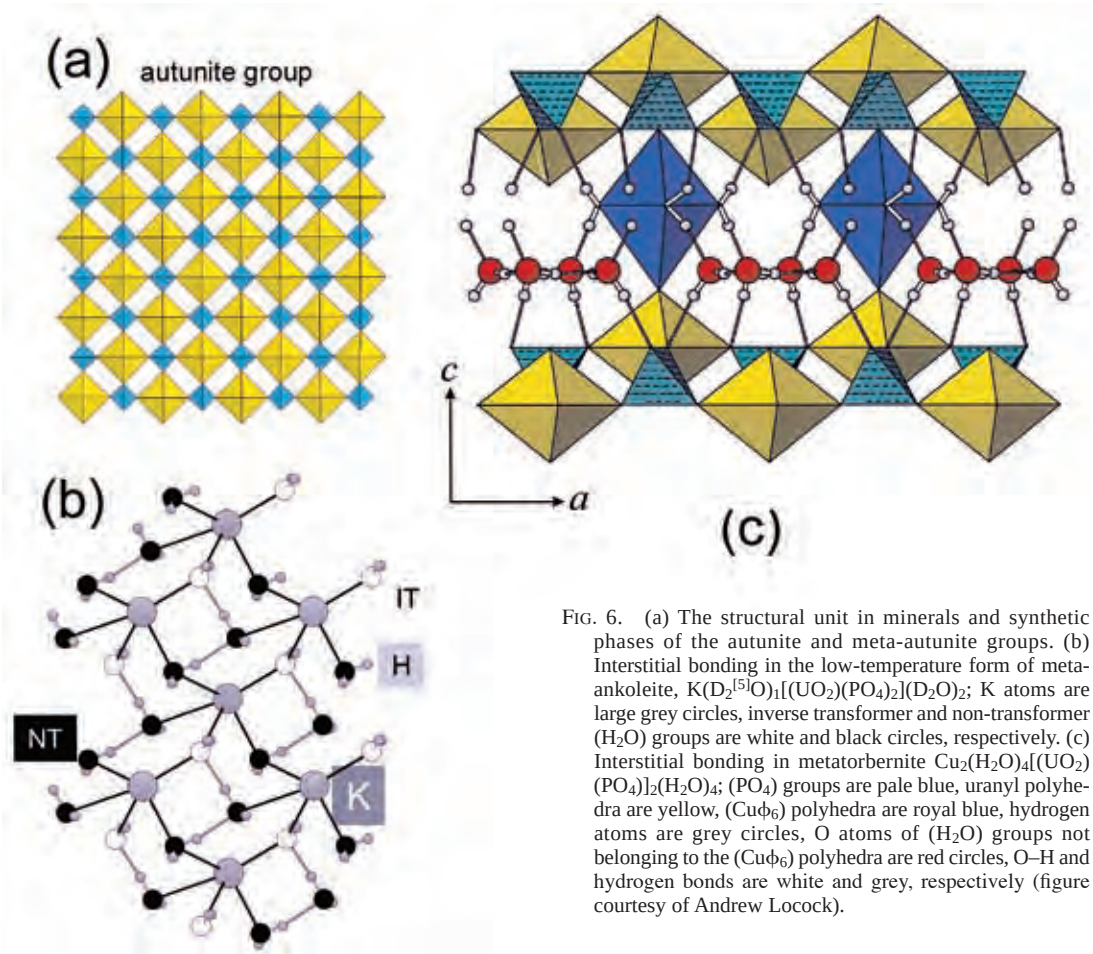

FIG. 6. (a) The structural unit in minerals and synthetic phases of the autunite and meta-autunite groups. (b) Interstitial bonding in the low-temperature form of meta-ankoleite, $K(D_2^{[5]}O)_1[(UO_2)(PO_4)_2](D_2O)_2$; K atoms are large grey circles, inverse transformer and non-transformer (H_2O) groups are white and black circles, respectively. (c) Interstitial bonding in metatorbernite $Cu_2(H_2O)_4[(UO_2)(PO_4)]_2(H_2O)_4$; ($PO_4$) groups are pale blue, uranyl polyhedra are yellow, ($Cu\phi_6$) polyhedra are royal blue, hydrogen atoms are grey circles, O atoms of (H_2O) groups not belonging to the ($Cu\phi_6$) polyhedra are red circles, O–H and hydrogen bonds are white and grey, respectively (figure courtesy of Andrew Locock).

Negative numbers of transformer and total number of (H_2O) groups

The predicted numbers of transformer and total number of (H_2O) groups can be negative for a specific mineral or synthetic phase, if there are more $(OH)^-$ groups or inverse-transformer (H_2O) groups than transformer or total number of (H_2O) groups. This has the advantage that a negative predicted value of transformer (H_2O) groups can be used to predict the number of inverse transformer (H_2O) groups, because an interstitial complex rarely contains both, transformer and inverse-transformer (H_2O) groups. If the number of transformer and total number of (H_2O) groups is negative, $(OH)^-$ groups must occur in the interstitial complex. These groups can be also predicted if one also considers the charge balance between interstitial cations and structural unit.

THE NUMBER OF (H_2O) GROUPS AND THE *D* FACTOR FOR SHEET STRUCTURAL UNITS

For the correlation between number of transformer or total number of H_2O groups and *D*, we again considered minerals and selected synthetic phases that (1) form in or from aqueous solution (*i.e.*, below the critical point of water and generally in damp, as distinct from wet, environments), and (2) do not contain any disordered cations in their interstices (except boltwoodite, see above). As mentioned above, knowledge of the hydrogen-bonding scheme is not required for the determination of the total number of (H_2O) groups and the parameter *D*. Hence for the correlation between the latter two parameters, we also considered the chemical composition of minerals where the hydrogen-bonding scheme could be equivocally resolved. The names of the corresponding minerals are marked with (*) in Table 3.

For the correlation between *D* and the number of (H_2O) groups per cation or the number of transformer (H_2O) groups per cation, we cannot treat lone-pair stereoactive cations (*e.g.*, Pb^{2+} and Bi^{3+}) as part of the structural unit, because the latter two parameters are expressed in terms of interstitial cations. Also, we cannot consider uranyl-sheet minerals that do not contain interstitial cations (*e.g.* schoepite, $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$).

For the correlation between *D* and the total number of (H_2O) groups, we did not consider any structural data from highly hydrated minerals of the autunite, carnotite and zippeite groups (*e.g.*, autunite, torbernite, zeunerite, marecottite). In the interlayer of these minerals, there are additional layers of (H_2O) groups that do not bond to any interstitial cation (Locock & Burns 2003c, d, Locock *et al.* 2004a, 2005, Brugger *et al.* 2003). Many of these minerals are not stable in air and dehydrate to phases with a lower degree of hydration. For example, Locock & Burns (2003d) and Locock *et al.* (2004a) reported the occurrence of two or three possible hydration states for phases with the structural unit of the autunite group $[(UO_2)(TO_4)]^-$ (T = P, As) and octahedrally coordinated divalent cations ($^{[6]}M^{2+}$= Cu^{2+}, Mg, Mn^{2+}, and Fe^{2+}) in the interstitial complex: octahydrates, decahydrates and dodecahydrates. In this paper, we consider only the structural data for the octahydrates, which Gaines *et al.* (1997) and Finch & Murakami (1999) listed as members of the meta-autunite group.

The total number of (H_2O) groups per cation versus D

Figure 7a shows the variation in *D* as a function of the number of (H_2O) groups per cation for minerals and selected synthetic phases containing sheet structural-units. The total number of (H_2O) groups per cation

TABLE 3. OBSERVED AND PREDICTED CHEMICAL COMPOSITION OF SELECTED URANYL-OXYSALT MINERALS WITH SHEET-STRUCTURAL UNITS

Mineral	Observed chemical composition	Predicted chemical composition	Ref.
	Meta-autunite group		
Meta-ankoleite	$^{[8]}K[(UO_2)(PO_4)](D_2O)_3$	$^{[8]}M[(UO_2)(PO_4)](H_2O)_{2.0}$	1
Metazeunerite	$^{[6]}Cu[(UO_2)(AsO_4)]_2(H_2O)_8$	$^{[6]}Cu[(UO_2)(AsO_4)]_2(H_2O)_8$	2
Metatorbernite	$^{[6]}Cu[(UO_2)(PO_4)]_2(H_2O)_8$	$^{[6]}Cu[(UO_2)(PO_4)]_2(H_2O)_8$	2
Threadgoldite*	$^{[6]}Al(OH)[(UO_2)(PO_4)]_2(H_2O)_8$	$Al(^{[3]}OH)[(UO_2)(PO_4)]_2(H_2O)_9$	3
Metakahlerite*	$^{[6]}Fe^{2+}[(UO_2)AsO_4]_2(H_2O)_8$	$^{[6]}Fe^{2+}[(UO_2)AsO_4]_2(H_2O)_8$	4
Metakirchheimerite*	$^{[6]}Co^{2+}[(UO_2)AsO_4]_2(H_2O)_8$	$^{[6]}Co^{2+}[(UO_2)AsO_4]_2(H_2O)_8$	4
Metauranocircite (I)	$^{[9]}Ba[(UO_2)(PO_4)_2](H_2O)_7$	$^{[9]}Ba[(UO_2)(PO_4)_2](H_2O)_5$	5
Metauranocircite (II)	$^{[9]}Ba[(UO_2)(PO_4)_2](H_2O)_6$	$^{[9]}Ba[(UO_2)(PO_4)_2](H_2O)_5$	5
	Uranophane group		
Uranophane	$^{[7]}Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$	$^{[7]}Ca[(UO_2)SiO_3(OH)]_2(H_2O)_4$	6
Uranophane-beta*	$^{[8]}Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$	$^{[8]}Ca[(UO_2)SiO_3(OH)]_2(H_2O)_{3.5}$	7
Boltwoodite	$^{[7]}K[(UO_2)(SiO_3OH)](H_2O)_1$	$^{[7]}K[(UO_2)SiO_3(OH)](H_2O)_2$	8
Natroboltwoodite	$^{[6]}Na[(UO_2)(SiO_3OH)](H_2O)_1$	$^{[6]}Na[(UO_2)SiO_3(OH)](H_2O)_{2.5}$	8
Sklodowskite*	$^{[6]}Mg[(UO_2)(SiO_3OH)]_2(H_2O)_6$	$^{[6]}Mg[(UO_2)SiO_3(OH)]_2(H_2O)_5$	9
Cuprosklodowskite	$^{[6]}Cu[(UO_2)(SiO_3OH)]_2(H_2O)_6$	$^{[6]}Cu[(UO_2)SiO_3(OH)]_2(H_2O)_5$	10
Kasolite	$^{[2+6]}Pb[(UO_2)(SiO_4)](H_2O)_1$	$^{[2+6]}Pb^{2+}[(UO_2)(SiO_4)](H_2O)_2$	11
	Phosphuranylite group		
Phuralumite*	$^{[6]}Al_2(OH)_4[(UO_2)_3(PO_4)_2(OH)_2](H_2O)_{10}$	$^{[6]}Al_2(OH)_4[(UO_2)_3(PO_4)_2(OH)_2](H_2O)_{10}$	12
Dewindtite*	$^{[8]}Pb_2{}^{[11]}Pb[(UO_2)_3(PO_4)_2(OH)O]_2(H_2O)_{12}$	$^{[8]}Pb_2{}^{[11]}Pb[(UO_2)_3(PO_4)_2(OH)O]_2(H_2O)_9$	13
Upalite	$^{[6]}Al[(UO_2)_3(PO_4)_2(OH)O](H_2O)_7$	$^{[6]}Al[(UO_2)_3(PO_4)_2(OH)O](H_2O)_9$	14
Françoisite(-Nd)*	$^{[9]}Nd[(UO_2)_3(PO_4)_2(OH)O](H_2O)_6$	$^{[9]}Nd[(UO_2)_3(PO_4)_2(OH)O](H_2O)_6$	15
Dumonite	$^{[7]}Pb_2[(UO_2)_3(PO_4)_2O_2](H_2O)_5$	$^{[8]}Pb_2[(UO_2)_3(PO_4)_2O_2](H_2O)_6$	16
Hügelite*	$^{[8]}Pb_2[(UO_2)_3(AsO_4)_2O_2](H_2O)_5$	$^{[7]}Pb_2[(UO_2)_3(AsO_4)_2O_2](H_2O)_7$	17
Phurcalite	$^{[6]}Ca^{[7]}Ca[(UO_2)_3(PO_4)_2O_2](H_2O)_7$	$^{[8]}Ca^{[7]}Ca[(UO_2)_3(PO_4)_2O_2](H_2O)_6$	18
Bergenite*	$^{[6]}Ca_2{}^{[9.5]}Ba_4[(UO_2)_3(PO_4)_2O_2]_3(H_2O)_{16}$	$^{[8]}Ca_2{}^{[9.5]}Ba_4[(UO_2)_3(PO_4)_2O_2]_3(H_2O)_{13}$	19
	Carnotite group		
Francevillite*	$^{[9]}Ba[(UO_2)_2(V_2O_8)](H_2O)_5$	$^{[9]}Ba[(UO_2)_2(V_2O_8)](H_2O)_5$	20
Curienite*	$^{[8]}Pb[(UO_2)_2(V_2O_8)](H_2O)_5$	$^{[8]}Pb[(UO_2)_2(V_2O_8)](H_2O)_5$	21
Sengierite	$^{[6]}Cu_2(OH)_2[(UO_2)_2(V_2O_8)](H_2O)_6$	$^{[6]}Cu_2(^{[4]}OH)_2[(UO_2)_2(V_2O_8)](H_2O)_9$	22

Zippeite group

Zippeite*	$^{[7,33]}K_3[(UO_2)_4(SO_4)_2O_3(OH)](H_2O)_3$	$^{[7,33]}K_3[(UO_2)_4(SO_4)_2O_3(OH)](H_2O)_5$	23
Natrozippeite	$^{[6,6]}Na_4[(UO_2)_8(SO_4)_4O_5(OH)_3](H_2O)_{12}$	$^{[6,6]}Na_5[(UO_2)_8(SO_4)_4O_5(OH)_3](H_2O)_{15}$	23
Marecottite*	$^{[6]}Mg_3[(UO_2)_4(SO_4)_2O_3(OH)]_2(H_2O)_{28}$	$^{[6]}Mg_3[(UO_2)_4(SO_4)_2O_3(OH)]_2(H_2O)_{23}$	24
Magnesiozippeite	$^{[6]}Mg[(UO_2)_2(SO_4)O_2](H_2O)_{3.5}$	$^{[6]}Mg[(UO_2)_2(SO_4)O_2](H_2O)_6$	23
Zinczippeite	$^{[6]}Zn[(UO_2)_2(SO_4)O_2](H_2O)_{3.5}$	$^{[6]}Zn[(UO_2)_2(SO_4)O_2](H_2O)_6$	23
Cobaltzippeite	$^{[6]}Co[(UO_2)_2(SO_4)O_2](H_2O)_{3.5}$	$^{[6]}Co[(UO_2)_2(SO_4)O_2](H_2O)_6$	23

Uranyl-hydroxy-hydrates

Becquerelite	$^{[7]}Ca[(UO_2)_3O_2(OH)_3]_2(H_2O)_8$	$^{[7]}Ca[(UO_2)_3O_2(OH)_3]_2(H_2O)_6$	25
Compreignacite*	$^{[7]}K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$	$^{[7]}K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_6$	26
Fourmarierite*	$^{[8]}Pb[(UO_2)_4O_3(OH)_4](H_2O)_4$	$^{[8]}Pb[(UO_2)_4O_3(OH)_4](H_2O)_4$	27
Protasite*	$^{[10]}Ba[(UO_2)_3O_3(OH)_2](H_2O)_3$	$^{[10]}Ba[(UO_2)_3O_3(OH)_2](H_2O)_2$	28
Masuyite*	$^{[10]}Pb[(UO_2)_3O_3(OH)_2](H_2O)_3$	$^{[10]}Pb[(UO_2)_3O_3(OH)_2](H_2O)_2$	29
Curite	$^{[10]}Pb_3[(UO_2)_8O_8(OH)_6](H_2O)_2$	$^{[10]}Pb_3[(UO_2)_8O_8(OH)_6](H_2O)_5$	30
Sayrite*	$^{[9]}Pb_2[(UO_2)_5O_6(OH)_2](H_2O)_4$	$^{[9]}Pb_2[(UO_2)_5O_6(OH)_2](H_2O)_4$	31
Agrinierite	$^{[7]}K^{[9]}K(^{[9]}Ca,Sr)[(UO_2)_3O_3(OH)_2]_2(H_2O)_5$	$^{[7]}K^{[9]}K(^{[9]}Ca,Sr)[(UO_2)_3O_3(OH)_2]_2(H_2O)_3$	32

Miscellaneous

Guilleminite	$^{[10]}Ba[(UO_2)_3O_2(SeO_3)_2](H_2O)_3$	$^{[10]}Ba[(UO_2)_3O_2(SeO_3)_2](H_2O)_{4.5}$	33
Marthozite	$^{[6]}Cu[(UO_2)_3O_2(SeO_3)_2](H_2O)_8$	$^{[6]}Cu[(UO_2)_3O_2(SeO_3)_2](H_2O)_9$	34
Roubaultite	$^{[6]}Cu_2[(UO_2)_3(CO_3)_2O_2(OH)_2](H_2O)_4$	$^{[6]}Cu_2[(UO_2)_3(CO_3)_2O_2(OH)_2](H_2O)_5$	35
Johannite	$^{[6]}Cu[UO_2)_2(OH)_2(SO_4)_2](H_2O)_8$	$^{[6]}Cu[UO_2)_2(OH)_2(SO_4)_2](H_2O)_6$	36

* structure not refined. References: [1] Cole *et al.* (1993), [2] Locock & Burns (2003d), [3] Khosrawan-Sazedj (1982b), [4] Locock *et al.* (2004b), [5] Locock *et al.* (2005), [6] Ginderow (1988), [7] Viswanathan & Harneit (1986), [8] Burns (1998a), [9] Ryan & Rosenzweig (1977), [10] Rosenzweig & Ryan (1975), [11] Rosenzweig & Ryan (1977a), [12] Piret *et al.* (1979), [13] Piret *et al.* (1990), [14] Piret & Declercq (1983), [15] Piret *et al.* (1988), [16] Piret & Piret-Meunier (1988), [17] Locock & Burns (2003f), [18] Atencio *et al.* (1991), [19] Locock & Burns (2003e), [20] Mereiter (1986d), [21] Borene & Cesbron (1971), [22] Piret *et al.* (1980), [23] Burns *et al.* (2003), [24] Brugger *et al.* (2003), [25] Burns & Li (2002), [26] Burns (1998b), [27] Piret (1985), Li & Burns (2000c), [28] Pagoaga *et al.* (1987), [29] Burns & Hanchar (1999), [30] Taylor *et al.* (1981), [31] Piret *et al.* (1983), [32] Cahill & Burns (2000), [33] Cooper & Hawthorne (1995), [34] Cooper & Hawthorne (2001), [35] Ginderow & Cesbron (1985), [36] Mereiter (1982b).

increases with increasing *D* values, and the synthetic phases and minerals are both in agreement with this general trend. Figure 7b shows the analogous data for minerals, for which the linear trend can be described with the following equation.

$$\text{Total number of } (H_2O) \text{ groups} = 5.1\,D - 2.17 \quad R^2 = 0.83,\ \sigma = 1.1 \qquad (4)$$

In order to test the quality of the regression parameters refined, the observed number of (H_2O) groups values for minerals is plotted against the predicted values (Fig. 7c). Closer inspection of the plot indicates that approximately 70% of the data points fall into the range of ± one H_2O group from the one-to-one reference line (shown as a shaded band), which indicates a good agreement between observed and predicted number of total H_2O groups in uranyl-oxysalt minerals.

We also show the total number of (H_2O) groups per cation as a function of *D*, the bond-valence distribution factor, where the latter parameter does not include the number of hydrogen bonds emanating from $(OH)^-$ groups in the structural unit (Fig. 8a). In Figure 8a, the data for minerals both with and without (OH) groups are distinguished, and it is apparent that predictions for minerals with (OH) groups are systematically lower than predictions for minerals without (OH) groups in the structural unit. Hence the number of (OH) groups in the structural unit must be included in the expression for *D*.

The linear equations and the corresponding linear regression parameters for the plots of minerals with structural units without ([5]) and with ([6]) $(OH)^-$ groups are as follows:

$$\text{total number of } (H_2O) \text{ groups} = 4.88\,D - 2.53; \quad R^2 = 0.87,\ \sigma = 1.00 \qquad (5)$$

$$\text{total number of } (H_2O) \text{ groups} = 3.5\,D - 1.84; \quad R^2 = 0.80,\ \sigma = 0.96 \qquad (6)$$

Figure 8b shows the observed and predicted number of (H_2O) groups per cation using equations (5) and (6). Comparison of Figures 7c and 8b indicates similarly

good agreement between the observed and predicted numbers of (H_2O) groups per cation. However, the disadvantage with Figure 8b is that two different linear equations must be used to predict the number of (H_2O) groups per cation.

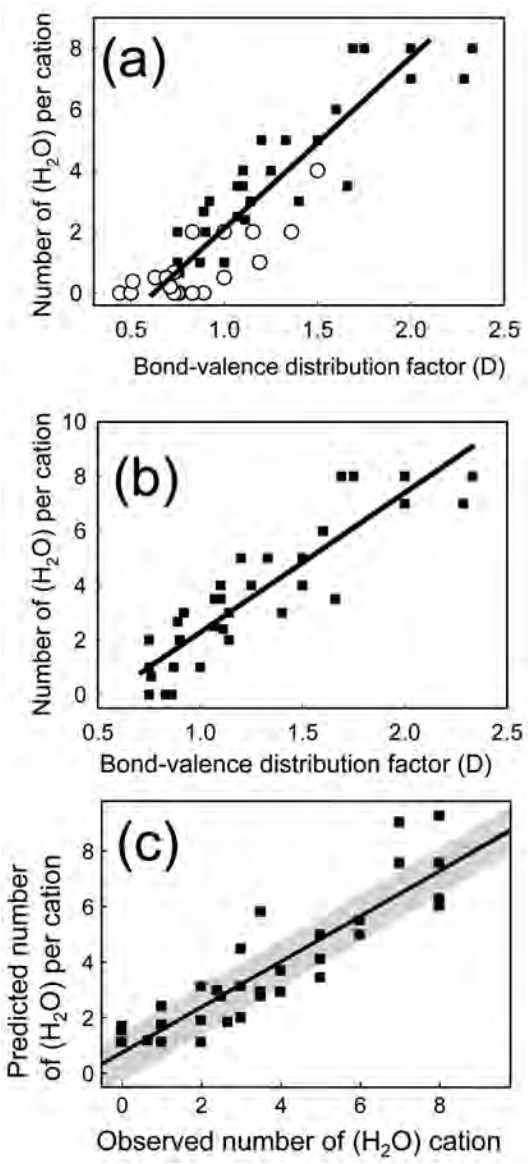

FIG. 7. Variation in the number of (H_2O) groups per cation as a function of the bond-valence distribution factor (a) for minerals (black squares) and selected synthetic compounds (circles) with sheet structural units, and (b) for uranyl-oxysalt minerals with sheet structural-units. (c) The predicted *versus* observed total number of (H_2O) groups per cation in minerals using equation (4); the plus-minus one (H_2O) group spread from the one-to-one reference line is indicated as a grey band.

Figure 8c shows the *D* values as a function of the number of transformer (H_2O) groups per cation for uranyl-oxide and -oxysalt minerals with sheet structural units. A linear trend is apparent, and can be described with the following equation:

$$\text{number of transformer } (H_2O) \text{ groups per cation} = 3.90\,D - 3.60; \quad R^2 = 0.89,\ \sigma = 0.7 \qquad (7)$$

In Figure 8d, the observed numbers of transformer (H_2O) groups per cation are compared with the predicted values. Approximately 70% of the data points fall into the range of plus or minus one (H_2O) group, which indicates good agreement between observed and predicted number of transformer (H_2O) groups per cation.

PREDICTION OF THE NUMBER AND TYPE OF (H_2O) GROUPS IN INTERSTITIAL COMPLEXES

In earlier papers (Schindler *et al.* 2000, Schindler & Hawthorne 2001a, b, c), we focused on possible chemical composition of minerals; we did not include data from synthetic compounds, as these form either in a system with only one type of cation (where no other possible interstitial cations are available) or under extreme thermodynamic conditions. Here, we do not consider data for synthetic uranyl-compounds in developing quantitative relations between structural and chemical parameters. However, we test their predictive capability with selected synthetic structures.

The correlation between [CN_{in}] and CDA for minerals results in a band of data (Fig. 2a) that should be representative of natural conditions, as it contains data from uranyl minerals of a wide range of chemical composition (*i.e.*, sulfates, phosphates, vanadates, selenates and oxy-hydroxides). It gives well-defined maximum and minimum values of [CN_{in}] for structural units with CDA values between 0.05 and 0.40 *vu*. These values can be used to calculate the range in Lewis basicity of all sheet structural-units. Using this range in Lewis basicity, we can calculate the range of transformer and inverse transformer (H_2O) groups for a given interstitial cation.

The correlations between [1] the total number of (H_2O) groups per interstitial cation and *D*, and [4] the number of transformer (H_2O) groups per interstitial cation and *D*, allow us now to predict more accurately the number of (H_2O) groups for a specific cation.

Recent determinations of the structures of uranyl-oxysalt minerals (*e.g.*, Burns *et al.* 2003) have shown that the chemical compositions of many uranyl-oxide and oxysalt minerals were wrongly determined. Hence we will only compare predicted and observed chemical

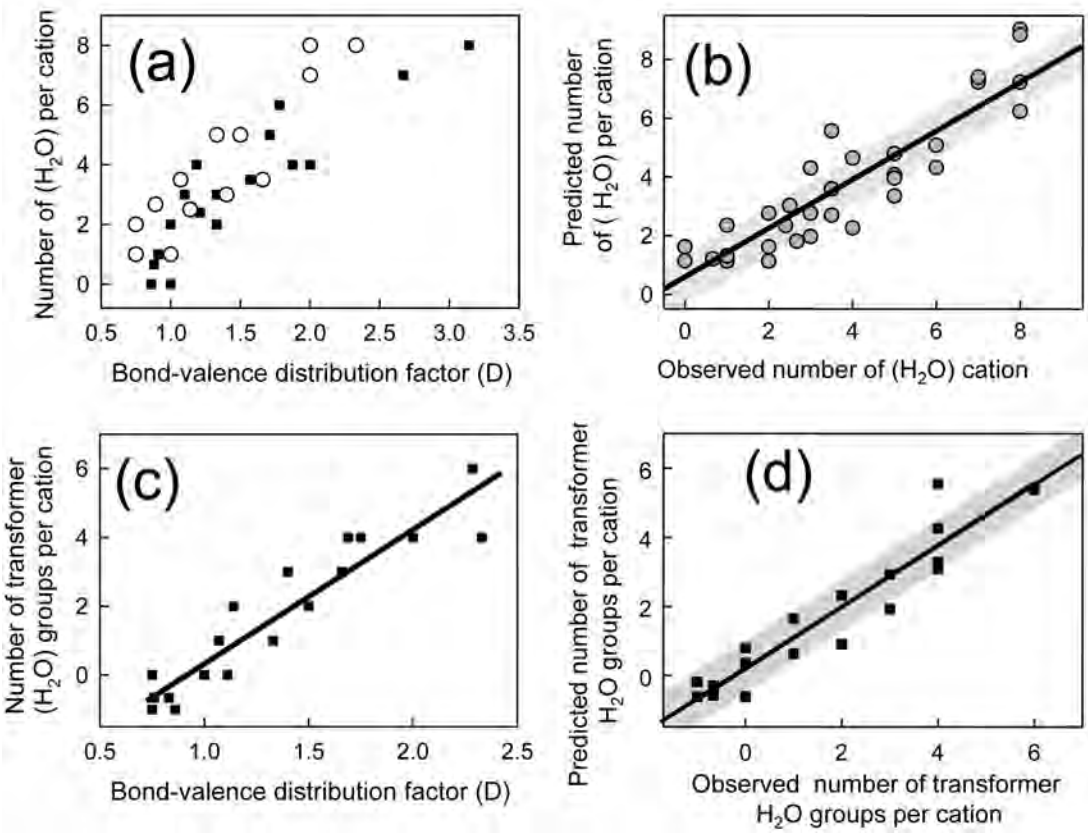

FIG. 8. (a) Variation in number of (H_2O) groups per cation as a function of the bond-valence distribution factor for minerals with sheet structural units without $(OH)^-$ groups (circles) and for minerals with sheet structural units with $(OH)^-$ groups (squares). (b) The predicted *versus* observed number of (H_2O) groups per cation in minerals using equations (5) and (6); the grey band indicates ± one (H_2O) group from the one-to-one reference line. (c) The variation in number of transformer (H_2O) groups per cation as a function of the bond-valence distribution factor for minerals with sheet structural units. (d) The predicted *versus* observed total number of transformer (H_2O) groups per cation in minerals calculated using equation (7); the ± one (H_2O) group range from the one-to-one reference line is indicated as a grey band.

compositions of interstitial complexes where the corresponding structure has been accurately determined. In Table 3, we list selected uranyl-oxysalt minerals with sheet structural units, their chemical composition, and the predicted chemical composition based on the coordination numbers of the interstitial cations. The observed and predicted chemical compositions of the interstitial complex are given as $^{[z]}M$[structural unit] $(H_2O)_n$, where n is the number of (H_2O) groups in the interstitial complex. In Table 4, we list the observed and predicted numbers of transformer (TR), inverse-transformer (INV) and non-transformer (NTR) H_2O groups for the selected uranyl-oxysalt minerals. No numbers are given for the different types of observed interstitial (H_2O) groups if the hydrogen-bonding scheme in the structure is not known.

In the following sections, we will compare predicted and observed chemical compositions for minerals of the meta-autunite, uranophane, phosphuranylite, carnotite and zippeite groups. For the meta-autunite group, we will show in detail how the possible cations and the number of transformer (H_2O) groups and the total number of (H_2O) groups can be predicted reasonably accurately for a specific structural unit.

THE META-AUTUNITE GROUP

The meta-autunite group has the general formula $M^{z+}[(UO_2)(TO_4)]_2(OH)_m(H_2O)_n$ with T = As, P, z in the range 1–3, m = 0,1 and n in the range 2–10; this group contains over 26 mineral species of diverse chemical composition, and has been investigated in detail by

Locock & Burns (2003d), and Locock *et al.* (2004a, b, 2005). Figure 6a shows the corresponding structural unit $[(UO_2)(TO_4)]^{-}$. It contains U^{6+} in [6]-coordination and (TO_4) tetrahedra arranged in a checkerboard pattern. The effective charge of the structural unit is 2^{-}, and the number of O atoms in the structural unit is 12. Hence the structural unit has a CDA value of 0.17 *vu*. We may use the values of CDA, together with Figure 2a, to predict the maximum and minimum values of $[CN_{in}]$: 0.66 and 1.17, respectively. There are twelve atoms of oxygen in the structural unit; thus there are a minimum of $12 \times 0.62 = 8$ and a maximum of $12 \times 1.17 = 14$ bonds from the interstitial complex to the structural unit. This results in a range of Lewis basicity from 2 / 14 = 0.14 to 2 / 8 = 0.25 *vu*. The valence-matching principle requires that the Lewis acidities of interstitial complexes in the minerals of the meta-autunite group should be in the range 0.14–0.25 *vu*; this range is shown in Figure 9a.

Interstitial complexes with monovalent cations

Inspection of Figure 9a indicates that interstitial monovalent cations must bond to inverse-transformer (H_2O) groups if the interstitial cation has a coordination number higher than [7]. For example, the low-temperature form of meta-ankoleite (Table 1) contains the interstitial complex with $^{[8]}K$, and hence the interstitial cation must bond to at least one inverse transformer (H_2O) group. We can now use the linear equations [1] and [4] to predict the total number of (H_2O) groups and the number of transformer (H_2O) groups. For an [8]-coordinated monovalent cation and the meta-ankoleite structural unit, $D = N^{SU}_{A} / (N^{IC}_{B} + N^{SU}_{(OH)})$, $= 6 / 8 = 0.75$, and the predicted total number of (H_2O) groups is therefore $5.1 \times 0.75 - 2.7 = 1.1$. The predicted number of transformer (H_2O) groups is $3.9 \times 0.75 - 3.6 = -0.7$; the negative value means that there are more inverse-transformer (H_2O) groups or $(OH)^{-}$ groups than transformer (H_2O) groups in the interstitial complex. An inverse-transformer (H_2O) group is more likely to occur

TABLE 4. OBSERVED AND PREDICTED NUMBER OF TRANSFORMER (TR), INVERSE-TRANSFORMER (INV) AND NON-TRANSFORMER (NTR) (H_2O)-GROUPS IN URANYL-OXYSALT MINERALS WITH SHEET-STRUCTURAL UNITS

Mineral	Chemical composition	Observed			Predicted			Ref.
		TR	INV	NTR	TR	INV**	NTR	
Meta-autunite group								
Meta-ankoleite	$^{[8]}K[(UO_2)(PO_4)](D_2O)_3$	0	1	2	0	1	1	1
Metazeunerite	$^{[6]}Cu[(UO_2)(AsO_4)]_2(H_2O)_8$	4	0	4	4	0	4	2
Metatorbernite	$^{[6]}Cu[(UO_2)(PO_4)]_2(H_2O)_8$	4	0	4	4	0	4	2
Threadgoldite*	$^{[6]}Al(OH)[(UO_2)(PO_4)]_2(H_2O)_8$	n.d.	n.d.	n.d.	5	0	4	3
Metakahlerite*	$^{[6]}Fe^{2+}[(UO_2)AsO_4]_2(H_2O)_8$	n.d.	n.d.	n.d.	4	0	4	4
Metakirchheimerite*	$^{[6]}Co^{2+}[(UO_2)AsO_4]_2(H_2O)_8$	n.d.	n.d.	n.d.	4	0	4	4
Metauranocircite (II,I)	$^{[9]}Ba[(UO_2)(PO_4)_2](H_2O)_5$	n.d.	n.d.	n.d.	2	0	3	5
Uranophane group								
Uranophane	$^{[7]}Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$	1	0	4	1.5	0	2.5	6
Uranophane-beta*	$^{[8]}Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$	n.d.	n.d.	n.d.	1	0	2.5	7
Boltwoodite	$^{[7]}K[(UO_2)(SiO_3OH)](H_2O)_1$	0	1	0	0	1	1	8
Natroboltwoodite	$^{[6]}Na[(UO_2)(SiO_3OH)](H_2O)_1$	0	1	0	0	0.5	2	8
Sklodowskite*	$^{[6]}Mg[(UO_2)(SiO_3OH)]_2(H_2O)_6$	n.d.	n.d.	n.d.	2	0	3	9
Cuprosklodowskite	$^{[6]}Cu[(UO_2)(SiO_3OH)]_2(H_2O)_6$	2	0	4	2	0	3	10
Kasolite	$^{[2+6]}Pb[(UO_2)(SiO_4)](H_2O)_1$	0	0	1	0	1	1	11
Phosphuranylite group								
Phuralumite*	$^{[6]}Al_2(OH)_4[(UO_2)_3(PO_4)_2(OH)_2](H_2O)_{10}$	n.d.	n.d.	n.d.	6	0	4	12
Dewindtite*	$^{[8]}Pb_2{}^{[11]}Pb[(UO_2)_3(PO_4)_2(OH)O]_2(H_2O)_{12}$	n.d.	n.d.	n.d.	2	0	7	13
Upalite	$^{[6]}Al[(UO_2)_3(PO_4)_2(OH)O](H_2O)_7$	6	0	1	5	0	4	14
Françoisite(-Nd)*	$^{[9]}Nd[(UO_2)_3(PO_4)_2(OH)O](H_2O)_6$	n.d.	n.d.	n.d.	3	0	3	15
Dumonite	$^{[7]}Pb_2[(UO_2)_3(PO_4)_2O_2](H_2O)_5$	2	0	3	2	0	4	16
Hügelite*	$^{[8]}Pb_2[(UO_2)_3(AsO_4)_2O_2](H_2O)_5$	n.d.	n.d.	n.d.	0	0	5	17
Phurcalite	$^{[8]}Ca^{[7]}Ca[(UO_2)_3(PO_4)_2O_2](H_2O)_7$	3	0	4	1	0	5	18
Bergenite*	$^{[8]}Ca_2{}^{[9]}Ba_4[(UO_2)_3(PO_4)_2O_2]_3(H_2O)_{16}$	n.d.	n.d.	n.d.	0	1	12	19
Carnotite group								
Francevillite*	$^{[9]}Ba[(UO_2)_2(V_2O_8)](H_2O)_5$	n.d.	n.d.	n.d.	2	0	3	20
Curienite*	$^{[8]}Pb[(UO_2)_2(V_2O_8)](H_2O)_5$	n.d.	n.d.	n.d.	2	0	3	21
Sengierite	$^{[6]}Cu_2(OH)_2[(UO_2)_2(V_2O_8)](H_2O)_6$	4	0	2	4	0	5	22

Zippeite group								
Zippeite*	$^{[7.33]}K_3[(UO_2)_4(SO_4)_2O_3(OH)](H_2O)_3$	n.d.	n.d.	n.d.	0	1	5	23
Natrozippeite	$^{[6.6]}Na_5[(UO_2)_8(SO_4)_4O_5(OH)_3](H_2O)_{12}$	0	0	12	3	0	12	23
Marecottite*	$^{[6]}Mg_3[(UO_2)_4(SO_4)_2O_3(OH)]_2(H_2O)_{28}$	n.d.	n.d.	n.d.	12.5	0	10	24
Magnesiozippeite	$^{[6]}Mg[(UO_2)_2(SO_4)O_2](H_2O)_{3.5}$	3	0	0.5	3	0	3	23
Zinczippeite	$^{[6]}Zn[(UO_2)_2(SO_4)O_2](H_2O)_{3.5}$	3	0	0.5	3	0	3	23
Cobaltzippeite	$^{[6]}Co[(UO_2)_2(SO_4)O_2](H_2O)_{3.5}$	3	0	0.5	3	0	3	23
Uranyl-hydroxy-hydrates								
Becquerelite	$^{[7]}Ca[(UO_2)_3O_2(OH)_3]_2(H_2O)_8$	4	0	4	3	0	3	25
Compreignacite*	$^{[7]}K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$	n.d.	n.d.	n.d.	1	0	5	26
Fourmarierite*	$^{<[8]>}Pb[(UO_2)_4O_3(OH)_4](H_2O)_4$	n.d.	n.d.	n.d.	1	0	3	27
Protasite*	$^{[10]}Ba[(UO_2)_3O_3(OH)_2](H_2O)_3$	n.d.	n.d.	n.d.	0	0	2	28
Masuyite*	$^{[10]}Pb[(UO_2)_3O_3(OH)_2](H_2O)_3$	n.d.	n.d.	n.d.	0	0	2	29
Curite	$^{[10]}Pb_3[(UO_2)_8O_8(OH)_6](H_2O)_2$	0	2	0	0	1	4	30
Sayrite*	$^{[9]}Pb_2[(UO_2)_5O_6(OH)_2](H_2O)_4$	n.d.	n.d.	n.d	0	0	4	31
Agrinierite	$^{[7]}K^{[9]}K(^{[9]}Ca,Sr)[(UO_2)_3O_3(OH)_2]_2(H_2O)_5$	1	3	1	0	2	1	32
Miscellaneous								
Guilleminite	$^{[10]}Ba[(UO_2)_3O_2(SeO_3)_2](H_2O)_3$	3	0	0	1.5	0	3	33
Marthozite	$^{[6]}Cu[(UO_2)_3O_2(SeO_3)_2](H_2O)_8$	4	0	4	5	0	4	34
Roubaultite	$^{[6]}Cu_2[(UO_2)_3(CO_3)_2O_2(OH)_2](H_2O)_4$	4	0	0	2	0	4	35
Johannite	$^{[6]}Cu[UO_2)_2(OH)_2(SO_4)_2](H_2O)_8$	4	0	4	3	0	3	36

* structure not refined. ** predicted from equations [4] and [7]. References: [1] Cole *et al.* (1993), [2] Locock & Burns (2003d), [3] Khosrawan-Sazedj (1982b), [4] Locock *et al.* (2004b), [5] Locock *et al.* (2005), [6] Ginderow (1988), [7] Viswanathan & Harneit (1986), [8] Burns (1998a), [9] Ryan & Rosenzweig (1977), [10] Rosenzweig & Ryan (1975), [11] Rosenzweig & Ryan (1977a), [12] Piret *et al.* (1979), [13] Piret *et al.* (1990), [14] Piret & Declercq (1983), [15] Piret *et al.* (1988), [16] Piret & Piret-Meunier (1988), [17] Locock & Burns (2003f), [18] Atencio *et al.* (1991), [19] Locock & Burns (2003e), [20] Mereiter (1986d), [21] Borene & Cesbron (1971), [22] Piret *et al.* (1980), [23] Burns *et al.* (2003), [24] Brugger *et al.* (2003), [25] Burns & Li (2002), [26] Burns (1998b), [27] Piret (1985), Li & Burns (2000c), [28] Pagoaga *et al.* (1987), [29] Burns & Hanchar (1999), [30] Taylor *et al.* (1981), [31] Piret *et al.* (1983), [32] Cahill & Burns (2000), [33] Cooper & Hawthorne (1995), [34] Cooper & Hawthorne (2001), [35] Ginderow & Cesbron (1985), [36] Mereiter (1982b).

with an [8]-coordinated monovalent cation than an (OH) group, because the O atom of an $(OH)^-$ group must bond to at least eight $^{[8]}M^+$cations in order to satisfy its bond-valence requirements. Hence, a stable structure with a monovalent [8]-coordinated cation has the predicted chemical composition $^{[8]}M(H_2{}^{[5]}O)_{1.0}[(UO_2)(TO_4)](H_2O)_{1.0}$, which is in good agreement with the observed composition of the low-temperature form of meta-ankoleite. A [9]-coordinated interstitial cation occurs in synthetic $Cs_2[(UO_2)(PO_4)]_2(H_2O)_5$ (Locock *et al.* 2004b). Using equations [1] and [4], the predicted chemical composition of an interstitial complex with a [9]-coordinated monovalent cation is $^{[9]}M_2(H_2{}^{[5]}O)_{2.0}[(UO_2)(PO_4)]_2(H_2O)_{1.5}$. The hydrogen bonding scheme of $Cs_2[(UO_2)(PO_4)]_2(H_2O)_5$ was not unequivocally determined, but there are no transformer and at least two inverse-transformer (H_2O) groups. Hence, its chemical composition is either $Cs_2(H_2{}^{[5]}O)_2[(UO_2)(PO_4)]_2(H_2O)_3$ or $Cs_2(H_2{}^{[5]}O)_3[(UO_2)(PO_4)]_2(H_2O)_2$, in reasonable accord with our predictions.

The Lewis acidity of a monovalent cation in [7]-coordination matches the range in Lewis basicity of the structural unit of the meta-autunite-group minerals with no transformer (H_2O) groups. For a [7]-coordinated monovalent cation, $D = N^{SU}{}_A / (N^{IC}{}_B + N^{SU}{}_{(OH)}) = 6 / 7 = 0.86$; the predicted total number of (H_2O) groups is $5.1 \times 0.86 - 2.7 = 1.7$, and the predicted number of transformer (H_2O) groups is $3.9 \times 0.86 - 3.6 = -0.25$. Thus, a stable mineral with two monovalent [7]-coordinated cations has the predicted chemical composition $^{[7]}M_2(H_2O)_0[(UO_2)(TO_4)](H_2O)_2$.

Locock *et al.* (2004b) showed that the monovalent cations Na^+, K^+, Rb^+, Ag^+ and Tl^+ substitute for (H_2O) in minerals and synthetic compounds of the meta-autunite type. Furthermore, they showed that all cations occur in [7]-coordination, despite differences in ionic radii. None of these minerals were included in the correlation between D and the number of (H_2O) groups per cation, but their general chemical composition $^{[7]}M(H_2O)_3[(UO_2)(TO_4)]$ ($T = As^{5+}$, P) is in accord with our predictions. Note that in the low-temperature form of meta-ankoleite $K(H_2O)_3[(UO_2)(PO_4)]$, K is ordered and in [8]-coordination, whereas it is disordered and in [7]-coordination in the room-temperature form.

Another monovalent cation is the complex cation $(H_3O)^+$, which usually has a coordination number of [3], corresponding to the number of hydrogen bonds emanating from the complex cation. In order for $(H_3O)^+$ to have a Lewis acidity that overlaps the range in Lewis basicity of the structural unit of meta-autunite, it has to link to from one (0.25 *vu*) to four (0.14 *vu*) transformer (H_2O) groups. Using equations [1] and [4], the predicted total number of (H_2O) groups is 7.5 for a [3]-coordinated cation, and the number of transformer

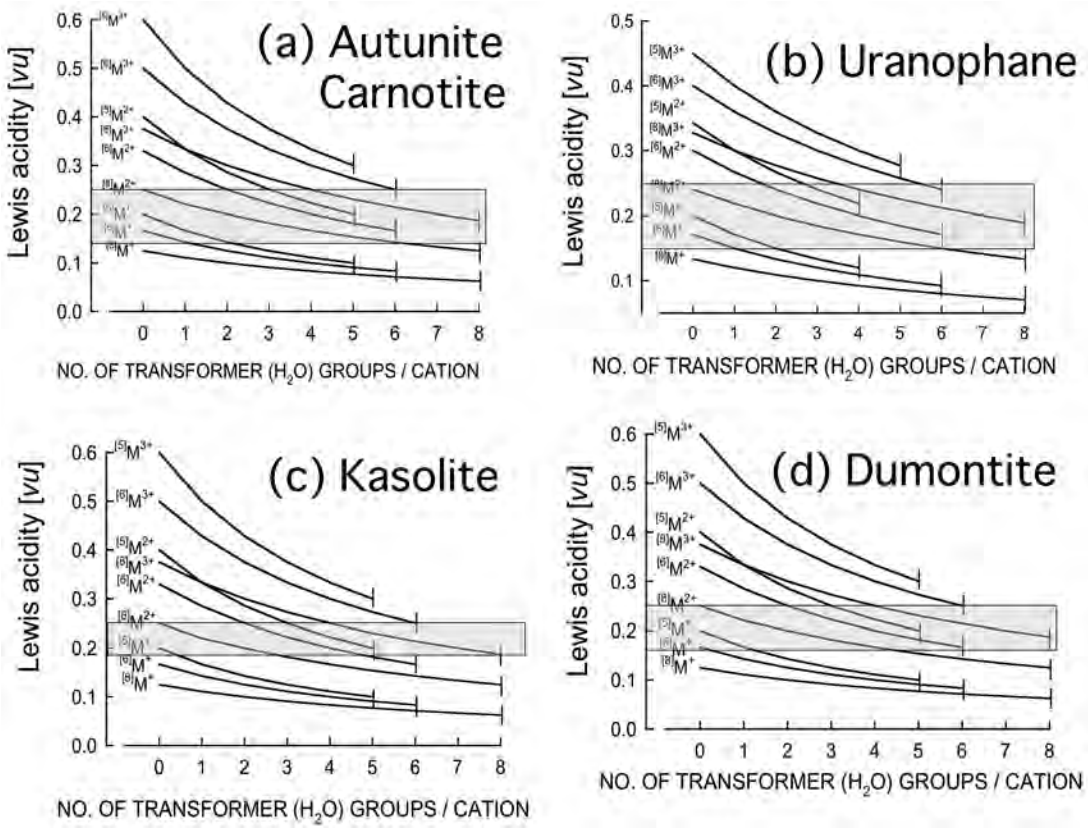

FIG. 9. Variation in Lewis acidity with the number of transformer (H_2O) groups for different interstitial-cation charges and coordination numbers for a general interstitial complex; the range of basicity of the different structural units are shown by the dotted lines: (a) autunite, $[(UO_2)(PO_4)]_2^{2-}$, and carnotite, $[(UO_2)_2(M_2O_8)]^{2-}$; (b) uranophane, $[(UO_2)SiO_3(OH)]^{-}$; (c) kasolite, $[(UO_2)(SiO_4)]^{2-}$; (d) dumontite, $[(UO_2)_3O_2(PO_4)_2]^{4-}$.

(H_2O) groups is 4.2. The resulting predicted chemical formula is $(H_3O)^+(H_2O)_4[(UO_2)(TO_4)]_2(H_2O)_4$, which does not agree with the compositions of chernikovite, $(H_3O)^+[(UO_2)(PO_4)](H_2O)_3$ and trögerite, $(H_3O)^+[(UO_2)(AsO_4)](H_2O)_3$ (Fitch *et al.* 1983, Morosin 1978). However, the $(H_3O)^+$ group is disordered in the interstitial complex [in the same fashion as K^+, Na^+, Ag^+, Tl^+, Rb^+, $(NH_4)^+$], which might be an explanation why fewer (H_2O) groups are required to distribute bond valence from the cation to the anions of the structural unit.

Tetrahedrally coordinated monovalent cations such as Li have a Lewis acidity of 0.25 *vu*, and thus 0–2 transformer (H_2O) groups are needed to reduce the Lewis acidity of interstitial $^{[4]}$Li such that it falls into the range of Lewis basicity of the structural unit. The maximum number of transformer (H_2O) groups is three: 1 / (4 + 3) = 0.14 *vu*. The predicted total number of (H_2O) groups for a [4]-coordinated cation is 5.5, and the number of transformer (H_2O) groups is 2. Thus, the predicted chemical composition is $Li(H_2O)_2[(UO_2)(TO_4)](H_2O)_{3.5}$, in reasonable agreement with the composition of synthetic $Li(D_2O)_0[(UO_2)(AsO_4)(D_2O)_4$ (Fitch *et al.* 1982), and $Li(H_2O)_0[(UO_2)(PO_4](H_2O)_4$ (Locock *et al.* 2004b).

Interstitial complexes with divalent cations

The most common coordination numbers for divalent cations are [6], [7] and [8]. Interstitial complexes with divalent cations in [6]-, [7]- and [8]-coordination and no transformer (H_2O) groups have Lewis acidities of 0.33, 0.285 and 0.25 *vu*, respectively. These values are larger than the range of Lewis basicity of the meta-autunite structural unit (Fig. 9a), and transformer (H_2O) groups are required to reduce the Lewis acidity such that it falls into the range of the Lewis basicity of the structural unit. Consider the case for [*N*]-coordination. If the interstitial divalent cation is bonded to *d* trans-

former (H_2O) groups, its Lewis acidity may be written as $2 / (2d + N - d) = 2 / (N + d)$ *vu*. For the Lewis acidity to fall at the maximum range of the Lewis basicity of the structural unit (*i.e.*, 0.25 *vu*), then $2 / (N + d) = 0.25$. For $N = 6$, d is equal to 2; thus an octahedrally coordinated divalent interstitial cation must bond to a *minimum* of two transformer (H_2O) groups to concur with the valence-matching principle. For the Lewis basicity to fall at the minimum of the range of Lewis basicity of the structural unit (*i.e.*, 0.14 *vu*), then $2 / (N + d) = 0.14$, whence d is equal to 8; however, six is the maximum possible value of d (Fig. 9a). Thus an octahedrally coordinated divalent cation must bond to a *maximum* of six transformer (H_2O) groups to concur with the valence-matching principle.

The predicted total number of (H_2O) groups and the predicted number of transformer (H_2O) groups from equations [1] and [4] for minerals with a divalent octahedrally coordinated interstitial cation is 7.5 and 4.2, in excellent agreement with almost all minerals of the meta-autunite groups containing those types of cations, *e.g.*, metatorbernite, $Cu^{2+}(H_2O)_4[(UO_2)_2(PO_4)_2](H_2O)_4$, metazeunerite, $Cu^{2+}(H_2O)_4[(UO_2)_2(AsO_4)_2](H_2O)_4$ (Locock & Burns 2003d), metakahlerite, $Fe^{2+}(H_2O)_4[(UO_2)(AsO_4)]_2(H_2O)_4$, and metakirchheimerite, $Co^{2+}(H_2O)_4[(UO_2)(AsO_4)]_2(H_2O)_4$ (Locock *et al.* 2004a) (Tables 3, 4).

Locock *et al.* (2005) showed the existence of two modifications of meta-uranocircite: I: $^{[9]}Ba[(UO_2)(PO_4)]_2(H_2O)_7$, and II: $Ba[(UO_2)(PO_4)]_2(H_2O)_6$. The two major differences distinguish these structures: in the structure of meta-uranocircite I, (1) ($Ba\phi_9$) polyhedra do not share common edges, and (2) one interstitial (H_2O) group does not bond to Ba (Locock *et al.* 2005). The structure of meta-uranocircite II has fully occupied $^{[9]}Ba^{2+}$ and (H_2O) sites (Khosrawan-Sazedj 1982a). On the basis of [9]-coordinated Ba, the predicted chemical composition of both meta-uranocircite modifications is $^{[9]}Ba[(UO_2)(PO_4)]_2(H_2O)_5$, in reasonable agreement with the observed chemical compositions (Tables 3, 4).

Meta-autunite was not considered in the above correlations, but the predicted chemical composition of $^{[7]}Ca[(UO_2)(PO_4)_2](H_2O)_6$ is in good agreement with the observed chemical composition.

Interstitial complexes with trivalent cations

The trivalent cations possible in this type of environment are octahedrally coordinated small cations (*e.g.*, Al, Fe^{3+}) and (usually) [8]- or [9]-coordinated REE (Y and rare-earth elements). Consider the case for [6]-coordination of Al or Fe^{3+}. If the cation is bonded to d transformer (H_2O) groups, its Lewis acidity may be written as $3 / (2d + 6 - d) = 3 / (6 + d)$ *vu*. For the Lewis acidity to fall at the maximum of the range of Lewis basicity of the structural unit (*i.e.*, 0.25 *vu*), then $3 / (6 + d) = 0.25$, whence d is equal to 6. For the Lewis acidity to fall at the minimum of the range of Lewis basicity of the structural unit (*i.e.*, 0.14 *vu*), then $3 / (6 + d) = 0.14$, whence d is equal to 15. This range of d values exceeds the coordination number [6] (the maximum possible for Al), and hence only an $[Al(H_2O)_4(H_2O)_e]$ complex can occur with this structural unit [unless there are additional (H_2O) groups not coordinated to Al and where the O atom has a coordination number of [3] only]. This result may also be seen directly by inspection of Figure 9a.

This situation can change if interstitial ($Al\phi_6$) octahedra polymerize. Consider two octahedra that link together. The bridging anions will receive an incident bond-valence of $\sim 0.5 \times 2 \approx 1.0$ *vu*; hence these anions will be (OH) rather than (H_2O). This being the case, the interstitial complex may be written as $[Al_2(H_2O)_{12-2f}(OH)_f]^{(6-f)+}$, and the Lewis acidity is $(6 - f) / [(12 - 2f) \times 2 + f] = (6 - f) / (24 - 3f)$. Where $f = 2$, the Lewis acidity of the complex is 0.24 *vu*; where $f = 4$, the Lewis acidity of the complex is 0.17 *vu*. Thus the complex has the appropriate Lewis acidity for $f = 1$, 2, 3 and 4. However, two octahedra cannot share four anions, and hence f = 1(corner-sharing), $f = 2$ (edge-sharing) or $f = 3$ (face-sharing) only are possible. Face-sharing of ($Al\phi_6$) octahedra is unlikely in an interstitial environment, and the complexes $[Al_2(H_2O)_{8-10}(OH)]^{5+}$ seem more likely.

If there are no $(OH)^-$ groups in the interstitial complex, the predicted total numbers of (H_2O) groups and transformer (H_2O) groups from equations [1] and [4] are 13(1) and 7.7(0.9), and the predicted chemical composition is $Al(H_2O)_8[(UO_2)(TO_4)]_3(H_2O)_5$. If there is only one $(OH)^-$ group per Al in the interstitial complex, $D = 12 / (6 + 0) = 2$, and the predicted values for the total numbers of (H_2O) groups and transformer (H_2O) groups are 7.5 and 4.2, respectively. The predicted and observed values of total (H_2O) and transformer (H_2O) are the number of (H_2O) or transformer (H_2O) groups minus the number of bonds reduced by action of interstitial $(OH)^-$ groups and inverse transformer (H_2O) groups. Taking this fact into account, the predicted chemical composition is $Al(^{[3]}OH)(H_2O)_5[(UO_2)(TO_4)]_2(H_2O)_4$. This prediction is in good agreement with the composition of threadgoldite, $Al(^{[3]}OH)[(UO_2)(PO_4)]_2(H_2O)_8$, in which Al bonds to four (H_2O) groups (Tables 3, 4).

For REE in [7]- and [8]-coordination, transformer (H_2O) will provide Lewis acidities in the range 0.14–0.25 *vu*. From a dimer with f (OH) groups and a coordination number N, the Lewis acidity is $(6 - f) / ([2N - 2f] \times 2 + f) = (6 - f) / (4N - 3f)$. For $N = [7]$, the dimer has Lewis acidity for $f = 0$, 1, 2 and 3; for $N = [8]$, the dimer has the appropriate range of Lewis acidity for $f = 0$ and 1 (Lewis acidity = 0.15 *vu*). Thus $[^{[7]}Y_2(H_2O)_{13}(OH)]^{5+}$, and $[^{[7]}Y_2(H_2O)_{12}(OH)_2]^{4+}$ and $[^{[7]}Y_2(H_2O)_{11}(OH)_3]^{3-}$ are possible cation complexes with (OH). However, as the charge of the structural unit is 2^-, $[^{[7]}Y_2(H_2O)_{12}(OH)_2]^{4+}$ produces a stoichiometrically simpler formula.

The *D* value for one trivalent cation in [7]-coordination is 1.71, and the predicted values for total (H_2O) per cation and transformer (H_2O) per cation are 5 and 3, respectively. For the dimer $[^{[7]}Y_2(H_2O)_{12}(OH)_2]^{4+}$, the numbers of ($H_2O$) groups and transformer (H_2O) groups are 12 and 7.4, respectively. Hence, the predicted chemical composition is $^{[7]}Y_2(H_2O)_7(OH)_2[(UO_2)(TO_4)]_4(H_2O)_5$.

The Uranophane Group

The minerals of the uranophane group are based on $[(UO_2)SiO_3(OH)]^-$ sheets that contain $(U^{6+}\phi_7)$ pentagonal bipyramids and acid $[(SiO_3(OH)]$ groups (Fig. 10a) [except kasolite, which contains SiO_4 groups]. The pentagonal bipyramids form edge-sharing chains that are connected by ($Si\phi_4$) tetrahedra. There are two distinct types of sheets in the structural units of the uranophane-group minerals: uranophane, uranophane-beta, boltwoodite and sklodowskite are based on the $[(UO_2)(SiO_3OH)]^-$ sheet, whereas kasolite is based on the $[(UO_2)(SiO_4)]^{2-}$ sheet. The $(OH)^-$ groups are located at the free apices of the ($Si\phi_4$) tetrahedra and form hydrogen bonds to interstitial (H_2O) groups. The anion topology of the uranophane structural unit can be described as an arrangement of triangles, squares and pentagons (Burns 1999a).

The CDA of the structural unit $[(UO_2)SiO_3(OH)]^-$ is $(1 + h) / 6 = 1.2 / 6 = 0.20$ *vu* (using $h = 0.20$ *vu*). Using Figure 2a, we may derive the corresponding minimum and maximum values of $[CN_{in}]$: [0.80] and [1.30], respectively. We may now use these values to calculate the range in Lewis basicity. The minimum and maximum numbers of bonds from the interstitial complex to the structural unit are 4.8 and 7.8, respectively. The corresponding minimum and maximum values of the Lewis basicity of the $[(UO_2)SiO_3(OH)]^-$ structural unit are $1.2 / 7.8 = 0.15$ and $1.2 / 4.8 = 0.25$ *vu*, respectively; this range of Lewis basicity is marked on Figure 9b.

For monovalent interstitial cations, [5]-, [6]-, [7]- and [8]-coordinations are predicted to be possible. Using equation [7], the predicted numbers of transformer (H_2O) groups are 0.3, –0.3, –0.7 and –1, which means that [7] and [8]-coordinated monovalent cations must bond to more inverse-transformer (H_2O) groups than transformer (H_2O) groups. Considering also the predicted total number of (H_2O) groups, possible compositions of minerals are $^{[5]}M^+[(UO_2)SiO_3(OH)](H_2O)_2$, $^{[6]}M^+[(UO_2)SiO_3(OH)](H_2O)_2$, $^{[7]}M^+(H_2{}^{[5]}O)_1[(UO_2)SiO_3(OH)](H_2O)_1$ and $^{[8]}M^+(H_2{}^{[5]}O)_1[(UO_2)SiO_3(OH)]$. These predictions are in good agreement with the observed chemical compositions of boltwoodite, $^{[7]}K(H_2{}^{[5]}O)[(UO_2)(SiO_3OH)]$, natroboltwoodite, $^{[6]}Na(H_2{}^{[5]}O)[(UO_2)(SiO_3OH)]$ (Burns 1998a), and synthetic Cs-substituted boltwoodite, $^{[7.5]}Cs[(UO_2)(SiO_3OH)]$ (Burns 1999b) (Tables 3, 4).

For divalent cations, [6]-, [7]- and [8]-coordinations are possible, and the predicted compositions of the interstitial complexes are $^{[6]}M^{2+}(H_2O)_2[(UO_2)SiO_3(OH)]_2(H_2O)_3$, $^{[7]}M^{2+}(H_2O)_{1.5}[(UO_2)SiO_3(OH)]_2(H_2O)_{2.5}$, and $^{[8]}M^{2+}(H_2O)_1[(UO_2)SiO_3(OH)]_2(H_2O)_{2.5}$. Minerals with divalent cations are cuprosklodowskite, $^{[6]}Cu^{2+}(H_2O)_2[(UO_2)(SiO_3OH)]_2(H_2O)_4$ (Rosenzweig & Ryan 1975), sklodowskite, $^{[6]}Mg[(UO_2)(SiO_3OH)]_2(H_2O)_6$ (Ryan & Rosenzweig 1977), uranophane $^{[7]}Ca(H_2O)_1\,[(UO_2)(SiO_3OH)]_2(H_2O)_4$, (Ginderow 1988), and uranophane-beta, $^{[8]}Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$; the number of transformer (H_2O) groups was not determined for sklodowskite and uranophane-beta. Except for uranophane-beta, the differences between the predicted and observed values of the total number of (H_2O) groups do not exceed one (H_2O) group per cation (Table 3).

The structural unit $[(UO_2)(SiO_4)]^{2-}$ has a CDA value of $2 / 6 = 0.33$ *vu*. The corresponding minimum and maximum values of $[CN_{in}]$ are [1.30] and [1.84] (Fig. 2a), and the minimum and maximum numbers of bonds to the structural unit are 7.8 and 10.8, respectively. The resulting range in Lewis basicity is 0.185 to 0.25 *vu*, and this is shown for $[(UO_2)(SiO_4)]$ on Figure 9c. Using equations [41] and [7], the predicted composition of a mineral containing a [8]-coordinated divalent cation is $^{[8]}Pb(H_2{}^{[5]}O)_1[(UO_2)(SiO_4)](H_2O)_1$, in good agreement with the observed composition of kasolite, $^{[2+6]}Pb(H_2{}^{[5]}O)_0[(UO_2)(SiO_4)](H_2O)_1$.

We are now able to answer the question why uranophane-beta, $^{[8]}Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$, has more ($H_2O$) groups than kasolite, $^{[8]}Pb[(UO_2)(SiO_4)](H_2O)$. The *D* value in uranophane-beta is 1.2, whereas it is only 0.75 in kasolite. In order to transfer the bond valence from the interstitial cation to the anions, uranophane-beta must contain more non-transformer (H_2O) groups than kasolite.

The Phosphuranylite Group

The structural unit of minerals of the phosphuranylite group is the sheet $[(UO_2)_3(PO_4)_2(O,OH)_2]^{n-}$ that contains ($P\phi_4$) tetrahedra, and ($U\phi_7$) pentagonal bipyramids and ($U\phi_8$) hexagonal bipyramids in the ratio 2 : 1 (Fig. 10b). The anion topology of the sheet consists of triangles, squares, pentagons and hexagons. These anion sheets can be further distinguished by the orientation of the phosphate tetrahedra (Burns 1999a, Locock & Burns 2003e). In addition, phosphuranylite, $KCa(H_3O)_3[(UO_2)\{(UO_2)_3(PO_4)_2O_2\}_2](H_2O)_8$ (Demartin *et al.* 1991), or $Ca[(UO_2)\{(UO_2)_3(PO_4)_2(OH)_2\}_2](H_2O)_{12}$ (Piret & Piret-Meunier 1991), and althupite, $AlTh^{4+}[(UO_2)\{(UO_2)_3(PO_4)_2(OH)O\}_2](OH)_3(H_2O)_{15}$ (Piret & Deliens 1987), contain U^{6+} in the interlayers that link adjacent $[(UO_2)_3(PO_4)_2(O,OH)]^{n-}$ sheets *via* equatorial bonds. The resulting structural units of phosphuranylite and althupite are formally frameworks, with the general composition $[(UO_2)\{(UO_2)_3(PO_4)_2(OH,O)\}_2]^{n-}$ and

therefore are not considered here. There are three different compositions of sheet structural-units with slightly different ranges in Lewis basicity:

$[(UO_2)_3(PO_4)_2(OH)_2]^{2-}$ (0.14–0.25 *vu*)

$[(UO_2)_3(PO_4)_2(O)(OH)]^{3-}$ (0.15–0.26 *vu*)

$[(UO_2)_3(TO_4)_2O_2]^{4-}$, T = P, $A^{5+}{}_3$ (0.16–0.25 *vu*)

The structural unit $[(UO_2)_3(PO_4)_2(OH)_2]^{2-}$ occurs in phuralumite, the structural unit $[(UO_2)_3(PO_4)_2O(OH)]^{2-}$ occurs in dewindtite, upalite and françoisite-(Nd), and the structural unit $[(UO_2)_3(TO_4)_2O_2]^{4-}$ occurs in dumontite, phurcalite, bergenite and hügelite (Table 3). The Lewis basicity range of the $[(UO_2)_3(P(As)O_4)_2O_2]^{4-}$ structural unit is shown in Figure 9d, which indicates that the cations $^{[4]-[6]}M^{+}$, $^{[5]-[10]}M^{2+}$, $^{[7]-[10]}M^{3+}$ and $\{^{[6]}M^{3+}(OH)\}^{2+}$ can be compatible with the structural unit if they bond to a specific number of transformer (H_2O) groups. Monovalent cations with coordination numbers higher than [6] can also occur if they bond to a specific number of inverse-transformer (H_2O) groups.

Table 3 shows that differences between total numbers of (H_2O) groups per cation observed and predicted from equation [1] do not exceed one (H_2O) group per cation. In the case of phuralumite, $^{[6]}Al_2(OH)_4[(UO_2)_3(PO_4)_2(OH)_2](H_2O)_{10}$, the predicted total number of (H_2O) groups is identical with the observed number of (H_2O) groups. In the reported structures of dumontite and hügelite, the coordination number of the Pb^{2+} cations can be assigned as either [7] or [8]. However, the observed total number of (H_2O) groups per cation is 2.5, and agrees well with the predicted numbers of either 3.0 and 2.5 for cations in [7]- or [8]-coordination, respectively (Table 3). For upalite and phurcalite, the predicted numbers of transformer (H_2O) groups per cation are smaller than the observed values, but the differences do not exceed one (H_2O) group per cation (Table 4).

The Carnotite Group

The minerals of the carnotite group contain the structural unit $[(UO_2)_2(V_2O_8)]^{2-}$, an anion sheet with (UO_7) pentagonal bipyramids and ($V^{5+}O_5$) square pyramids. The ($V^{5+}O_5$) square pyramids share common edges and form a $[V_2O_8]$ dimer that shares corners with dimers of edge-sharing (UO_7) pentagonal bipyramids (Fig. 10c). The anion topology can be described as an arrangement of triangles, squares and pentagons (Burns 1999a). The $[(UO_2)_2(V_2O_8)]^{2-}$ structural unit has a CDA value of 2 / 12 = 0.17 *vu*, which results in a range in Lewis basicity of 0.14 to 0.25 *vu*. This range, the number of anions and (OH) groups in the structural unit, and the effective charge of the structural unit, are identical to those for minerals of the meta-autunite group (Fig. 9a). Hence, predictions of cations, transformer and total numbers of (H_2O) groups are identical with the predictions for the minerals of the meta-autunite group (see above).

The range in Lewis basicity for the structural unit $[(UO_2)_2(V_2O_8)]^{2-}$ (0.14–0.25 *vu*) requires that monovalent cations with coordination numbers higher than [7] must bond to inverse-transformer (H_2O) groups. This may be the case in carnotite, $K_2[(UO_2)_2(V_2O_8)](H_2O)_3$, and margaritasite, $(Cs,K)_2[(UO_2)_2(V_2O_8)](H_2O)_n$ (n = 1–3) (Gaines *et al.* 1997), in which the large cations K and Cs normally occur in coordination numbers higher than [7] . The predicted composition for monovalent cations with coordination numbers [8], [10] and [12] are $^{[8]}M(H_2{}^{[5]}O)_1[(UO_2)_2(V_2O_8)](H_2O)_1$, $^{[10]}M(H_2{}^{[5]}O)_3[(UO_2)_2(V_2O_8)](H_2O)_0$ and $^{[12]}M(H_2{}^{[5]}O)_5[[(UO_2)_2(V_2O_8)](H_2O)_0$, respectively.

The compositions of only three minerals of the carnotite group have been determined on the basis of structural data: francevillite, $^{[9]}Ba[(UO_2)_2(V_2O_8)](H_2O)_5$, curienite, $^{[8]}Pb[(UO_2)_2(V_2O_8)](H_2O)_5$, and sengierite, $^{[6]}Cu_2(OH)_2(H_2O)_4[(UO_2)_2(V_2O_8)](H_2O)_2$. For francevillite and curienite, the predicted compositions of the interstitial complex, $^{[9]}Ba(H_2O)_2[(UO_2)_2(V_2O_8)](H_2O)_3$ and $^{[8]}Pb(H_2O)_2[(UO_2)_2(V_2O_8)](H_2O)_3$, are in good agreement with the observed compositions. For a [6]-coordinated cation such as $^{[6]}Cu^{2+}$ in sengierite, the possible interstitial complex can be calculated without or with ($^{[4]}OH$) groups. In the first case, the predicted composition is $^{[6]}Cu(H_2O)_4[(UO_2)_2(V_2O_8)](H_2O)_3$. In the second case, four transformer (H_2O) groups are required by the interstitial complex because each $(^{[4]}OH)^{-}$ group reduces by two the number of bonds from $^{[6]}Cu^{2+}$ to the structural unit. Hence, the predicted chemical composition is $^{[6]}Cu_2(^{[4]}OH)_2(H_2O)_4[(UO_2)_2(V_2O_8)](H_2O)_5$, in reasonable agreement with the observed composition.

The Zippeite Group

The structures of the zippeite-group minerals contain topologically identical sheets in which uranyl pentagonal bipyramids link together by sharing edges and vertices to form chains that are cross-linked by sulfate tetrahedra (Fig. 10d). Burns *et al.* (2003) showed that the symmetries and chemical compositions of the uranyl sheets are not identical for all members of this group. There are three different sheet structural units with similar ranges in Lewis basicity:

$[(UO_2)_4(SO_4)_2O_3(OH)]^{3-}$ (0.14–0.25 *vu*)

$[(UO_2)_8(SO_4)_4O_5(OH)_3]^{5-}$ (0.14–0.25 *vu*)

$[(UO_2)_2(SO_4)O_2]^{2-}$ (0.15–0.25 *vu*)

The structural unit $[(UO_2)_4(SO_4)_2O_3(OH)]^{3-}$ occurs in zippeite, $^{[7.33]}K_3[(UO_2)_4(SO_4)_2O_3(OH)](H_2O)_3$ (Burns *et al.* 2003), and marecottite, $^{[6]}Mg_3[(UO_2)_4$

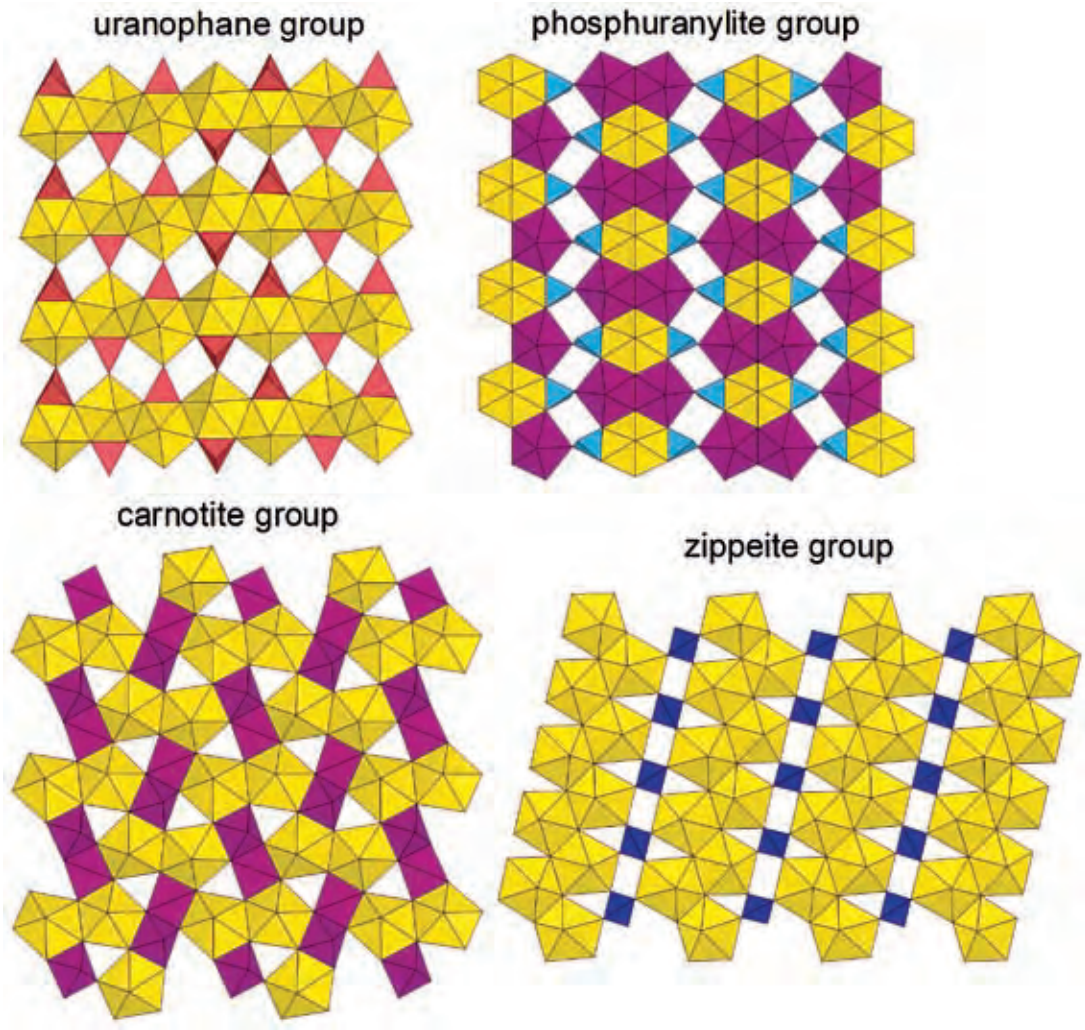

FIG. 10. Structural units in selected uranyl-oxysalt minerals. Uranophane: orange: (SiO_4) group, yellow: uranyl polyhedron. Phosphuranylite: turquoise: (PO_4) group, yellow: [8]-coordinated uranyl polyhedron, fuschia: [7]-coordinated uranyl polyhedron. Carnotite: fuschia: (VO_4) group, yellow: [7]-coordinated uranyl polyhedron. Zippeite: dark blue: (SO_4) group, yellow: [7]-coordinated uranyl polyhedron.

$(SO_4)_2O_3(OH)]_2(H_2O)_{28}$ (Brugger *et al.* 2003). The calculated range in Lewis basicity indicates that [7]-coordinated monovalent cations are possible if they bond to one inverse-transformer (H_2O) group, whereas three [6]-coordinated divalent cations must bond to at least 3.5 transformer (H_2O) groups. The predicted chemical compositions are as follows: zippeite $^{[7.33]}K_3(H_2{}^{[5]}O)[(UO_2)_4(SO_4)_2O_3(OH)](H_2O)_5$; marecottite, $^{[6]}Mg_3(H_2O)_{12.5}[(UO_2)_4(SO_4)_2O_3(OH)]_2(H_2O)_{10}$. Brugger *et al.* (2003) described the paragenesis of marecottite and magnesiozippeite at several localities, suggesting that marecottite dehydrates to magnesiozippeite. Hence, the data for marecottite were not considered in the correlation of Figure 7c, even though its composition is in good agreement with the general trend of uranyl oxysalt minerals.

The structural unit $[(UO_2)_8(SO_4)_4O_5(OH)_3]^{5-}$ occurs in natrozippeite, $^{[6.6]}Na_5[(UO_2)_8(SO_4)_4O_5(OH)_3](H_2O)_{12}$, and its Lewis basicity indicates that monovalent cations in [6]- and [7]-coordination can occur in the interstitial complex without bonding to any transformer (H_2O) groups. The predicted chemical composition on the basis of the average coordination number of Na

is $^{[6.6]}Na_5(H_2O)_3[(UO_2)_8(SO_4)_4O_5(OH)_3](H_2O)_{12}$, in reasonable agreement with the observed composition.

The structural unit $[(UO_2)_2(SO_4)O_2]^{2-}$ occurs in magnesiozippeite, zinczippeite and cobaltzippeite, $^{[6]}M(H_2O)_3[(UO_2)_2(SO_4)O_2]\ (H_2O)_{0.5}$ with M = Mg, Zn and Co^{2+} (Burns *et al.* 2003). The predicted chemical composition for a [6]-coordinated divalent cation is $^{[6]}M(H_2O)_3[(UO_2)_2(SO_4)O_2](H_2O)_3$, which shows good agreement between the predicted and observed numbers of transformer (H_2O) groups (Table 4).

The Uranyl-Hydroxy-Hydrate Group

Schindler & Hawthorne (2004) have examined the predicted and observed chemical compositions of interstitial complexes in uranyl-hydroxy-hydrate minerals. However, their predictions were based on CDA *versus* [CN_{in}] (Fig. 2a). Predicted compositions of interstitial complexes were given with a possible range of transformer (H_2O) groups. Here, we are now able to predict more exactly the number of transformer (H_2O) groups and total number of (H_2O) groups.

For uranyl-hydroxy-hydrate minerals, the total numbers of (H_2O) groups per cation predicted from equation [1], are in good agreement with the observed values (Table 3); the largest difference is for becquerelite (Table 3). For curite, $^{[9]}Pb^{2+}{}_{3+x}(H_2{}^{[5]}O)_2[(UO_2)_4O_{4+x}(OH)_{3-x}]_2$, the predicted number of transformer (H_2O) groups per cation is –0.35, which is equivalent to one "reduced" bond for three cations. Three divalent cations cannot occur with $(OH)^-$ groups in the interstitial complex because of the charge of the $[(UO_2)_8O_8(OH)_6]^{6-}$ structural unit. Hence, the divalent cations must bond to one inverse-transformer (H_2O) groups, and the predicted chemical composition is $^{[9]}Pb^{2+}{}_3(H_2{}^{[5]}O)[(UO_2)_4O_4(OH)_3]_2(H_2O)_4$ (Table 4).

Miscellaneous Uranyl-Oxysalt Minerals

For the selenate and carbonate minerals of this group, the predicted and observed values for the total number of (H_2O) groups per cation and the number of transformer (H_2O) groups per cation show good agreement (Tables 3, 4). However, closer inspection of the predicted and observed values indicates that more (H_2O) groups are predicted than are actually observed. The reason for this could involve the size of the $(SeO_3)^{2-}$ and $(CO_3)^{2-}$ triangles and the number of anions in the structural unit. These triangles are the smallest of all oxyanion groups in the structural units of uranyl-oxysalt minerals, and fewer non-transformer (H_2O) groups are required in comparison to minerals with larger anionic groups [*e.g.*, $(PO_4)^{3-}$ and $(SiO_3OH)^{3-}$].

The structural data for fontanite, $Ca[(UO_2)_3(CO_3)_2O_2](H_2O)_6$ (Hughes & Burns 2003) were not included in the data of Figures 7b and 8c. Thus, we can test the applicability of our regression model by comparing the predicted and observed number of (H_2O) groups per cation. In fontanite, there are 14 anions in the phosphophyllite-type structural unit, and Ca is in [8]-coordination, bonding to six (H_2O) groups and two O atoms of the uranyl groups. Hence, the bond-valence distribution factor, D, is 14 / 8 = 1.75. The predicted number of (H_2O) groups per cation is 7, in good agreement with the observed value. The interstitial hydrogen bonding, and hence the number of transformer (H_2O) groups, were not unequivocally determined. However, O–O distances between (H_2O) groups indicate the occurrence of at least two transformer (H_2O) groups; the predicted number of transformer (H_2O) groups is 3, in good agreement with this value.

The sheets of polymerized uranyl and selenate polyhedra in guilleminite, $^{[10]}Ba[(UO_2)_3O_2(SeO_3)_2](H_2O)_3$, and marthozite, $^{[6]}Cu[(UO_2)_3O_2(SeO_3)_2](H_2O)_8$, have the same anion topologies as the sheets of polymerized uranyl and phosphate polyhedra in the minerals of the phosphuranylite group. However, the geometry and bonding in the selenate group differ significantly from those in the phosphate group, and we discuss separately the chemical composition of guilleminite and marthozite. The range in Lewis basicity of the $[(UO_2)_3O_2(SeO_3)_2]^{2-}$ structural unit is 0.14–0.25 *vu*. Hence divalent cations in [6]-coordination must bond to 2–6 transformer (H_2O) groups, and the interstitial complex in marthozite, $\{^{[6]}Cu(H_2O)_5(H_2O)_4\}^{2+}$, is in accord with this value. Divalent cations in [10]-coordination must bond to 0–1 transformer (H_2O) groups, and the interstitial complex in guilleminite, $\{Ba(H_2O)_{1.5}(H_2O)_3\}^{2+}$, is in accord with this value.

Summary

Structures and chemical compositions of uranyl-oxysalt minerals with sheet structural units have been investigated in detail. The following correlations between structural parameters and chemical compositions have been developed:

(1) the CDA (Charge Deficiency per Anion) of the structural unit correlates with the range in coordination numbers of the O atoms in the structural unit ([CN_{in}]);

(2) the bond-valence distribution factor, D, correlates with the number of (H_2O) groups per interstitial cation in the interstitial complex;

(3) the bond-valence distribution factor, D, correlates with the number of inverse-transformer and transformer (H_2O) groups per interstitial cation in the interstitial complex.

Correlation (1) has been used to calculate a characteristic range in Lewis basicity for a structural unit in a uranyl-oxysalt mineral. The range in Lewis basicity and correlations (2) and (3) have been used to predict the chemical composition of interstitial complexes in minerals of the autunite, uranophane, phosphuranylite, carnotite, zippeite, uranyl-hydroxy-hydrate and "miscellaneous" groups of uranyl minerals. These predictions

included (1) the type of interstitial cations in the interstitial complex, (2) the number of (H_2O) groups per interstitial cation, (3) the number of transformer, non-transformer and inverse-transformer (H_2O) groups per interstitial cation.

The good agreement between observed and predicted values of the different types of (H_2O) groups show that the ideas developed by Hawthorne (1985, 1990, 1997), Schindler & Hawthorne (2001a, b, c, 2004) and in this paper are fairly successful in understanding aspects of the stereochemistry and chemical composition of the interstitial complexes of uranyl-oxysalt minerals.

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APPENDIX A. GLOSSARY

Bond valence: a measure of the strength of a bond, which varies with the corresponding bond-length. The bond valence, s, may be expressed as a function of bond length, R, in the following way: $s = \exp\{(R_0 - R) / b\}$, where R_0 and b are constant characteristic of cation–anion pairs.

Characteristic bond-valence: the formal valence of a cation or an anion divided by its mean coordination-number. The characteristic bond-valence of an oxyanion is its formal charge divided by the mean number of bonds to the oxyanion. For example, an O atom of an (SO_4) group is, on average, [4]-coordinated, which means it receives three bonds in addition to that from the central S atom; thus, there are, on average, twelve bonds to the oxyanion, and its characteristic bond-valence is $2 / 12 = 0.17$ *vu*.

Lewis acid strength (Lewis acidity): the characteristic bond-valence of a cation; the Lewis acidity of a cation correlates with its electronegativity.

Lewis base strength (Lewis basicity): the characteristic bond-valence of an anion or an oxyanion.

Valence-matching principle: The most stable structures will form where the Lewis acidity of the cation closely matches the Lewis basicity of the anion or oxyanion.

Structural unit: the strongly bonded part of the structure; it is usually anionic, but can be neutral or cationic.

Interstitial complex: the weakly bonded part of the structure, consisting of large low-valence alkali and alkaline-earth cations, (H_2O) groups and monovalent anions such as $(OH)^-$ and Cl^-.

Binary structural representation: interstitial complex and structural unit are each considered as single components, whose interaction can be examined using the valence-matching principle.

Transformer (H_2O) groups: (H_2O) groups in which the O atoms accept only one bond from a cation (inclusive of hydrogen bonds). Hence, they receive only one bond but propagate two hydrogen bonds, *i.e.*, they split one bond into two bonds. This effect transforms the higher bond-valence of one cation–(H_2O) bond into the lower bond-valences of two hydrogen bonds.

Non-transformer (H_2O) groups: (H_2O) groups in which the O atoms accept two additional bonds from cations (inclusive of hydrogen bonds). Hence, they receive two bonds and also propagate two bonds (*i.e.*, they do not transform bonds). Non-transformer (H_2O) groups propagate bond-valence to acceptor O atoms of the structural unit.

General formula of a mineral: this indicates the *interstitial complex* and the *structural unit*, and is written as follows:

$$\{^{[m]}M^{+}_{a}\ ^{[n]}M^{2+}_{b}\ ^{[l]}M^{3+}_{c}\ (H_2O)_d\ (H_2O)_e\ ^{[q]}(OH)_f\}^{(a+2b+3c-f)+}\ [M^{z+}\ (H_2O)_i\ (OH)_j\ (SO_4)_k]^{(a+2b+3c-f)-}\ (H_2O)_g$$

where d is the number of interstitial transformer (H_2O) groups, e is the number of interstitial non-transformer (H_2O) groups, f is the number of interstitial (OH) groups, and g is the number of interstitial (H_2O) groups that do not bond to interstitial cations.

Effective charge of a structural unit: the formal charge plus the amount of bond-valence contributed to the interstitial complex from hydrogen bonds of (H_2O) and (OH) groups in the structural unit. For example, the formal charge of the structural unit $[Fe^{2+}(H_2O)_4(SO_4)_2]^{2-}$ is 2^-, and there are eight hydrogen bonds emanating from the structural unit; thus, the effective charge of the structural unit is $(2 + 8h)^-$, where h is the bond valence of the hydrogen bond. The corresponding interstitial complex must have the same effective charge with an opposite sign.

Charge deficiency per anion (CDA) of the structural unit: the effective charge of the structural unit divided by the number of O atoms in the structural unit.

Effective Lewis basicity (Lewis basicity) of the structural unit: the effective charge of the structural unit divided by the number of bonds from the structural unit.

Effective Lewis acidity (Lewis acidity) of an interstitial complex: the effective charge of the interstitial complex divided by the number of bonds emanating from the interstitial complex.

APPENDIX B: DERIVATION OF HYDROGEN-BOND ARRANGEMENTS

Many crystal structures of uranyl-oxysalt minerals have no details of the arrangements of hydrogen bonds in their structures because of the difficulty in locating the H atoms among such heavy scatterers as U. For our work, we need the arrangement of hydrogen bonds in each structure as they play such an important role in affecting the stability of specific chemical compositions. As a result, we have derived the arrangements of hydrogen bonds in some uranyl-oxysalt structures by crystal-chemical argument in order to have the data relevant to our ideas of structure stability. Here, we present an example of the determination of hydrogen-bond arrangements from stereochemical considerations. All H_2O–O and H_2O–H_2O distances less than 3.2 Å were examined in terms of potential hydrogen-bond acceptors (excluding pairs of anions that are edges of coordination polyhedra), and both hydrogen-bond donors and hydrogen-bond acceptors were identified.

Phurcalite: $Ca_2[(UO_2)_3(PO_4)_2O_2](H_2O)_7$

The bond-valence table for phurcalite (Table A1) indicates the bond-valence sums around the O atoms of the structure, exclusive of bond valences resulting from hydrogen bonds. Inspection of the bond-valence sums around the anions allows identification of the (H_2O) groups by their low incident bond-valence (sums >> 1 *vu*); these anions are labeled $(H_2O)_{17–23}$ in the table. Note that $(H_2O)_{18}$ accepts two bonds from Ca, $(H_2O)_{17}$, $(H_2O)_{19}$, $(H_2O)_{20}$, $(H_2O)_{21}$ and $(H_2O)_{23}$ accept one bond from Ca, and $(H_2O)_{22}$ does not bond to Ca.

TABLE A1. BOND-VALENCE TABLE (*vu*) FOR PHURCALITE, $Ca_2[(UO_2)_3(PO_4)_2O_2](H_2O)_7$

	U(1)	U(2)	U(3)	P(1)	P(2)	Ca(1)	Ca(2)	Sum
O(1)	1.60					0.22		1.82
O(2)	1.58							1.58
O(3)		1.68						1.68
O(4)		1.62					0.12	1.74
O(5)			1.59			0.18		1.77
O(6)			1.54				0.16	1.80
O(7)	0.70	0.63	0.59					1.92
O(8)			0.55	1.20				1.75
O(9)	0.35		0.55	1.21				2.11
O(10)	0.64	0.64	0.68					1.96
O(11)	0.41	0.38			1.21			2.00
O(12)	0.21	0.46			1.18			1.85
O(13)			0.46		1.21		0.29	1.96
O(14)		0.53		1.34				1.87
O(15)				1.23		0.33	0.36	1.92
O(16)					1.36	0.46		1.82
$(H_2O)_{17}$							0.32	0.32
$(H_2O)_{18}$						0.22	0.19	0.41
$(H_2O)_{19}$						0.33		0.33
$(H_2O)_{20}$						0.30		0.30
$(H_2O)_{21}$							0.32	0.32
$(H_2O)_{22}$								0
$(H_2O)_{23}$							0.26	0.26
Sum	5.49	5.94	5.96	4.98	4.96	2.04	2.02	

Let us consider the hydrogen bonds about each (H_2O) group in turn.

Coordination of $(H_2O)_{17}$: $(H_2O)_{17}$ has six anions closer than 3.2 Å. Three of these pair with $(H_2O)_{17}$ to form edges of coordination polyhedra; O(2) and O(3) are in the right arrangements to be hydrogen-bond acceptors, and $(H_2O)_{22}$ (at a distance of 2.772 Å) is a potential hydrogen-bond interaction.

Coordination of $(H_2O)_{18}$: $(H_2O)_{18}$ is bonded to two Ca atoms and has eight anions closer than 3.2 Å. seven of these pair with $(H_2O)_{18}$ to form edges of coordination polyhedra; O(12) and O(15) are in the right arrangements to be hydrogen-bond acceptors, and hence $(H_2O)_{18}$ is a non-transformer (H_2O) group.

Coordination of $(H_2O)_{19}$: $(H_2O)_{19}$ has eight anions closer than 3.2 Å. Four of these pair with $(H_2O)_{19}$ to form edges of coordination polyhedra; O(4) and O(6) are in the right arrangements to be hydrogen-bond acceptors, and $(H_2O)_{22}$ (at a distance of 2.727 Å) is a potential hydrogen-bond interaction.

Coordination of $(H_2O)_{20}$: $(H_2O)_{20}$ has five anions closer than 3.3 Å. Two of these pair with $(H_2O)_{20}$ to form edges of coordination polyhedra; O(2) is in the right arrangement to be a hydrogen-bond acceptor, and $(H_2O)_{22}$ (at a distance of 2.723 Å) and $(H_2O)_{23}$ (at a distance of 2.875 Å) are potential hydrogen-bond interactions.

Coordination of $(H_2O)_{21}$: $(H_2O)_{21}$ has six anions closer than 3.2 Å. Three of these anions pair with $(H_2O)_{19}$ to form edges of coordination polyhedra; two of the four O atoms are in suitable positions to be hydrogen-bond acceptors. All close (H_2O) groups form edges of coordination polyhedra with $(H_2O)_{21}$, and hence there are no hydrogen-bond donors. Thus $(H_2O)_{21}$ is a transformer (H_2O) group.

Coordination of $(H_2O)_{22}$: $(H_2O)_{22}$ has five anion neighbors within 3.2 Å, none of which are edges of coordination polyhedra. The O(8) anion has an incident bond-valence of 1.75 *vu*, and can accept a hydrogen bond from $(H_2O)_{22}$. The remaining $(H_2O)_{17}$, $(H_2O)_{19}$ and $(H_2O)_{20}$ are potential hydrogen-bond interactions.

Coordination of $(H_2O)_{23}$: $(H_2O)_{23}$ has six anions closer than 3.2 Å. Three of these pair with $(H_2O)_{23}$ to form edges of coordination polyhedra; O(3) and O(14) are in an appropriate arrangement to be hydrogen-bond acceptors, and $(H_2O)_{20}$ (at a distance of 2.875 Å) is a potential hydrogen-bond interaction.

We now need to determine the donor–acceptor relations for $(H_2O)_{17}$, $(H_2O)_{19}$, $(H_2O)_{20}$, $(H_2O)_{22}$ and $(H_2O)_{23}$. This may be done by considering the patterns of interactions that lead to reasonable bond-valence sums at the relevant anions, with the constraint that $(H_2O)_{22}$ is not bonded to Ca, and hence must both accept and receive hydrogen bonds. Two typical arrangements are shown in Figure A1. Note that although the

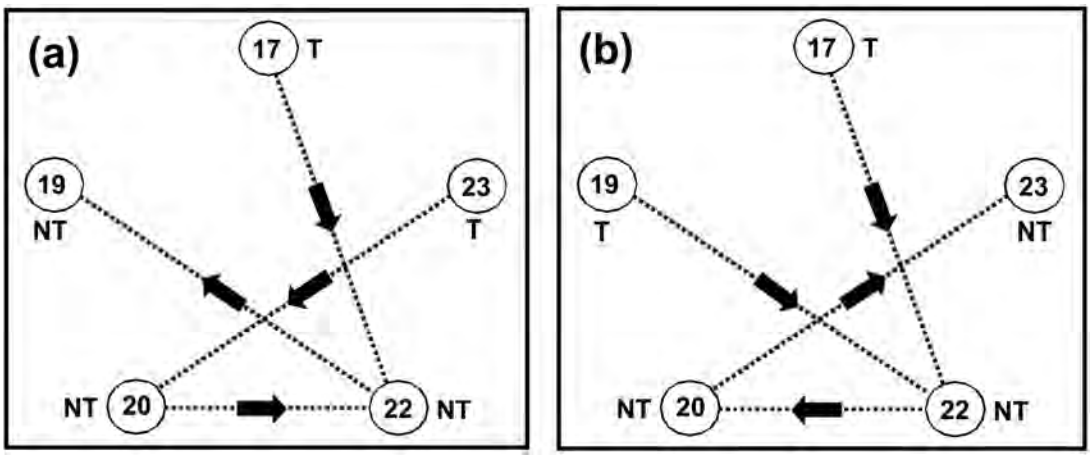

FIG. A1. (a), (b) Possible donor–acceptor relations for some of the (H_2O) groups in phurcalite; (H_2O) groups are shown as white circles with the enclosed number denoting the identification number of the group, dotted lines show donor–acceptor anions joined by a hydrogen bond, the arrows denote the direction from donor to acceptor, T denotes a transformer (H_2O) group, and NT denotes a non-transformer (H_2O) group. Note that the numbers of transformer and non-transformer (H_2O) groups are the same in each arrangement.

assignment of specific donors and acceptors is made in Figures A1a and A1b, the numbers of transformer and non-transformer (H_2O) groups is the same. Thus for phurcalite, we assign three transformer (H_2O) groups, three non-transformer (H_2O) groups and one non-transformer (H_2O) group not bonded to any cations: $\{Ca_2(H_2O)_3(H_2O)_3(H_2O)_1\}$.