References

Gabe, E. J., Le Page, Y., Charland, J. P., Lee, F. L., White, P. S.: NRCVAX – An interactive program system for structure analysis. J. Appl. Crystallogr. **22** (1989) 384–387.

Germain, G., Main, P., Woolfson, M. M.: Application of phase relations to complex structures III: Optimum use of phase relations. Acta Crystallogr. **A27** (1971) 368–378.

Prasad, S. N., Venugopalan, S., Billard, J.: Anomalous smectic mesomorphism of 4,4′-di-n-pentyloxyazoxybenzene. Mol. Cryst. Liq. Cryst. (Letters) **49** (1979) 271–278.

Shivaprakash, N. C., Rajalakshmi, P. K., Shashidhara Prasad, J.: Molecular packing coefficients of the homologous series 4,4′-di-n-alkyloxyazoxy benzene. *Liquid Crystals of One- and Two-Dimensional Order*, Ed. Helfrich, W., Heppke, G.: Springer-Verlag Berlin, New York (1980) 72–76.

Venkatramana Shastry, C. I., Sheshadri, T. P., Shashidhara Prasad, J.: Crystal Structure of trans-4-propyl cyclohexyl-4(trans-4-ethyl cyclohexyl) benzoate. Z. Kristallogr. **177** (1986) 271–276.

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The role of OH and H_2O in oxide and oxysalt minerals

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I am pleased to dedicate this to Professor Friedrich Liebau
on the occasion of his 65th birthday in recognition of the past 10 years
when I have been privileged to call him both a friend and a colleague

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Oxides / Oxysalt minerals / Crystal water / Hydrogen bonds

Abstract. Hydrogen plays an extremely important role in the structure and chemistry of the oxide and oxysalt minerals. The characteristics of this role can be profitably analyzed in a simple and intuitive fashion using bond-valence theory. For any crystal structure, the *structural unit* may be defined as the strongly bonded part of the structure; structural units are linked together by *interstitial species*, usually alkali or alkaline earth cations and $(H_2O)^0$ groups that are involved in much weaker bonding. This scheme gives a *binary representation* of even the most complex structure. The interaction between the structural unit and the interstitial species can be quantitatively evaluated using the *valence-matching principle* (Brown, 1981).

As components of the structural unit, $(OH)^-$ and $(H_2O)^0$ play a major role in dictating the dimensional polymerization of the structural unit because of the very asymmetric nature of the donor-hydrogen and hydrogen...acceptor interactions. As an interstitial component, $(H_2O)^0$ can play three different roles. Interstitial $(H_2O)^0$ may bond to an interstitial cation, essentially forming a *complex cation*. In this role, $(H_2O)^0$ acts as a bond-valence transformer, moderating the Lewis acidity of the interstitial cations such that it matches the Lewis basicity of the structural unit and the valence-matching principle is satisfied. Interstitial $(H_2O)^0$ need not bond to an interstitial cation to occupy well-ordered atomic positions; a stable hydrogen-bonded network can occur in the interstitial regions between structural units. The role of such $(H_2O)^0$ is to satisfy the bond-valence requirements of H atoms that are part of the structural unit, propagating the bonding

across the interstitial space to other parts of the structural unit. Occluded $(H_2O)^0$ may occur in some minerals. Such $(H_2O)^0$ is not bonded to interstitial cations and does not participate in a static ordered hydrogen-bond network. However, this type of $(H_2O)^0$ will still affect many of the physical properties of a mineral.

Introduction

The structures and chemistry of the oxide and oxysalt minerals are impressive in both their complexity and diversity, and it can be reasonably asserted that our understanding of these aspects lags far behind our experimental capabilities for their characterization. Nevertheless, there are some empirical rules that (sometimes weakly) govern the constitution of these minerals, rules that date back to early work on the modern electronic theory of valence (Lewis, 1916, 1923) and the structure of crystals. The most rigorous rule is that of electroneutrality: the sum of the formal charges of all the ions in a crystal is zero. Other rules grew out of observations on a few mineral and inorganic structures, and various ideas emerged during the 1920s: that atoms have a specific size, tables of atomic and ionic radii, the idea of coordination number, considering structures as polymerizations of coordination polyhedra. These ideas were refined by Pauling (1929, 1960) who synthesized them into his well-known rules for the behaviour of 'complex ionic crystals'. Some aspects of these ideas have been extensively developed up to the present time. There are now available tables of accurate empirical 'ionic' radii (Shannon, 1976) whereby mean interatomic distances for specific coordinations can be predicted typically to within ~ 0.01 Å. Individual bond lengths can be predicted via various developments of Pauling's second rule (e.g. Baur, 1970, 1971), and the relative strengths of bonds can be calculated (Brown and Shannon, 1973) given the observed bond lengths in a structure. Thus we can currently predict various geometrical aspects of a crystal structure quite accurately, provided that we know the connectivity (often called the topology) of the chemical bonds. This particular statement brings into focus our principal area of ignorance concerning crystals: *we still have very little understanding of the bond topology of crystals*, as distinct from their geometrical features which we can usually predict with reasonable accuracy.

Our lack of fundamental understanding is particularly apparent when we come to consider the oxide and oxysalt minerals. There are ~ 2000 oxide and oxysalt minerals, showing a bewildering variety of both chemical and structural complexity, from halite (NaCl) with 8 atoms in its unit cell (Wells, 1985) to mcgovernite $[Mn_{160}Mg_{77}Zn_{31}Fe_6As^{3+}_{12}As^{5+}_{29}Si_{41}O_{323}(OH)_{253}]$ with over 1200 atoms in its unit cell (Dunn et al., 1988). What feature(s) of chemistry and structure make the very complex minerals stable relative to an isochemical assemblage of other phases? In general, the coordination numbers will be the same in the complex phase and in the alternate possible phases; as the local environments are the same, there are thus no local energetic differences. The differences must arise in the way that the coordination polyhedra link together. This involves the longer-range bond topology of the structure which will thus (in the absence of any change in local coordination) dictate the energetics of the structures. Note that this argument comes to essentially the same conclusion as the arguments of Burdett (1986): the energy difference between structures can be expressed in terms of the first few disparate moments of their respective electronic energy density of states. Thus the important energetic differences between structures involve the most local topological differences in their bond networks.

Bond-valence theory

Brown (1981) has developed a coherent approach to chemical bonding in inorganic structures. Although the empirical bond-valence curves of Brown and Shannon (1973) and Brown and Wu (1976) are now widely used, the general ideas of bond-valence theory have not yet seen the use that they deserve. Consequently I shall briefly review these ideas, particularly as they can be developed further to deal in a very simple way with the complex hydroxy-hydrated oxysalt minerals.

The conceptual basis of bond-valence theory

A crystal, liquid or molecule can be defined as an array of atoms connected by a network of chemical bonds. For the oxide and oxysalt minerals, any path through this network contains alternating cations and anions, and the total network is subject to the *law of electroneutrality:* the total valence of the cations is equal to the total valence of the anions. A bond-valence can be assigned to each bond such that the *valence sum rule* is obeyed: *the sum of the bond-valences at each atom is equal to the magnitude of the atomic valence.* If the interatomic distances are known, then the bond-valences can be calculated from the curves of Brown (1981, 1988). If the interatomic distances are not known, then the bond-valences can be approximated by the Pauling bond-strength. So far, we are just dealing with formalizations and extensions of Pauling's rules. Although these ideas are important, they involve *a posteriore* analysis: the structure must be known in detail before these ideas can be applied. If we are to develop any *predictive* capability, we need an *a priore* approach to crystal structure. In this regard, Brown (1981) introduced a very important idea that abstracts the basic ideas of bond-valence theory and associates the resulting quantitative parameters with *ions* rather than with bonds between specific ion pairs.

Table 1. Lewis acid strengths (v. u.) for cations.*

Li	0.205	Sc	0.49	Ge	0.89
Be	0.501	Ti^{4+}	0.67	As^{5+}	1.13
B	0.87	V^{5+}	1.08	Se	1.50
C	1.35	Cr^{3+}	0.50	Rb	0.124
N	1.67	Cr^{6+}	1.50	Sr	0.233
Na	0.156	Mn^{2+}	0.344	Nb	0.823
Mg	0.334	Mn^{3+}	0.52	Sn^{4+}	0.68
Al	0.57	Fe^{2+}	0.340	Sb^{5+}	0.83
Si	1.00	Fe^{3+}	0.527	Te^{6+}	1.00
P	1.247	Co^{2+}	0.351	Cs	0.113
S	1.50	Ni^{2+}	0.339	Ba	0.195
Cl	1.75	Cu^{2+}	0.392	Ta	0.822
K	0.126	Zn	0.402	Pb^{2+}	0.29
Ca	0.274	Ga	0.65	Hg^{2+}	0.36

* Values taken from Brown (1988) for bonds to oxygen.

Lewis acid strength

The bond-valences around a specific cation in a wide range of crystal structures lie within ~20% of the mean value; this mean value is thus characteristic of that particular cation. If the cation only has one coordination number, then the mean bond-valence for that cation will be equal to the Pauling bond-strength. Thus S (sulphur) always occurs in tetrahedral coordination on oxysalts, and hence will have a mean bond-valence of 1.50 v.u. If the cation occurs with more than one coordination number, then the mean bond-valence will be equal to the weighted mean of the bond-valences in all the observed structures. Thus Ge has coordination numbers from [4] to [6] in oxysalt structures; [4] is more common than [5] and [6], and hence the mean bond-valence is 0.87 u.v. As the mean bond-valence correlates with formal charge and cation size (Brown, 1981), then it should vary systematically through the periodic table; this is in fact the case. Table 1 shows these characteristic values (Brown, 1988), smoothed across periods and down the groups of the periodic table.

The mean bond-valence of a cation correlates quite well with its electronegativity, indicating that it is a measure of the *Lewis acid strength* of the cation. Thus we have the following definition (Brown, 1981): *the Lewis acid strength of a cation is equal to the mean bond-valence incident to that cation [= atomic (formal) valence/mean coordination number].*

Lewis base strength

The *Lewis base strength* of an anion can be defined in exactly the same way as the characteristic valence of the bonds incident to the anion. However, variation in bond-valence incident to an anion is far greater than the analogous variation for cations. For example, in sodium alum {$Na[Al(SO_4)_2(H_2O)_6](H_2O)_6$; Cromer et al., 1967}, Na is [12]-coordinated and the oxygen to which it is bonded receives 0.08 v.u. from the Na–O bond; conversely, the oxygen receives 1.50 v.u. from the S–O bond. With this kind of variation, it is not particularly useful to define a Lewis base strength for a simple anion such as O^{2-} because the individual bond-valences have too great a dispersion for the mean to have any predictive value.

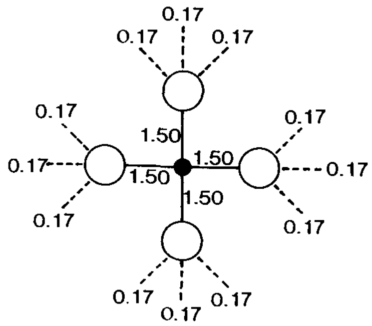

Fig. 1. Diagrammatic representation of the bond-valence structure of the $(SO_4)^{2-}$ oxyanion assuming [4]-coordination for each constituent oxygen.

The situation is entirely different for *complex oxyanions*. Consider the $(SO_4)^{2-}$ oxyanion shown in Figure 1. Each oxygen receives 1.5 v.u. from the central cation (S^{6+}), and hence each oxygen of the group needs an additional 0.50 v.u. to be supplied by additional cations. Oxygen coordination numbers [3] and [4] are by far the most common in mineral structures, with [4] predominating. With this the case, each oxygen of the $(SO_4)^{2-}$ oxyanion needs three more incident bonds to supply the necessary bond-valence of 0.50 v.u.; the resultant Lewis base strength is $0.50/3 = 0.17$ v.u. for each of the oxygens in the group and hence of the group itself. In this way, we can define the Lewis base strength of an oxyanion; we see that it has a very small dispersion and hence is very effective for predictive purposes.

The valence-matching principle

These definitions for Lewis acid and base strengths lead to a specific criterion for chemical bonding, the *valence-matching principle: the most stable structures will form when the Lewis acid strength of the cation(s) most closely matches the Lewis base strength of the anion(s).* We can consider this as the chemical equivalent of the handshaking principle in combinatorial

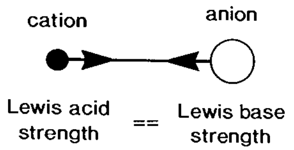

Fig. 2. Illustration of the valence-matching principle for a cation-anion bond; the valence of the bond from the cation to the anion is the same as the valence of the bond from the anion to the cation. For this to be the case, the Lewis acidity and basicity of the component ions must match.

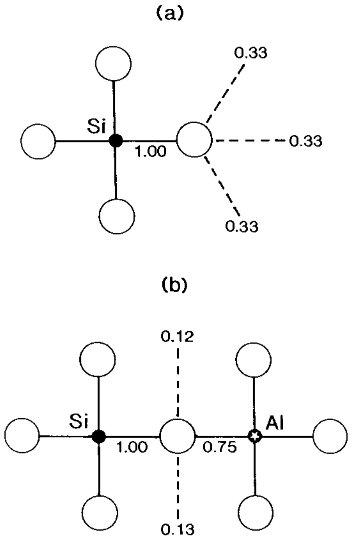

Fig. 3. Calculation of Lewis basicity for some complex oxyanions: (a) $(SiO_4)^{4-}$; (b) $[AlSiO_4]^{1-}$.

mathematics. As a chemical bond contains two ends (Fig. 2), the ends must match up for a stable configuration to form.

Simple applications of the valence-matching principle

Thenardite (Na_2SO_4; Hawthorne and Ferguson, 1975a) illustrates both the utility of defining a Lewis base strength for an oxyanion, and the working of the valence-matching principle. As discussed above, the $(SO_4)^{2-}$ oxyanion has a Lewis base strength of 0.17 v.u., which matches up very well with the Lewis acidity of 0.16 v.u. for Na (Table 1). Thus the Na–(SO_4) bond accords with the valence-matching principle, and thenardite is a stable mineral.

Consider the compound Na_4SiO_4; why is this not a mineral? Many rocks are rich in both Na_2O and SiO_2, and it seems reasonable that this stoichiometry might be a stable mineral. As shown in Figure 3a, the Lewis basicity of the $(SiO_4)^{4-}$ is 0.33 v.u., whereas the Lewis acidity of Na is 0.16 v.u. (Table 1). These values do not match up and a stable bond will not form; consequently, Na_4SiO_4 is not a stable mineral.

Consider $NaAlSiO_4$; a fragment of the structural unit (a 4-connected framework) is shown in Figure 3b, together with the bonds and bond-valences required for local bond-valence satisfaction. The Lewis basicity for the $[AlSiO_4]^{1-}$ unit is 0.13 v.u. Inspection of Table 1 shows that this matches up reasonably well with both Na (Lewis acidity = 0.16 v.u.) and K (Lewis acidity = 0.13 v.u.). Hence (Na, K)$[AlSiO_4]$ is a stable mineral, the nepheline-kalsilite series (Dollase and Thomas, 1978).

Thus we see the power of the valence-matching principle as a simple way to consider possible cation-anion interactions of interest. It is important to recognize that this is an *a priore* analysis; it is not necessary to have a refined crystal structure to apply these ideas.

A binary representation of complex structure

For any crystal structure, the *structural unit* may be defined as the strongly bonded part of the structure. Structural units are linked together by *interstitial species*, usually cations and $(H_2O)^0$ groups, that are (much) more weakly bonded. There is a degree of arbitrariness in these definitions in that there is no indication of how strong a bonding interaction must be for the constituent atoms to be considered as part of the structural unit. However, this does provide a necessary degree of flexibility, as the optimum division between bonds belonging to the structural unit and bonds to the interstitial species can depend on the relative distribution of bond-valences and the topology of the bond network. For the oxide and oxysalt minerals, the usual division is taken as 0.30 v.u.

In considering any structure as composed of a structural unit and interstitial species, we have in fact a *binary representation* of that structure, no matter how complex it may be. The structural unit is normally anionic (or neutral) whereas the interstitial species are usually cationic (or neutral). Consequently we may consider the structural unit as a very complex anion (Hawthorne, 1985) and calculate a Lewis basicity for it in exactly the same way as is done for more conventional oxyanions [e.g. $(SO_4)^{2-}$]; similarly we may calculate an average Lewis acidity for the interstitial species. We can then use the valence-matching principle to examine the interaction between the structural unit and the interstitial species to get some quantitative insight into the weak bonding interactions in these minerals. Such weak anharmonic interactions are of particular importance in controlling the

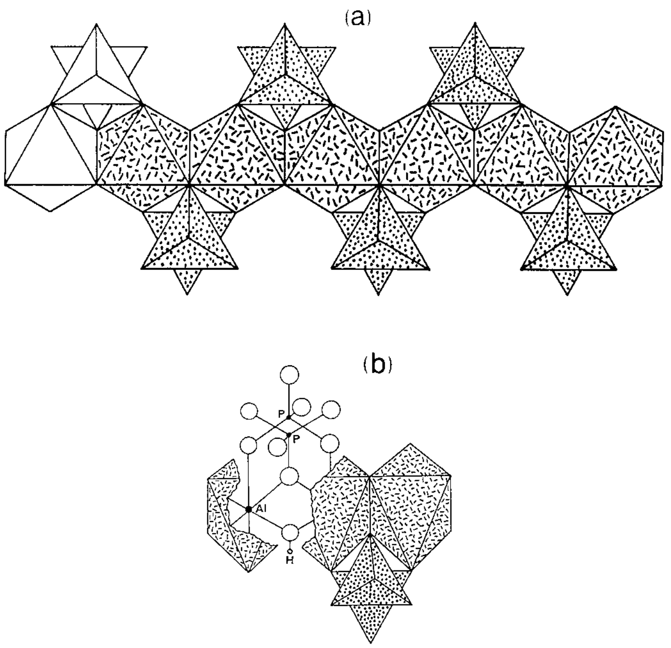

Fig. 4. The structure of goedkenite: (a) the structural unit, an edge-sharing chain of (AlO_6) octahedra (dashed) flanked by (PO_4) tetrahedra (dotted); (b) bonds within the smallest repeat fragment of the structural unit, showing the coordination of the individual anions.

stability and properties (e.g. solubility) of these oxysalt structures. It is worth emphasizing that we consider structures in this way *not* to convey the most complete picture of the bond topology, but to express structure in such a way as to apply bond-valence arguments in an *a priore* fashion to problems in structural chemistry. We can do this in a relatively simple fashion because this binary representation of structure gives a simple yet quantitative representation of even the most complex structure.

We may illustrate these arguments by considering the structure of goedkinite {$Sr_2[Al(PO_4)_2(OH)]$; Moore et al., 1975}. The structural unit is an edge-sharing chain of (AlO_6) octahedra flanked by (PO_4) tetrahedra (Fig. 4a); these chains are cross-linked by interstitial Sr atoms. A sketch of the smallest repeat fragment is shown in Figure 4b. There are nine oxygens in this fragment and the residual anionic charge is 4^-. In order to calculate the basicity of this structural unit, we must assign simple anion coordination numbers to the unit. Obviously we must have an objective process for doing this, as the calculation of structural unit basicity hinges on this assignment. Fortunately, this is fairly well-constrained by the general observation that

most minerals have oxygen in [3]- or [4]-coordination. Of course, it is easy to come up with exceptions, quartz for example, but the fact that these exceptions are few demonstrates the utility of this scheme. Normally it is adequate to use the coordination number [4].

However, there are the following exceptions:

(i) minerals with M^{3+} and T^{6+}, for which the oxygen coordination number [3] is more appropriate;

(ii) a coordination number of [3] is more appropriate for $(H_2O)^0$, and is also used for $(OH)^-$ when bonded to M^{3+} (this includes the strong O–H bonds).

To attain an oxygen coordination number of [4], the cluster of Figure 3 needs additional bonds from the interstitial species. From the connectivity of the structural unit, the cluster needs an additional 20 bonds; however, it will receive one hydrogen bond from an adjacent structural unit, which leaves 19 bonds to be received from the interstitial species. These 19 bonds must come from 4 positive charges, and thus the average bond-valence required by the cluster is $4/19 = 0.22$ v.u.; this is the Lewis basicity of the structural unit in goedkenite. Examination of the table of Lewis acid strengths (Table 1) shows that the cations of appropriate Lewis acidity are Sr (0.23 v.u.) and Ba (0.20 v.u.); in agreement with this, Sr is the interstitial cation in goedkenite. Note that Ca, with a Lewis basicity of 0.27 v.u., does not match with the Lewis basicity of the structural unit, and thus the valence-matching principle also accounts for the fact that goedkenite has Sr rather than Ca as the interstitial cation. In this way of treating minerals, we have a simple binary interaction: the structural unit bonds with the interstitial species. We may evaluate the stability of this interaction via the valence-matching principle, using the Lewis basicity of the structural unit and the Lewis acidity of the interstitial species as measures of their interaction. This reduces the most complex structure to a fairly simple representation, and characterizes the interaction of the component parts in a very simple but quantitative manner.

Hydrogen bonds

Hydrogen is electropositive and can be considered as a monovalent cation, H^+, that usually has the coordination number [2]. The geometrical details of the local stereochemistry around the hydrogen atom in inorganic structures has been examined in detail by Ferraris and Franchini-Angela (1972), Brown (1976a, b) and Ferraris and Ivaldi (1984). There is usually a spontaneous distortion from the most symmetrical arrangement, the H^+ cation moving off-centre towards one of the two coordinating anions. The H^+ cation forms a strong bond with the closer anion and a weak bond with the more distant anion. This arrangement can be written as D–H...A,

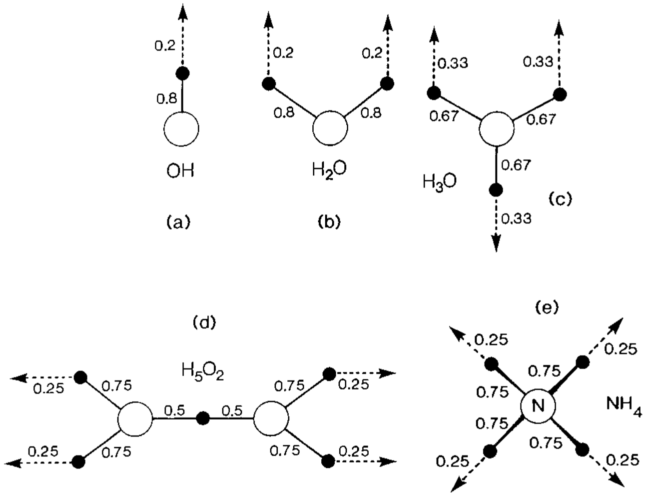

Fig. 5. Geometry and bond-valence structure in the hydrogen-bearing groups: (a) $(OH)^-$; (b) $(H_2O)^0$; (c) $(H_3O)^+$; (d) $(H_5O_2)^+$; (e) $(NH_4)^+$.

where D is the strongly bonded *donor* anion, A is the weakly bonded *acceptor* anion and H...A is called a *hydrogen bond.* D – H...A angles range between ~100° and 180° with an average value of ~165°; large angles usually involve strong hydrogen bonds (Brown, 1976a). Coordination numbers greater than [2] do occur for H^+. In this case, there is one short D – H bond and two (or more) weak H...A hydrogen bonds; the latter are usually designated as *bifurcated* (or *trifurcated*) hydrogen bonds.

Hydrogen-bearing groups

As hydrogen is strongly bonded to its donor anion, it is customary to consider the anion together with its associated hydrogen atom(s) as a complex species or group. There are five different hydrogen-bearing groups in oxide and oxysalt minerals: $(OH)^-$, $(H_2O)^0$, $(H_3O)^+$, $(H_5O_2)^+$ and $(NH_4)^+$. Others have designated larger groupings in synthetic inorganic crystals [e.g. $(H_7O_2)^{3+}$, $(H_{14}O_6)^{2+}$; Emsley et al., 1981]. However, these must involve hydrogen bonds as integral linkages of the group, and hence they cannot be considered as strongly bonded complexes according to the approach of Hawthorne (1985, 1990). Sketches of the bond geometry and bond-valence structure of the five naturally occurring groups are shown in Figure 5; note that none of the intra-group bonds have a bond-valence of less than 0.5 v.u.

The positively-charged groups act as *complex cations* and are extremely uncommon, although they have been identified in such minerals as hydronium jarosite ($\{H_3O\}[Fe_3^{3+}(SO_4)_2(OH)_6]$; Ripmeester et al., 1986), rhomboclase ($\{H_5O_2\}[Fe^{3+}(SO_4)_2(H_2O)_2]$; Mereiter, 1974) and tobelite ($\{NH_4\}[Al_2(Si_3Al)O_{10}(OH)_2]$; Higashi, 1982). On the other hand, the negatively-charged and neutral groups $(OH)^-$ and $(H_2O)^0$ are very common constituents of oxide and oxysalt minerals. Indeed, it is the presence of these groups that gives rise to the great diversity of structures exhibited by minerals.

$(OH)^-$ and $(H_2O)^0$ in oxysalt structures

The reason for the importance of $(OH)^-$ and $(H_2O)^0$ in oxysalt mineral structures stems from the very directional nature of the chemical bonding associated with them; on the oxygen side of each group, they function as an anion, whereas on the hydrogen side of each group, they function as a cation. This property allows them to play a variety of structural roles that are unique to $(OH)^-$ and $(H_2O)^0$.

$(OH)^-$ and $(H_2O)^0$ as components of the structural unit

In this context, the most important aspect of both these groups is their (usual) bond-valence distribution, as shown in Figure 5a, b. On the anionic side of each group, the bond-valence is relatively strong, ~1.2 v.u. for $(OH)^-$ and ~0.4 v.u. for $(H_2O)^0$. The remainder of the bond-valence requirements of the oxygen atom is satisfied by its bonds to the hydrogen(s); on the cationic side of the group, the bond-valence is relatively weak, ~0.2 v.u. for each group. Thus on the anionic side of the group, the strong bonding constitutes part of the structural unit, whereas on the cationic part of the group, the weaker (hydrogen) bonds do not form an integral part of the structural unit. The role played by these two groups is thus to limit the polymerization of the structural unit in specific directions. Hence they play a crucial role in controlling the character of the structural unit, particularly its dimensionality, and hence many of its physical, chemical and thermodynamic properties. This is best illustrated by some examples.

Newberyite ($[MgPO_3OH(H_2O)_3]$; Sutor, 1967) has a structural unit consisting of a sheet of corner-sharing (MgO_6) octahedra and (PO_4) tetrahedra, with the polyhedra arranged at the vertices of a 6_3 net (Fig. 6). Three of the (PO_4) ligands link to (MgO_6) octahedra within the plane of the sheet. The other ligand is 'tied off' orthogonal to the sheet by the fact that it is a hydroxyl anion, and hence cannot strongly bond to another cation as its bond-valence requirements are already satisfied by the P (together with its attendant hydrogen). The long P – O bond of 1.59 Å

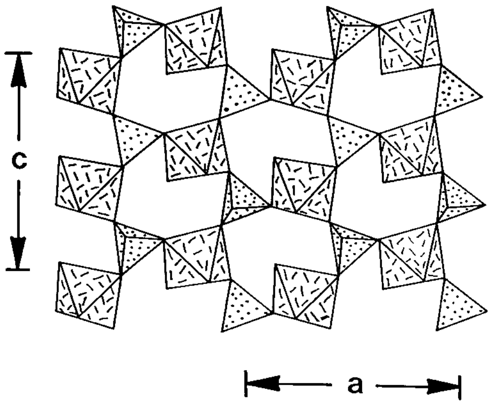

Fig. 6. The structural unit in newberyite, a sheet of corner-sharing (MgO_6) octahedra and (PO_4) tetrahedra.

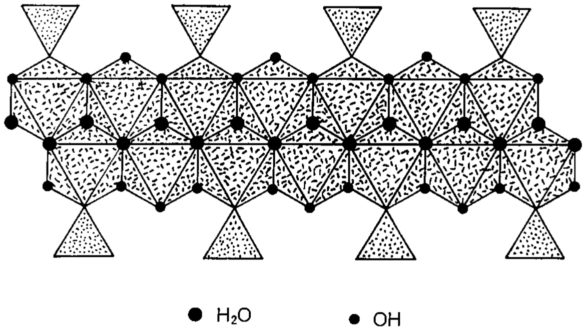

Fig. 7. The structural unit in artinite, a ribbon of (MgO_6) octahedra flanked by (CO_3) triangles.

contributes a bond-valence of 1.10 v.u. to the oxygen, and the remaining 0.90 v.u. is contributed by the hydrogen which then weakly hydrogen-bonds to the adjacent sheet. Three of the (MgO_6) ligands link to (PO_4) tetrahedra within the sheet; the other ligands are again 'tied off' by the fact that they are (H_2O) groups. The Mg–O bonds contribute a bond-valence of ~0.32 v.u. to each oxygen, and the remaining 1.68 v.u. is contributed by the two attendant hydrogen atoms which then weakly hydrogen-bond to adjacent sheets. Thus the chemical formula of the structural unit, [$Mg(PO_3OH)(H_2O)_3$], is also the chemical formula of the mineral, and the structural units are held together solely by hydrogen bonding directly from one unit to another.

In newberyite, all linkage within the structural unit was terminated at the $(OH)^-$ and $(H_2O)^0$ groups. This does not have to be the case; in specific arrangements, both $(OH)^-$ and $(H_2O)^0$ groups can allow polymerization in some directions but not in others. Artinite ([$Mg_2CO_3(OH)_2(H_2O)_3$]; Akao and Iwai, 1978) is an excellent example of this. The structural unit (Fig. 7) is a ribbon of edge-sharing (MgO_6) octahedra flanked by (CO_3) triangles linked to alternate outer octahedral vertices of the ribbon and occurring in a staggered arrangement on either side of the ribbon. The anions along the centre of the ribbon are bonded to three Mg cations; they receive $\sim 0.36 \times 3 = 1.08$ v.u. from the Mg cations, and thus receive 0.92 v.u. from their associated hydrogen atoms which then weakly hydrogen-bond (~0.08 v.u.) to an adjacent ribbon. The $(OH)^-$ group thus allows polymerization in the X and Y directions but prevents it in the Z direction. The anions along the edge of the ribbon are bonded to one Mg, two Mg, or one Mg and one C, with bond-valence contributions of about 0.3, 0.6 and 1.7 v.u. respectively. The first two anions are therefore $(H_2O)^0$ groups, which hydrogen bond fairly strongly to anions both in the same structural unit and in adjacent structural units. Thus the $(H_2O)^0$ group bonded to one Mg prevents further linkage in all three directions, whereas the $(H_2O)^0$ group bonded to two Mg atoms allows polymerization in the Y direction but prevents it in the other two directions. The bond-valence requirements to the two anions bonded only to C are satisfied by hydrogen bonding involving donor atoms from more than one structural unit. Thus the chemical formula of the structural unit is again the chemical formula of the mineral, and all inter-unit linkage is via hydrogen bonding. The $(OH)^-$ group allows polymerization in two directions within the structural unit, whereas the two types of $(H_2O)^0$ allow polymerization of the structural unit in one and no directions respectively.

To summarize, as components of the structural unit, both $(OH)^-$ and $(H_2O)^0$ play crucial roles in controlling its dimensional character.

$(H_2O)^0$ groups bonded to interstitial cations

Structural units are often linked together by interstitial cations. These are usually large and of low charge; generally they are alkali or alkaline-earth cations with Lewis acidities significantly less than the cations of the structural unit. Consequently $(H_2O)^0$ can function as a ligand for these cations whereas $(OH)^-$ usually cannot because the interstitial cation cannot contribute sufficient bond-valence (i.e. ~1.0 v.u.) for the $(OH)^-$ bond-valence requirements to be satisfied. There are at least three possible reasons for $(H_2O)^0$ groups to act as ligands for interstitial cations:

(i) to satisfy the bond-valence requirements around the interstitial cation in cases where there are insufficient neighboring anions from adjacent structural units;

(ii) to 'carry' the bond-valence from the interstitial cation to a distant unsatisfied anion via a hydrogen bond;

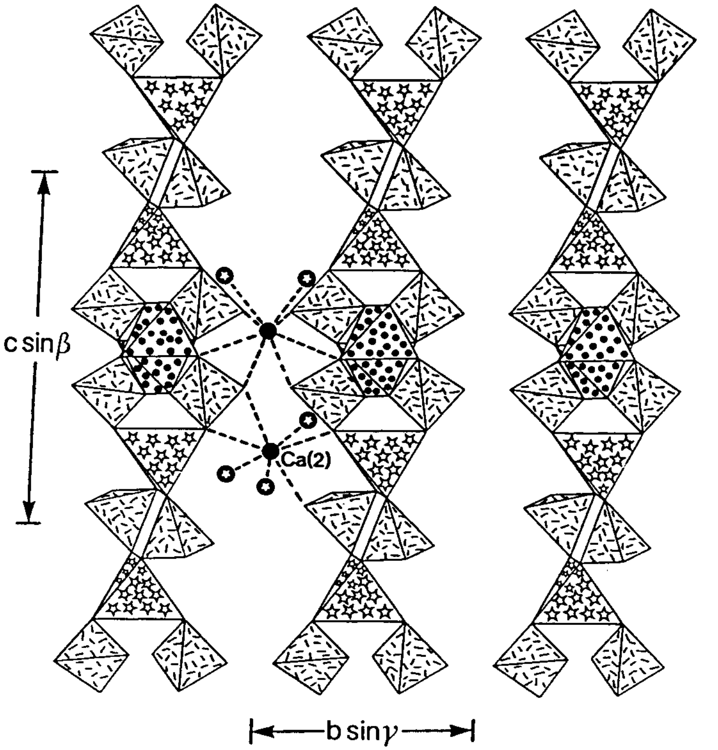

Fig. 8. The structure of ehrleite, complex sheets of corner-linked (ZnO_4), (BeO_4) and (PO_4) tetrahedra cross-linked by interstitial Ca and (H_2O) groups (✪); note the coordinations of the two interstitial Ca cations.

(iii) to act as a bond-valence transformer between the interstitial cation and the structural unit.

The structure of ehrleite $(Ca_2[ZnBe(PO_4)_2(PO_3OH)](H_2O)_4$; Hawthorne and Grice, 1987) is a good example of this (Fig. 8). The structural unit is a sheet of tetrahedra involving Zn, Be and P as the tetrahedrally coordinated cations. The (ZnO_4) and (BeO_4) tetrahedra are 4-connected (that is, they link to four other tetrahedra) whereas the (PO_4) tetrahedra are 3-connected [linking to two (BeO_4) and one (ZnO_4) tetrahedra] and the (PO_3OH) tetrahedra is 2-connected [linking to two (ZnO_4) tetrahedra]. These sheets are linked together by interstitial Ca atoms. The two distinct Ca atoms link to 6 and 4 structural unit oxygen anions respectively. These are fairly low coordination numbers for Ca (especially in the case of that coordinated by only 4 oxygens), and the coordinations are augmented by additional ligands in the form of interstitial $(H_2O)^0$ groups; two and three $(H_2O)^0$ groups complete the coordination around the interstitial Ca atoms (Fig. 7).

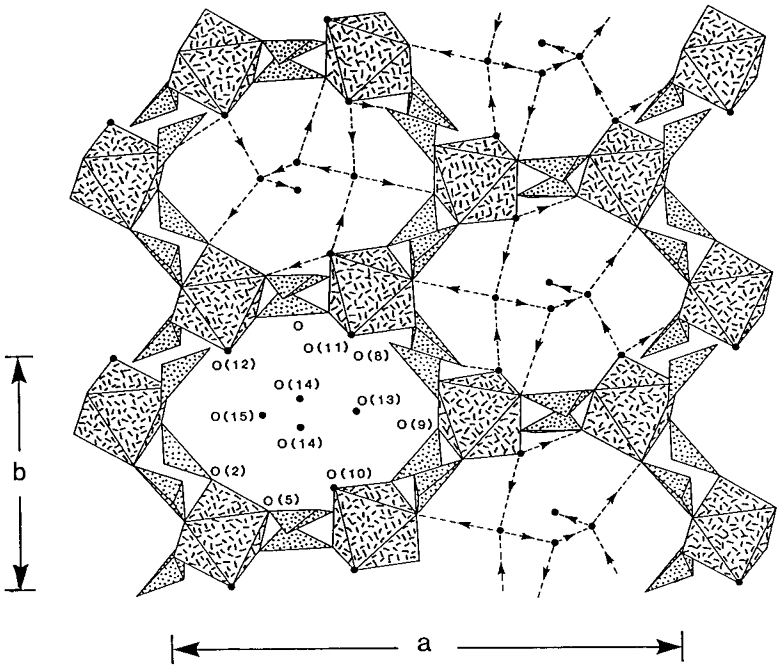

Fig. 9. The structure of mandarinoite, a framework of corner-linked (SeO_3) triangular pyramids and (FeO_6) octahedra; note the large cavities occupied by a well-ordered array of hydrogen-bonded (H_2O) groups.

The $(H_2O)^0$ groups that are bonded solely to interstitial cations thus play a very different role than those $(H_2O)^0$ groups that form part of the structural unit.

Interstitial $(H_2O)^0$ not bonded to cations

Many structures have interstitial $(H_2O)^0$ groups that are not bonded to any interstitial cation and yet participate in a well-ordered hydrogen-bonded network. The $(H_2O)^0$ groups of this sort act both as hydrogen-bond donors and hydrogen-bond acceptors. Any hydrogen-containing group can act as a hydrogen-bond donor to $(H_2O)^0$ groups of this sort, and any anion or $(H_2O)^0$ group can act as a hydrogen-bond acceptor. Minerals with such hydrogen-bonded networks can be thought of as intermediate between anhydrous structures and clathrates.

Such a structure is the mineral mandarinoite $([Fe^{3+}_2(SeO_3)_3(H_2O)_3](H_2O)_3$; Hawthorne, 1984). The structural unit is a heteropolyhedral framework of corner-linked (SeO_3) triangular pyramids and

(FeO_6) octahedra (Fig. 9) with large cavities that are occupied by hydrogen-bonded $(H_2O)^0$ groups in well-defined positions. Thus of the six $(H_2O)^0$ groups in the formula unit, three are bonded to Fe^{3+} and are part of the structural unit, whereas the remaining three are interstitial $(H_2O)^0$ groups not bonded to any cation at all, but held in place solely by hydrogen bonding.

Occluded $(H_2O)^0$ groups

In some structures, there are $(H_2O)^0$ groups that are not bonded to any cation or associated with any ordered hydrogen-bonding network; usually such $(H_2O)^0$ groups are located in holes within or between structural units. Such groups can occupy well-defined crystallographic positions, but their interaction with the rest of the structure is solely via a Van der Waals mechanism.

Beryl offers a good example of this. The alkali-free beryl structure can have nonbonded $(H_2O)^0$ groups occurring down the channels of the tetrahedral beryllo-silicate framework (Gibbs et al., 1968). Most natural beryls contain alkali cations partially occupying sites within this channel, and these interstitial cations are bonded to the interstitial channel $(H_2O)^0$ groups. However, Hawthorne and Cerny (1977) have shown that many natural beryls contain (H_2O) in excess of that required to coordinate the channel cations, and hence some of the $(H_2O)^0$ groups must be occluded rather than bonded components of the mineral. Although such (H_2O) does not play an important chemical role in the structure, it can have an important effect on such physical properties as specific gravity, refractive index and dielectric behaviour.

(H_2O): a bond-valence transformer

In Figure 10a, we see a cation, M, bonded to an anion, X, with a bond-valence of v v.u. Consider an $(H_2O)^0$ group bonded to a cation, M (Fig. 10b). From the cation, the oxygen receives a bond-valence of v v.u., and its bond-valence requirements are completed by two short O – H bonds of valence $(1-v/2)$ v.u. To satisfy the bond-valence requirements around each hydrogen atom, each hydrogen forms at least one hydrogen bond with neighbouring anions. Comparing Figures 10a and 10b, we see that when M bonds directly to X, the anion receives an incident bond-valence of v v.u., whereas when M bonds to an $(H_2O)^0$ group which then hydrogen bonds to X, the anion receives an incident bond-valence of v/2 v.u. Thus the $(H_2O)^0$ group is acting as a *bond-valence transformer*, causing one stronger bond to be split into two (or more) weaker bonds; it is this transformer effect that is the key to understanding the role of interstitial $(H_2O)^0$ groups in oxide and oxysalt minerals.

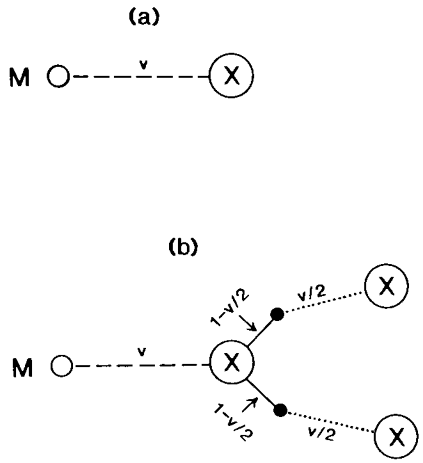

Fig. 10. The bond-valence structure of an M – X interaction: (a) direct M – X bonding; (b) M – (H_2O)...X bonding; M is a cation, X is an anion (usually oxygen).

The roles of interstitial H_2O in oxysalt structures

H_2O plays a major role in controlling the character of the structural unit. Such $(H_2O)^0$ groups are part of the structural unit and the amount is stoichiometrically fixed by the topology of the bond connectivity of the unit. Interstitial $(H_2O)^0$ is very different in character: it may coordinate an interstitial cation, or it may occur solely as a component of a hydrogen-bonded network. Whatever is the case, $(H_2O)^0$ occupies fixed atomic positions and must play a role in the stability of the structure. The details of these roles are different, depending on the type of interstitial $(H_2O)^0$ group involved. Nevertheless, they are susceptible to analysis and even prediction using some of the ideas outlined above.

Interstitial (H_2O) bonded to a cation

The key to understanding the role of this type of $(H_2O)^0$ group is in the coupling of two distinct ideas of bond-valence theory:

(1) the role of $(H_2O)^0$ as a bond-valence transformer;

(2) application of the valence-matching principle to the interaction between the structural unit and the interstitial cations.

According to the valence-matching principle, the valence of the bonds from the interstitial cations to the structural unit must match the Lewis basicity of that structural unit. If they do not match, then there cannot be a stable interaction and that particular structural arrangement will not occur. However, if the Lewis acidity of the interstitial cation is too large,

Table 2. Details of the interstitial (H_2O) in botryogen.

Bonded atoms	Number of anions	Ideal coord. no.	Bonds needed for ideal coord.
S	10	3	2×10
$S+Fe^{3+}$	6	3	$1\times\ 6$
$2Fe^{3+}+H$	2	3	0
$Fe^{3+}+H$	2	3	0

Bonds needed to structural unit $= 2\times 10+1\times 6=26$
No. of H bonds to structural unit $= 2\times 2+2\times 1=6$
No. of additional bonds needed $= 26-6=20$
Charge on structural unit $= 4^-$
Lewis basicity of structural unit $= 4/20 = 0.20$ v. u.

Interstitial cation = Mg Mg coordination $= [5(H_2O)+O]$
Bonds from Mg to structural unit $= 5\times 2+1=11$
Effective Lewis acidity of Mg $= 2/11 = 0.19$ v. u.

the cation may bond to an interstitial $(H_2O)^0$ group which then acts as a bond-valence transformer, taking the strong bond and transforming it into two weaker bonds (Fig. 10). In this way, *incorporation of interstitial (H_2O) into the structure can moderate the Lewis acidity of the interstitial cations such that the valence-matching principle is satisfied.*

The ferric iron sulphate mineral botryogen (Süsse, 1968) is an excellent example of this principle. The chemical formula of botryogen is $Mg_2[Fe^{3+}_2(SO_4)_4(OH)_2(H_2O)_2](H_2O)_{10}$; why does this mineral have 10 interstitial (H_2O) groups per formula unit? The structural unit of botryogen and the coordinations of the various anions in the structural unit are shown in Table 2. Using the ideal coordination numbers discussed in a previous section for all the simple anions, the structural unit of botryogen needs an additional 26 bonds to achieve ideal coordination of all its simple anions. Six of these bonds will be hydrogen bonds from (OH) and (H_2O) groups that are part of the structural unit, leaving 20 bonds to be provided by the interstitial cations. Thus the Lewis basicity of the structural unit in botryogen is the charge divided by the number of additional bonds required: $4/20=0.20$ v. u. The interstitial cations in botryogen are Mg, which has a Lewis acidity of 0.33 v. u. The valence-matching principle is violated and a stable structure should not form. However, the interstitial Mg cations are coordinated by $[(H_2O)_5+O]$, and this will moderate the effective Lewis acidity of the Mg via the transformer effect of the $(H_2O)^0$. The effective Lewis acidity of the $[Mg(H_2O)O]$ group is approximately the charge divided by the number of bonds to the structural unit: $2/(5\times 2+1)=0.19$ v. u. The moderated Lewis acidity of the complex interstitial species now matches the Lewis basicity of the structural unit and thus a stable mineral is formed.

We can think of this type of interstitial $(H_2O)^0$ as combining with a simple cation to form a *complex cation*. Our binary structure components are now an anionic structural unit and one or more complex cations. It is apparent from the stereochemistry of interstitial $(H_2O)^0$ groups observed in recent neutron structure refinements of zeolite structures that this may be a profitable way in which to consider this type of $(H_2O)^0$ group.

Prediction of cation-bonded interstitial (H_2O) in oxysalt minerals

According to the above arguments, the amount of interstitial $(H_2O)^0$ bonded to an interstitial cation in a structure should be capable of prediction. The Lewis basicity of the structural unit can be calculated and the Lewis acidity of the interstitial cation(s) is known. The amount of such $(H_2O)^0$ is simply that required to moderate the interstitial cation acidity to match the Lewis basicity of the structural unit according to the valence-matching principle.

Let a be the Lewis acidity of the cation, Z be the cation charge and b be the Lewis basicity of the structural unit. The (mean) coordination number, C, of the cation is given by

$$C = Z/a\,.$$

For each $(H_2O)^0$ group participating in bonding between the cation and the structural unit, the number of bonds between the cation and the structural unit is increased by one relative to a direct interaction between the cation and the structural unit. We may therefore write the moderated Lewis acidity, a', of the cation as

$$a' = Z/(C+n) = aZ/(Z+an)\,,$$

where n is the number of $(H_2O)^0$ groups participating in the bonding. The valence-matching principle requires that $a' \sim b$ for a stable interaction to occur. Replacing a' by b and rearranging gives

$$n \sim Z(a-b)/ab$$

as an estimate of the amount of interstitial $(H_2O)^0$. If $a=b$, there is no interstitial $(H_2O)^0$. If $a<b$, there is no way of achieving an acidity-basicity match and a stable mineral is unlikely to form. If $a>b$, an acidity-basicity match may be achieved by the incorporation of this type of interstitial $(H_2O)^0$, and n gives an estimate of how much will occur.

The results for a cross-section of oxysalt minerals are shown in Table 3. By-and-large, the predictions are quite reasonable, even with such complex minerals as gordonite, suggesting that the general idea that such interstitial $(H_2O)^0$ is structurally incorporated to satisfy the valence-matching principle is sound. There are some glaring examples where quantitative prediction fails. Thus in apjohnite (Menchetti and Sabelli, 1976), the observed

Table 3. Prediction of interstitial (H_2O) in selected oxysalt minerals.

Mineral	Formula	Observed H_2O	Predicted H_2O	Ref.
Gordonite	$Mg[Al_2(PO_4)_2(OH)_2(H_2O)_2](H_2O)_4 \cdot 2H_2O$	6	6	[1]
Leucophosphite	$K[Fe_2^{3+}(PO_4)(OH)(H_2O)](H_2O)_2$	2	4	[2]
Lawsonite	$Ca[Al_2(Si_2O_7)(OH)_2](H_2O)$	1	2	[3]
Dresserite	$Ba[Al_2(CO_3)_2(OH)_4](H_2O)$	1	0	[4]
Sodium alum	$Na[Al(SO_4)_2(H_2O)_6](H_2O)_6$	6	4	[5]
Apjohnite	$Mn[Al_2(SO_4)_4(H_2O)_{12}](H_2O)_{10}$	10	2	[6]
Fleischerite	$Pb_3[Ge(SO_4)_2(OH)_6](H_2O)_3$	3	3	[7]
Roemerite	$Fe^{2+}[Fe_2^{3+}(SO_4)_4(H_2O)_8](H_2O)_6$	6	6	[8]
Sideronatrite	$Na_2[Fe^{3+}(SO_4)_2(OH)](H_2O)_3$	3	0	[9]
Jahnsite	$CaMnMg_2[Fe_2^{3+}(PO_4)_4(OH)_2](H_2O)_8$	8	12	[10]
Guildite	$Cu[Fe^{3+}(SO_4)_2(OH)](H_2O)_4$	4	6	[11]
Krausite	$K[Fe^{3+}(SO_4)_2(H_2O)]$	0	1	[12]
Olmsteadite	$KFe_2^{2+}[Nb(PO_4)_2O_2](H_2O)_2$	2	2	[13]
Hilairite	$Na_2[Zr(Si_3O_9)](H_2O)_3$	3	3	[14]
Cyanochroite	$K_2[Cu(SO_4)_2(H_2O)_6]$	0	0	[15]
Krohnkite	$Na_2[Cu(SO_4)_2(H_2O)_2]$	0	1	[16]
Bayldonite	$Pb[Cu_3(AsO_4)_2(OH)_2](H_2O)$	1	1	[17]

References: [1] Leavens and Rheingold (1988); [2] Moore (1972); [3] Baur (1978); [4] Jambor et al. (1969); [5] Cromer et al. (1967); [6] Menchetti and Sabelli (1976); [7] Otto (1975); [8] Fanfani et al. (1970); [9] Scordari (1981a); [10] Moore and Araki (1974); [11] Wan et al. (1978); [12] Graeber et al. (1965); [13] Moore et al. (1976); [14] Ilyushin et al. (1981); [15] Carapezza and Riva di Sanseverino (1968); [16] Hawthorne and Ferguson (1975b); [17] Ghose and Wan (1979).

amount of interstitial $(H_2O)^0$ is 10 pfu (per formula unit), whereas the predicted amount is 2 pfu; possibly some of the $(H_2O)^0$ takes a more passive role (see next section). As a predictive tool, the current method is capable of significant improvement. The accuracy of the procedure hinges on the best assignment of anion coordination numbers, and systematic examination of a large number of structures should result in better predictive values. In addition, H^+ is assumed to have a coordination number of [2]. Certainly this is not always the case, as many (OH)-bearing structures have principal infrared stretching frequencies in the region of $\sim 3700\ cm^{-1}$, indicative of negligible hydrogen-bonding interaction.

Interstitial (H_2O) not bonded to an interstitial cation

Several examples of minerals with this type of $(H_2O)^0$ are given in Table 4. As emphasized previously, such $(H_2O)^0$ groups are usually well-ordered and participate in a hydrogen-bonding network; the example of mandarinoite (Hawthorne, 1984) is shown in Figure 9. Mandarinoite contains $(H_2O)^0$ groups as an integral part of the structural unit, and inspection of Table 4 shows that all these minerals contain $(H_2O)^0$ and/or $(OH)^-$ groups as part of their structural unit.

Table 4. Selected minerals with interstitial $(H_2O)^0$ not bonded to an interstitial cation.

Name	Formula	Ref.
Chalcanthite	$[Cu^{2+}(SO_4)(H_2O)_4](H_2O)$	[1]
Fibroferrite	$[Fe^{3+}(SO_4)(OH)(H_2O)_2](H_2O)_4$	[2]
Amarantite	$[Fe_2^{3+}(SO_4)_2O(H_2O)_4](H_2O)_3$	[3]
Hohmannite	$[Fe_2^{3+}(SO_4)_2O(H_2O)_4](H_2O)_4$	[4]
Nesquehohnite	$[Mg(CO_3)(H_2O)_2](H_2O)$	[5]
Mandarinoite	$[Fe_2^{3+}(SeO_3)_3(H_2O)_3](H_2O)_3$	[6]
Sonoraite	$[Fe_2^{3+}(TeO_3)_2(OH)_2(H_2O)](H_2O)$	[7]
Emmonsite	$[Fe_2^{3+}(TeO_3)_3(H_2O)](H_2O)$	[8]

References: [1] Bacon and Curry (1962); [2] Scordari (1981b); [3] Süsse (1968); [4] Scordari (1978); [5] Stephen and MacGillavry (1972); [6] Hawthorne (1984); [7] Donnay et al. (1970); [8] Pertlik (1972).

Hydrogen generally has a coordination number of [2]. In some cases, both coordinating anions are part of a structural unit. In other cases, the geometry of the structural unit does not allow such coordination (e.g. when the O – H bond projects out into a large interstitial cavity). In such cases, the bond-valence requirements of the hydrogen atom still need to be satisfied, and here is where this type of interstitial $(H_2O)^0$ group has its role. It provides the additional necessary coordination of this (structural unit) H by acting as an acceptor for the hydrogen bond. This $(H_2O)^0$ must then act as a donor for other hydrogen bonds, and a hydrogen-bond network of $(H_2O)^0$ groups is formed until the acceptor anions of the hydrogen bonds belong to a structural unit. Thus a mandarinoite (Fig. 9), the interstitial $(H_2O)^0$ groups essentially satisfy the bond-valence requirements of the H of the structural unit, and propagate its bonding through the interstitial space to other parts of the structural unit. The amount of such $(H_2O)^0$ depends on (i) the amount of 'unsatisfied' H in the structural unit, and (ii) the amount of interstitial void space between the structural units. In zeolite-like structures, the amount of available void space is constrained by the character of the structural unit (as in mandarinoite), whereas in structures with 0-, 1- and 2-dimensional structural units, there is no such constraint.

Summary

1. For any crystal structure, the *structural unit* may be defined as the strongly bonded part of the structure; structural units are linked together by *interstitial species*, usually alkali or alkaline earth cations and $(H_2O)^0$ groups that are involved in much weaker bonding. This scheme gives a *binary representation* of even the most complex structure.

2. The interaction between the structural unit and the interstitial species can be quantitatively evaluated using the *valence-matching principle* (Brown, 1981).

3. As components of the structural unit, $(OH)^-$ and $(H_2O)^0$ play a major role in dictating the dimensional polymerization of the structural unit because of the very asymmetric nature of the donor-hydrogen and hydrogen... acceptor interactions.

4. As an interstitial component, $(H_2O)^0$ can play three different roles:

5. Interstitial $(H_2O)^0$ may bond to an interstitial cation, essentially forming a *complex cation*. In this role, $(H_2O)^0$ acts as a bond-valence transformer, moderating the Lewis acidity of the interstitial cations such that it matches the Lewis basicity of the structural unit and the valence-matching principle is satisfied.

6. Interstitial $(H_2O)^0$ need not bond to an interstitial cation to occupy well-ordered atomic positions; a stable hydrogen-bonded network can occur in the interstitial regions between structural units. The role of such $(H_2O)^0$ is to satisfy the bond-valence requirements of H atoms that are part of the structural unit, propagating the bonding across the interstitial space to other parts of the structural unit.

7. Occluded $(H_2O)^0$ may occur in some minerals. Such $(H_2O)^0$ is not bonded to interstitial cations and does not participate in a static ordered hydrogen-bond network. However, this type of (H_2O) will still affect many of the physical properties of a mineral.

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References

Akao, M., Iwai, S.: The hydrogen bonding of artinite. Acta Crystallogr. **B33** (1978) 3951–3953.

Bacon, D. E., Curry, N. A.: The water molecules in $CuSO_4 \cdot 5H_2O$. Proc. Roy. Soc. **266** (1962) 95–108.

Baur, W. H.: Bond length variation and distorted coordination polyhedra in inorganic crystals. Trans. Am. Crystallogr. Assoc. **6** (1970) 129–155.

Baur, W. H.: The prediction of bond length variations in silicon-oxygen bonds. Am. Mineral. **56** (1971) 1573–1599.

Baur, W. H.: Crystal structure refinement of lawsonite. Am. Mineral. **63** (1978) 311–315.

Brown, I. D.: On the geometry of O–H...O hydrogen bonds. Acta Crystallogr. **A32** (1976a) 24–31.

Brown, I. D.: Hydrogen bonding in perchloric acid hydrates. Acta Crystallogr. **A32** (1976b) 786–793.

Brown, I. D.: The bond-valence method: an empirical approach to chemical bonding and structure. In: *Structure and Bonding in Crystals II* (M. O'Keeffe and A. Navrotsky, eds.). Academic Press, New York, 1–30 (1981).

Brown, I. D.: What factors determine cation coordination numbers. Acta Crystallogr. **B44** (1978) 545–553.

Brown, I. D., Shannon, R. D.: Empirical bond-strength–bond-length curves for oxides. Acta Crystallogr. **A29** (1973) 266–282.

Brown, I. D., Wu, K. K.: Empirical parameters for calculating cation-anion bond valences. Acta Crystallogr. **B32** (1976) 1957–1959.

Burdett, J. K.: Structural-electronic relationships in the solid state. In: *Molecular Structure and Energetics* (A. Greenberg and J. F. Leibman, eds.). VCH Publishers, Boca Raton, 209–275 (1986).

Carapezza, M., Riva di Sanseverino, L.: Crystallography and genesis of double sulfates and their hydrates. II. Structure, powder pattern and thermoanalysis of cyanochroite, $K_2Cu(SO_4)_2 \cdot 6H_2O$. Mineral. Petrol. Acta **14** (1968) 23–37.

Cromer, D. T., Kay, M. I., Larsen, A. C.: Refinement of the alum structures. II. X-ray and neutron diffraction of $NaAl(SO_4)_2 \cdot 12H_2O$, gamma-alum. Acta Crystallogr. **22** (1967) 182–187.

Dollase, W. A., Thomas, W. M.: The crystal chemistry of silica-rich, alkali-deficient nepheline. Contrib. Mineral. Petrol. **66** (1978) 311–318.

Donnay, G., Stewart, J. M., Preston, H.: The crystal structure of sonoraite, $Fe^{3+}Te^{4+}O_3(OH) \cdot H_2O$. Tschermaks Mineral. Petrogr. Mitt. **14** (1970) 27–44.

Dunn, P. J., Francis, C. A., Innes, J.: A mcgovernite-like mineral and leucophanite from the Kombat mine, Namibia. Am. Mineral. **73** (1988) 1182–1185.

Emsley, J., Jones, D. J., Lucas, J.: Detecting and measuring strong hydrogen bonds: recent developments. Rev. Inorg. Chem. **3** (1981) 105–140.

Fanfani, L., Nunzi, A., Zanazzi, P. F.: The crystal structure of roemerite. Am. Mineral. **55** (1970) 78–89.

Ferraris, G., Franchini-Angela, M.: Survey of the geometry and environment of water molecules in crystalline hydrates studied by neutron diffraction. Acta Crystallogr. B28 (1972) 3572–3583.

Ferraris, G., Ivaldi, G.: X–OH and O–H...O bond lengths in protonated oxyanions. Acta Crystallogr. **B40** (1984) 1–6.

Ghose, S., Wan, C.: The crystal structure of bayldonite. Acta Crystallogr. **B35** (1979) 819–823.

Gibbs, G. V., Breck, D. W., Meagher, E. P.: Structural refinement of hydrous and anhydrous beryl, $Al_2(Be_3Si_6)O_{18}$ and emerald, $Al_{1.9}Cr_{0.1}(Be_3Si_6)O_{18}$. Lithos **1** (1968) 275–285.

Graeber, E. J., Morosin, B., Rosenzweig, A.: The crystal structure of krausite, $KFe(SO_4)_2 \cdot H_2O$. Am. Mineral. **50** (1965) 1929–1936.

Hawthorne, F. C.: The crystal structure of mandarinoite, $Fe_2^{3+}Se_3O_9 \cdot 6H_2O$. Can. Mineral. **22** (1984) 475–480.

Hawthorne, F. C.: Towards a structural classification of minerals: the ${}^{vi}M{}^{iv}T_2O_n$ minerals. Am. Mineral. **70** (1985) 455–470.

Hawthorne, F. C.: Structural hierarchy in $M^{[6]}T^{[6]}O_n$ minerals. Z. Kristallogr. **192** (1990) 1–52.

Hawthorne, F. C., Cerny, P. C.: The alkali-metal positions in Cs–Li beryl. Can. Mineral. **15** (1977) 414–421.

Hawthorne, F. C., Ferguson, R. B.: Anhydrous sulphates: I. Refinement of the crystal structure of celestite, with an appendix on the structure of thenardite. Can. Mineral. **13** (1975a) 181–187.

Hawthorne, F. C., Ferguson, R. B.: Refinement of the crystal structure of krohnkite. Acta Crystallogr. **B31** (1975b) 1753–1755.

Hawthorne, F. C., Grice, J. D.: The crystal structure of ehrleite, a tetrahedral sheet structure. Can. Mineral. **25** (1987) 767–774.

Higashi, S.: Tobelite, a new ammonium dioctahedral mica. Mineral. Jour. (Japan) **11** (1982) 138–146.

Ilyushin, G. D., Voronkov, A. A., Nevskii, N. N., Ilyukhin, V. V., Belov, N. V.: Crystal structure of hilairite $Na_2ZrSi_3O_9 \cdot 3H_2O$. Sov. Phys. Dokl. **26** (1981) 916–917.

Jambor, J. L., Fong, D. G., Sabina, A. P.: Desserite, the new barium analogue of dundasite. Can. Mineral. **10** (1969) 84–89.

Leavens, P. B., Rheingold, A. L.: Crystal structures of gordonite, $MgAl_2(PO_4)_2$-$(OH)_2(H_2O)_6 \cdot 2H_2O$, and its Mn analog. Neues Jahrb. Mineral. Monatsch. **1988** (1988) 265–270.

Lewis, G. N.: *Valence and the Structure of Atoms and Molecules*. Am. Chem. Soc. Mon. Ser., New York (1923).

Menchetti, S., Sabelli, C.: The halotrichite group: the crystal structure of apjohnite. Mineral. Mag. **40** (1976) 599–608.

Mereiter, K.: Die Kristallstruktur von Rhomboklas, $H_5O_2\{Fe[SO_4]_2 \cdot 2H_2O\}^-$. Tschermaks Mineral. Petrog. Mitt. **21** (1974) 216–232.

Moore, P. B.: Octahedral tetramer in the crystal structure of leucophosphite, $K_2[Fe_4^{3+}(OH)_2(H_2O)_2(PO_4)_4] \cdot 2H_2O$. Am. Mineral. **57** (1972) 397–410.

Moore, P. B., Araki, T.: Jahnsite, $CaMn^{2+}Mg_2(H_2O)_8Fe_2^{3+}(OH)_2[PO_4]_4$: a novel stereoisomerism of ligands about octahedral corner-chains. Am. Mineral. **59** (1974) 964–973.

Moore, P. b., Araki, T., Kampf, A. R., Steele, I. M.: Olmsteadite, $K_2Fe_2^{2+}[Fe_2^{2+}$-$(Nb,Ta)_2^{5+}O_4(H_2O)_4(PO_4O)_4$, a new species, its crystal structure and relation to vauxite and montgomeryite. Am. Mineral. **61** (1976) 5–11.

Moore, P. B., Irving, A. J., Kampf, A. R.: Foggite, goedkenite and samuelsonite: three new species from the palermo No. 1 pegmatite, North Groton, New Hampshire. Am. Mineral. **60** (1975) 957–964.

Otto, H. H.: Die Kristallstruktur von Fleischerit, $Pb_3Ge[(OH)_6 \vert (SO_4)_2] \cdot 3H_2O$, sowie kristallchemische Untersuchungen an isotypen Verbindungen. Neues Jahrb. Mineral Abhandl. **123** (1975) 160–190.

Pauling, L.: The principles determining the structure of complex ionic crystals. Jour. Am. Chem. Soc. **51** (1929) 1010–1026.

Pauling, L.: *The Nature of the Chemical Bond*. 3rd. Ed. Cornell University Press, Ithaca, New York (1960).

Pertlik, F.: Der Strukturtyp von Emmonsit, $\{Fe_2[TeO_3]_3 \cdot H_2O\} \cdot xH_2O$ $(x = 0-1)$. Tschermaks Mineral. Petrogr. Mitt. **18** (1972) 157–168.

Ripmeester, J. A., Ratcliffe, C. I., Dutrizac, J. E., Jambor, J. L.: Hydronium ion in the alunite-jarosite group. Can Mineral. **24** (1986) 435–447.

Scordari, F.: The crystal structure of hohmannite, $Fe_2(H_2O)_4[(SO_4)_2O] \cdot 4H_2O$ and its relationship to amarantite, $Fe_2(H_2O)_4[(SO_4)_2O] \cdot 3H_2O$. Mineral. Mag. **42** (1978) 144–146.

Scordari, F.: Sideronatrite: a mineral with a $\{Fe_2(SO_4)_4(OH)_2\}$ guildite type chain. Tschermaks Mineral. Petrogr. Mitt. **28** (1981 a) 315–319.

Scordari, F.: Fibroferrite: a mineral with a $\{Fe(OH)(H_2O)_2SO_4\}$ spiral chain and its relationship to $Fe(OH)SO_4$, butlerite and parabutlerite. Tschermaks Mineral. Petrogr. Mitt. **28** (1981 b) 17–29.

Shannon, R. D.: Revised effective ionic radii and systematic studies of interatomic distances in halides and oxides. Acta Crystallogr. **A32** (1976) 751–767.

Stephan, G. W., MacGillavry, C. H.: The crystal structure of nesquehonite, $MgCO_2 \cdot 3H_2O$. Acta Crystallogr. **B28** (1972) 1031–1033.

Süsse, P.: The crystal structure of amarantite, $Fe_2(SO_4)_2O \cdot 7H_2O$. Z. Kristallogr. **127** (1968) 261–275.

Sutor, D. J.: The crystal and molecular structure of newberyite, $MgHPO_4 \cdot 3H_2O$. Acta Crystallogr. **23** (1967) 418–422.

Wan, C., Ghose, S., Rossman, G. R.: Guildite, a layer structure with a ferric hydroxy-sulphate chain and its optical absorption spectra. Am. Mineral. **63** (1978) 478–483.

Wells, A. F.: *Structural Inorganic Chemistry*. 5th. Ed. Oxford University Press, Oxford (1985).

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Redetermination of the crystal structure of diammine silver(I)-sulfate, $[Ag(NH_3)_2]_2SO_4$

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Linear chain structure / Diammine silver(I)-sulfate / Hydrogen bonds / Bent diammine silver(I)-cations

Abstract. The crystal structure of diammine silver(I)-sulfate, $[Ag(NH_3)_2]_2SO_4$, has been redetermined from X-ray single crystal data: space group $P\bar{4}2_1c$, $a = 8.442(2)$ Å, $c = 6.399(3)$ Å, $Z = 2$, $R/R_w = 0.016/0.017$ for 708 structure factors with $I > 3\sigma(I)$ and 38 variables. The structure consists of metal-over-metal stacks of diammine silver(I)-cations with $d(Ag-Ag) = 3.200$ Å that are held together by hydrogen bonds. The diammine silver(I)-cations are significantly bent with an N–Ag–N angle of 174.3° due to additional oxygen coordination of Ag(I).

Introduction

The crystal structure of diammine silver(I)-sulfate was first determined by Corey and Wyckoff (1934) on the basis of rotation and Laue photographs. The precision was rather low compared to that of present standards and led to a doubtful short Ag–N distance as already mentioned by Maurer and Weiss (1977).

Our interest in this compound was initiated by previous studies on di- and triammine nitrates of monovalent copper and silver with the composition $[M(NH_3)_2]NO_3$ and $[M(NH_3)_3]NO_3$ (Zachwieja and Jacobs, 1989). The crystal structures of these compounds contain linear chains of linear $[M(NH_3)_2]^+$ and trigonal planar $[M(NH_3)_3]^+$ cations analogous to those