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The role of H_2O in controlling bond topology: I. The $^{[6]}Mg(SO_4)(H_2O)_n$ ($n = 0–6$) structures

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In memoriam Professor Friedrich Liebau

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Abstract. Here, we examine the role of (H_2O) in controlling polymerization of structural units in simple hydrated oxysalt compounds of the form $Mg(SO_4)(H_2O)_n$. As the number of (H_2O) groups in the structure increases, the number of $M–M$ ($M = Mg$) linkages decreases in a 1 : 1 ratio with the (increasing) number of (H_2O) groups until no $M–M$ linkages are left, and then the number of $M–T$ ($T = S$) linkages decreases with the (increasing) number of (H_2O) groups until no $M–T$ linkages are left (at $n = 6$). The change in bond topology is monotonic as a function of (H_2O) content except for $n = 5$ where, instead of replacing an $M–T$ linkage, the fifth (H_2O) group is held in the structure by hydrogen bonds only. The valence-sum rule of bond-valence theory constrains the anion-coordination numbers to [2], [3] and [4] in these structures. The handshaking lemma of graph theory allows us to derive an equation relating the coordination numbers of the cations ($Mg = [6]$, $S^{6+} = [4]$, $H = [2]$) to the coordination numbers of the anions. There are four integer solutions to this equation, and the $Mg(SO_4)(H_2O)_n$ structures correspond to two of these solutions. Structures are known for $n = 0–2.5$, 4–7, 11; considering the variations in connectivity and coordination number as a function of n, a possible structural arrangement is proposed for $Mg(SO_4)(H_2O)_3$.

Introduction

Matchatski (1928) proposed to classify the silicate minerals according to the *dimensional polymerization* of their constituent silicate groups. Bragg (1930) extended this idea and described the classification that we use today: neso (ortho-), soro- (pyro-), cyclo- (ring-), ino- (chain-), phyllo- (sheet-) and tecto- (framework) silicates, and Zoltai (1960) proposed incorporating other tetrahedral oxyanions, *e.g.*, $(BeO_4)^{6-}$, $(BO_4)^{5-}$ into this classification. Liebau (1980) introduced several other classification criteria based on the topological character of the (alumino)silicate linkages, and comprehensively applied it to all silicate minerals known at that time (Liebau, 1985). In his classic work, Bowen (1928) proposed that silicate minerals in a basaltic magma crystallize in the sequence olivine → pyroxene → amphibole → mica → feldspar → quartz, a sequence that has subsequently become known as *Bowen's reaction series*. The parallels between this series and the Matchatski–Bragg–Liebau classification (*i.e.*, the bond topology of the minerals) is obvious. With progressive crystallization, we see a gradual condensation of the aluminosilicate tetrahedra, indicating that bond topology is intimately related to the crystallization of silicate minerals in basaltic magmas. For minerals in which the principal oxyanion does not commonly polymerize (*e.g.*, phosphates, sulphates), classification based on dimensional polymerization of the principal oxyanion does not work. Moore (1973) proposed classifying phosphate minerals according to the polymerization of their constituent divalent-metal octahedra, and also showed a relation between paragenesis and structural arrangement in pegmatite phosphate minerals.

This correlation between dimensional polymerization and paragenesis emphasizes the fundamental nature of dimensional polymerization and its basis as a natural way to organize crystal structures. However, the problem of non-polymerization of many geologically important oxyanions (*e.g.*, $(PO_4)^{3-}$, $(SO_4)^{2-}$) seemed a major obstacle. This problem was overcome by the idea of *binary representation* (Hawthorne, 1985a), whereby a crystal structure is divided into two components: the *structural unit* is the strongly bonded part of the structure and the *interstitial complex* is an assemblage of (usually monovalent and divalent) cations, anions and neutral species that weakly bind the structural units into a continuous crystal structure. These two structural elements are defined by bond valences (Brown, 2002) rather than by chemical groups, bonds stronger than 0.30 *v.u.* (valence units) generally belonging to the structural unit, and bonds weaker than 0.30 *v.u.* emanating from the constituents of the interstitial complex. Thus we can apply this idea to all minerals, irrespective of their chemical characteristics.

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The structural hierarchy hypothesis

Hawthorne (1983) introduced the *Structure Hierarchy Hypothesis*: *crystal structures may be hierarchically ordered according to the polymerization of the coordination polyhedra of higher bond-valences.* This hypothesis combines the Machatski–Bragg–Liebau approach, based on the dimensional polymerization of the oxyanion of interest, with the approach of Belov (1961) that describes mixed-polyhedron structures. This hypothesis can be rationalized *via* bond-valence theory in the following manner (Hawthorne, 1983). In a structure, the bond-valence requirements of the cations are satisfied by the formation of coordination polyhedra of anions around them. Thus we can think of the structure as an array of complex oxyanions that polymerize in order to satisfy their (simple) anion bond-valence requirements according to the valence-sum rule. Let the bond valences in an array of coordination polyhedra be $s_0^i = 1, n$) where $s_0^i > s_0^{i+1}$. The valence-sum rule indicates that polymerization can occur when $s_0^1 + s_0^i < |V_{\mathrm{anion}}|$ and the valence-sum rule is most easily satisfied when $s_0^1 + s_0^i = |V_{\mathrm{anion}}|$, where V is the formal valence of the simple anion. These relations suggest that the most important polymerizations involve those coordination polyhedra of higher bond-valence, subject to the constraint $s_0^1 + s_0^i < |V_{\mathrm{anion}}|$, as these linkages most easily satisfy the valence-sum rule. As outlined by Burdett *et al.* (1984), the topology of a bond network is a major feature controlling the energy of the structure. The polymerization of the principal coordination polyhedra is just another way of expressing the topology of the bond network, and at the intuitive level, we can recognize an energetic basis for the hierarchical organization of structures according to the details of the polymerization of their principal coordination polyhedra.

What affects dimensional polymerization?

The dimensional polymerization of a structural unit is intimately affected by its bonding interactions with the interstitial complex. Polymerization of the structural unit in a specific direction is terminated by the incidence of only one strong bond at the peripheral anion; all other bonds to that anion are weak. These weak bonds involve either ions of the interstitial complex or ions (usually H) from adjacent structural units. Thus dimensional polymerization may be limited by (1) the incidence of several weak bonds at peripheral anions of the structural unit, or (2) the occurrence of $(OH)^-$ or $(H_2O)^0$ as peripheral anions of the structural unit (Hawthorne, 1985a, 1986, 1990, 1992, 1994, 1997).

The *Principle of Correspondence of Lewis acidity-basicity* (Hawthorne and Schindler, 2008) states that *stable structures will form when the Lewis-acid strength of the interstitial complex closely matches the Lewis-base strength of the structural unit.* This is essentially the mean-field equivalent of the valence-matching principle (Brown, 2002), and allows quantitative assessment of this interaction. Schindler and Hawthorne (2001a, b, 2004, 2008) and Schindler *et al.* (2000, 2006) have used this principle to make quantitative predictions about the possible chemical compositions and crystal-chemical features of interstitial complexes in borate, vanadate, sulfate and uranyl-oxysalt minerals, and Schindler *et al.* (2004a, b) have extended these ideas to look at surface interactions between oxysalt minerals and aqueous solutions.

This work has focused primarily on examining the relations between the chemical compositions of the structural unit and the interstitial complex. There has been broad recognition of the relation between the degree of dimensional polymerization and the amount of $(OH)^-$ and $(H_2O)^0$ in the solid system (*e.g.*, Krivovichev, 2008) and the analogous effect has been recognized in inorganic chemistry (*e.g.*, Tulsky and Long, 2001) involving a much wider array of ligands. However, there has been little work done on the relation between the details of the bond topology of the structural unit and the amount of H in hydroxy-hydrate systems. A much better understanding of this issue is desirable, particularly for minerals as H plays a major role in controlling the diversity and distribution of mineral species within the Earth. Here, we will begin work on this issue by focusing on a system that, from a mineralogical perspective, is chemically relatively simple and yet shows a wide variation in H content and dimensional polymerization: $MgSO_4(H_2O)_n$.

The bond-valence structure of H_2O

Hawthorne (1992) considered this general issue in some detail, and Schindler and Hawthorne (2004) considered all possible arrangements involving (H_2O) as a constituent of the structural unit and the interstitial complex. In particular, he noted the importance of both (OH) and (H_2O) in affecting the mode of polymerization of the strongly bonded constituents of a structure (the structural unit) through their polar character. The bond-valence structure of the (H_2O) group is shown in Fig. 1 for the situation where (H_2O) is bonded to a single cation. The primary O atom of the (H_2O) group forms strong bonds (>0.50 *v.u.*, commonly 0.80 *v.u.*) with its associated H atoms, and is known as the *donor* anion. The valence-sum rule (Brown, 2002) requires that the sum of the bond valences incident

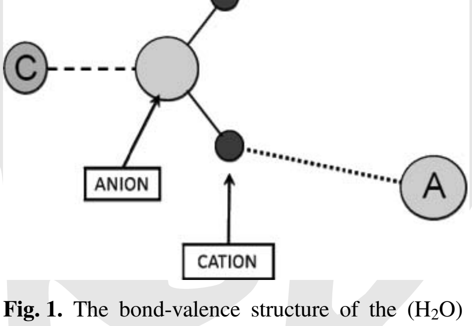

Fig. 1. The bond-valence structure of the (H_2O) group bonded to a cation C, showing how the (H_2O) group acts as an anion on the O side and a cation on the H side. Hydrogen atoms are black circles, the O of the (H_2O) group is a large grey circle, the acceptor anions are large grey circles labelled A, and the cation is a grey circle labelled C.

at H is 1 *v.u.*, and hence H must form weak bonds (<0.50 *v.u.*, commonly ~0.20 *v.u.*) with other anion(s) known as *acceptor* anions. Inspection of Fig. 1 shows that the (H_2O) group acts as an anion on the side of the O atom and as a cation on the side of the H atoms. On the anion side of the (H_2O) group, the incident bond-valence is often relatively strong, ~0.40 *v.u.*, whereas on the cation side, the exident bond-valence is weaker, ~0.20 *v.u.*. On the anion side of the (H_2O) group, the incident bond(s) commonly constitute part of the structural unit, whereas on the cation side of these groups, the exident bonds do not form part of the structural unit. Hence these exident bonds prevent continued polymerization of polyhedra of the structural unit in at least one direction.

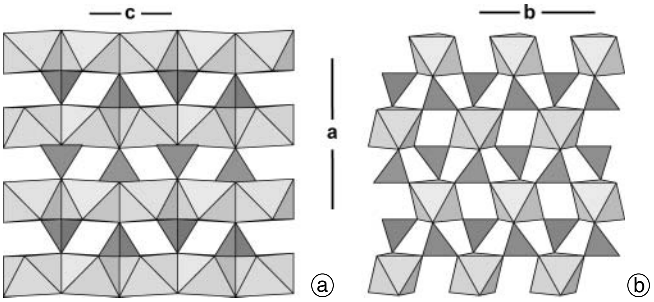

Fig. 2. The crystal structure of $Mg(SO_4)$ projected onto (**a**) (010), and (**b**) (001); tetrahedra are dark grey, octahedra are pale grey.

The $^{[6]}\mathrm{Mg(SO_4)(H_2O)}_n$ ($n = 0{-}11$) structures

This group of structures is ideal to examine the effects of (H_2O) on bond topology because (1) the ratio of the constituent polyhedra is 1 : 1, thereby simplifying discussions of connectivity, (2) the high Lewis basicity of the $(SO_4)^{2-}$ oxyanion prevents polymerization of this group (at least in the presence of H), simplifying the bond topologies to be considered, and (3) structures are known for nine values of n, allowing detailed examination of the change in bond topology as a function of *n*. The structures (mainly minerals) are listed in Table 1. Details of the octahedron-tetrahedron linkages are shown in Figs. 2–8 and bond valences are given in Tables 2–9. The (H_2O) groups are labelled O(a)W where a is the anion number used in the original publication; hydrogen atoms are labelled H(ab) where a indicates the donor anion, O(a)W, and b (= 1, 2) denotes the two H atoms bonded to O(a)W; note that only H(a1) is used where H(a1) and H(a2) are symmetrically equivalent (as in kieserite).

$n = 0$: $^{[6]}\mathrm{Mg(SO_4)}$

In the structure of α-$Mg(SO_4)$ (Fig. 2), chains of edge-sharing octahedra of the form $[M^{2+}\Phi_4]$ (Φ = unspecified anion = [O, (H_2O)] in the $^{[6]}\mathrm{Mg(SO_4)(H_2O)}_n$ structures) extend along **c** (Fig. 2a) and link to the (SO_4) tetrahedra in two different ways. Half the tetrahedra link to two adjacent vertices of the same chain, resulting in a staggered arrangement above and below the chain and forming an $[M^{2+}\Phi_2(SO_4)]$ unit that is a common arrangement in the structures of many minerals. These $[M^{2+}\Phi_2(SO_4)]$ units cross-link by sharing tetrahedron vertices with the anions of the $[M^{2+}\Phi_4]$ chain that are shared between two octahedra. The resulting arrangement (Fig. 2b) is a centered hexagonal net of chains of octahedra (viewed end-on) that are cross-linked along **a** and **c** by (SO_4) tetrahedra, and have anion-coordination numbers of [2] and [3] only (Table 2).

Table 1. Minerals and synthetic compounds of the form $Mg(SO_4)(H_2O)_n$.

n	Name	References
0	Synthetic	Weil (2007)
1	Kieserite	Hawthorne *et al.* (1987)
2	Sanderite	Ma *et al.* (2009a)
2.5	Synthetic	Ma *et al.* (2009b)
4	Starkeyite	Baur (1964)
4	Cranswickite	Peterson (2011)
5	Pentahydrite	Baur and Rolin (1972)
6	Hexahydrite	Zalkin *et al.* (1964)
7	Epsomite	Ferraris and Jones (1973)
11	Meridianiite	Peterson *et al.* (2007)

$n = 1$: $^{[6]}\mathrm{Mg(SO_4)(H_2O)}$

In the structure of kieserite (Fig. 3), each octahedron shares two *trans* vertices with adjacent octahedra to form a chain of corner-sharing octahedra of the form $[M^{2+}\Phi_5]$. These chains extend along **c** (Fig. 3a) and link to the (SO_4) tetrahedra in two different ways. Tetrahedra link to two adjacent vertices of this chain, resulting in a staggered arrangement on either side of the chain (Fig. 3a) and forming a unit of the form $[M^{2+}(SO_4)\,\Phi]$ that is a common arrangement in the structures of many minerals (*e.g.*, Moore, 1970, 1975; Hawthorne, 1985a, 1990; Burns and Hawthorne, 1995). These $[M^{2+}(SO_4)\,\Phi]$ chains cross-link by sharing tetrahedron vertices with octahedron vertices of adjacent $[M^{2+}(SO_4)\,\Phi]$ chains. The resulting arrangement (Fig. 3b) is a centered lattice of chains of octahedra (viewed end-on) that are cross-linked along **a** and **b** by (SO_4) tetrahedra.

The (H_2O) group (Fig. 3a, Table 3) bridges the $[M^{2+}\Phi_5]$ chain) and forms hydrogen bonds with the neighboring O(2) anions. Not considering the hydrogen bonds, the O(1) and O(2) anions are [2]-coordinated and have formal incident bond-valence sums of $1.50 + 0.33 = 1.83$ *v.u.*. Inspection of Table 3 shows that the structure accommodates this deficiency by shortening the bonds to O(1) in accord with the valence-sum rule (Brown, 2002). The other cation-anion bonds correspondingly lengthen, and the hydrogen atoms of the (H_2O) group hydrogen-bond to O(2) to accommodate the

Table 2. Bond-valence (*v.u.*) table for $Mg(SO_4)$.

	Mg	S	Σ
O(1)	$0.431^{\times 2}\downarrow$	$1.589^{\times 2}\downarrow$	2.020
O(2)	$0.330^{\times 2}\downarrow\rightarrow$	1.423	2.083
O(3)	$0.238^{\times 2}\downarrow\rightarrow$	1.481	1.957
$\sum$	1.998	6.082	

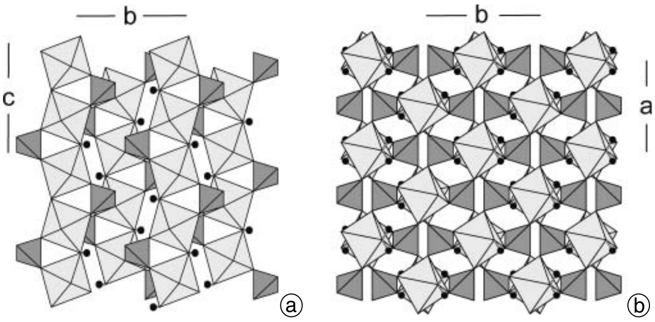

Fig. 3. The crystal structure of kieserite projected onto (**a**) (100), and (**b**) (001); legend as in Fig. 2, plus H atoms are shown as small black circles, and O(donor)-H bonds are shown as double lines.

Table 3. Bond-valence (*v.u.*) for kieserite.

	Mg	S	H(31)	Σ
O(1)	$0.42^{\times 2}\downarrow$	$1.53^{\times 2}\downarrow$		1.95
O(2)	$0.39^{\times 2}$	$1.48^{\times 2}\downarrow$	0.27	2.14
O(3)W	$0.27^{\times 2}\downarrow\rightarrow$		$0.73^{\times 2}\rightarrow$	2.00
$\sum$	2.16	6.02	1.00	

initial deficiency and the additional deficiency caused by lengthening of the Mg−O(2) and S−O(2) bonds.

$n = 2$: $^{[6]}Mg(SO_4)(H_2O)_2$

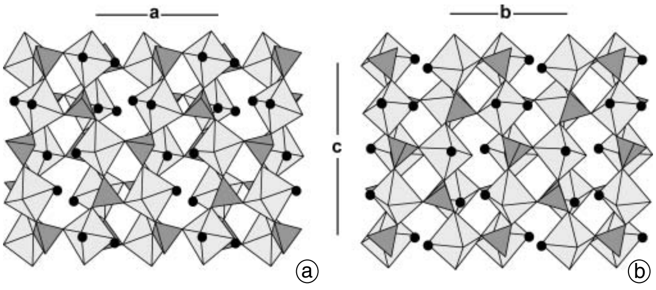

Fig. 4. The crystal structure of synthetic sanderite projected onto (**a**) (010), and (**b**) (100); legend as in Fig. 2, plus (H_2O) groups are shown as intermediate-sized black circles.

In the structure of synthetic sanderite (Fig. 4), the octahedra do not share edges or corners with each other. Each tetrahedron links to four octahedra, and each octahedron links to four tetrahedra. The two (H_2O) groups occupy two of the six vertices of the octahedron and are in a *cis* arrangement (Fig. 4). Hydrogen bonds were assigned here by identifying the possible O(donor)-O(acceptor) distances, and the resulting bond-valences are given in Table 4. The structure of sanderite bears a surprising similarity to that of starkeyite. In starkeyite (Fig. 6a), the structural unit consists of an $[Mg_2\varphi_6(SO_4)_2]$ cluster that occurs at the lattice points of a centered plane orthorhombic net. Careful inspection of the structure of sanderite (Fig. 4) shows that this structure also consists of an $[Mg_2\varphi_6(SO_4)_2]$ cluster that is centered at the lattice points of a centered plane orthorhombic net (Fig. 4a, b), but the clusters are joined by sharing octahedron-tetrahedron vertices in sanderite whereas they are not joined in starkeyite but are interrupted by (H_2O) groups (Fig. 6a).

$n = 2.5$: $^{[6]}Mg(SO_4)(H_2O)_{2.5}$

In the structure of synthetic $Mg(SO_4)(H_2O)_{2.5}$ (Fig. 5), the amount of (H_2O), 2.5 p.f.u. (per formula unit), forces there to be two distinct Mg sites, one of which is coordinated by two (H_2O) groups and one of which is coordi-

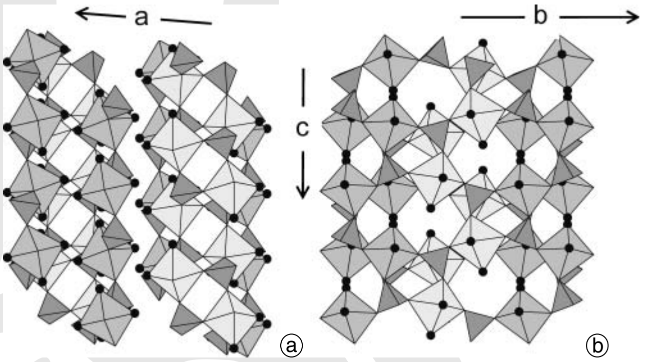

Fig. 5. The crystal structure of synthetic $Mg(SO_4)(H_2O)_{2.5}$ projected onto (**a**) (010), and (**b**) (100); legend as in Fig. 2, plus (H_2O) groups are shown as intermediate-sized black circles.

Table 4. Bond-valence (*v.u.*) table for sanderite.

	Mg(1)	Mg(2)	S(1)	S(2)	$\sum$	H(11)	H(12)	H(21)	H(22)	H(31)	H(32)	H(41)	H(42)	$\sum$
O(1)	0.370		1.503		1.873	0.10								1.97
O(2)		0.358	1.407		1.765						0.20			1.97
O(3)		0.359	1.415		1.774			0.20						1.97
O(4)	0.320		1.503		1.823							0.20		2.02
O(5)	0.353			1.363	1.716		0.20							1.92
O(6)		0.360		1.543	1.903								0.10	2.00
O(7)	0.388			1.557	1.945				0.10					2.05
O(8)		0.366		1.508	1.874					0.10				1.97
O(1)W	0.319				0.319	0.90	0.80							2.02
O(2)W	0.331				0.331			0.80	0.90					2.03
O(3)W		0.329			0.329					0.90	0.80			2.03
O(4)W		0.324			0.324							0.80	0.90	2.02
$\sum$	2.081	2.096	5.828	5.971		1	1	1	1	1	1	1	1	

Table 5. Bond-valence (*v.u.*) table for $Mg(SO_4)(H_2O)_{2.5}$.

	Mg(1)	Mg(2)	S(1)	S(2)	$\sum$	H(11)	H(12)	H(21)	H(22)	H(31)	H(32)	H(41)	H(42)	H(41)′	H(42)′	$\sum$
O(1)	0.381		1.637		2.018			0.05								2.07
O(2)	0.366		1.516		1.882				0.20							2.08
O(3)			1.503		1.503							0.20	0.20			1.90
O(4)		0.369	1.530		1.899		0.15									2.05
O(5)	0.371			1.407	1.778					0.25						2.04
O(6)		0.346		1.534	1.907	0.15										2.06
O(7)		0.356		1.561	1.917									0.15		2.07
O(8)		0.350		1.599	1.949										0.10	2.05
O(1)W	0.334				0.334	0.85	0.85									2.04
O(2)W	0.334				0.334			0.95	0.80							2.08
O(3)W	0.353				0.353					0.75	0.800.20					2.10
O(4)W		0.317			0.317							0.80	0.80			1.92
O(4)W′		0.336			0.336									0.85	0.90	2.09
$\sum$	2.139	2.074	6.186	6.101		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	

nated by three (H_2O) groups (coloured pale grey and very pale grey, respectively, in Fig. 5). Thus the octahedra also have the complementary number of linkages to (SO_4) tetrahedra. A prominent motif in this structure is the $[Mg_2\varphi_6(SO_4)_2]$ cluster (easily visible in Fig. 5b at the lower left) that also occurs in sanderite and starkeyite. These clusters link by sharing $M-T$ corners to form thick slabs (Fig. 5a) that are held together by hydrogen bonds that were assigned by inspection of potential O(donor)-O(acceptor) distances (Table 5).

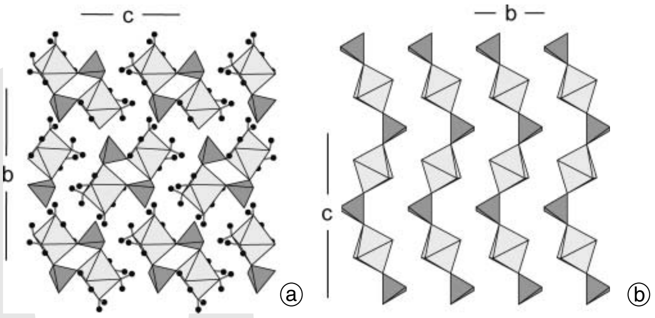

Fig. 6. The crystal structure of (**a**) starkeyite projected onto (100), and (**b**) cranswickite projected onto (100); legend as in Fig. 2.

$n = 4$: $^{[6]}Mg(SO_4)(H_2O)_4$

There are two distinct structures of stoichiometry $Mg(SO_4)(H_2O)_4$, starkeyite and cranswickite (Table 1, Fig. 6). In starkeyite, two octahedra and two tetrahedra share *cis* corners to form a cluster of composition $[M^{2+}{}_2\Phi_8(SO_4)_2]$. These clusters occur at the vertices of an orthorhombic net, and adjacent clusters are rotated ~90° relative to each other (Fig. 6a); this pattern of clusters also occurs with the $[M(TO_4)_2\,\Phi_4]$ cluster ($T = S^{6+}$, P) in bloedite and related minerals (Hawthorne, 1985b). The clusters are linked by hydrogen bonds, the topology of which is shown in Table 6. In cranswickite, octahedra and tetrahedra link via *trans* vertices of the octahedra to form $[M^{2+}{}_2\Phi_8(SO_4)_2]$ chains (Fig. 6b) that extend along the **c**-axis and are cross-linked by hydrogen bonds. As with sanderite, hydrogen bonds for cranswickite are assigned via the possible O(donor)-O(acceptor) distances and the resulting bond-valences are given in Table 7.

$n = 5$: $^{[6]}Mg(SO_4)(H_2O)_5$

The structure of pentahydrite (Fig. 7) consists of chains of alternating octahedra and tetrahedra parallel to [110]. As in cranswickite, octahedra and tetrahedra link via *trans* vertices of the octahedra to form a $[M^{2+}{}_2\Phi_8(SO_4)_2]$ chain. These chains are cross-linked directly by hydrogen bonds from the meridional (H_2O) groups of the octahedron, and

Table 6. Bond-valence (*v.u.*) for starkeyite.

	Mg	S	H(51)	H(52)	H(61)	H(62)	H(71)	H(72)	H(81)	H(82)	$\sum$
O(1)	0.35	1.48						0.17			2.00
O(2)	0.35	1.52				0.13					2.00
O(3)		1.48	0.19	0.19						0.14	2.00
O(4)		1.53			0.21		0.21		0.15		2.10
O(5)W	0.38		0.81	0.81							2.00
O(6)W	0.34				0.79	0.87					2.00
O(7)W	0.38						0.79	0.83			2.00
O(8)W	0.36								0.85	0.86	2.07
$\sum$	2.16	6.01	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	

Table 7. Bond-valence (*v.u.*) table for cranswickite.

	Mg	S	H(31)	H(32)	H(41)	H(42)	$\sum$
O(1)		$1.318^{\times 2}\downarrow$	0.20		0.20	0.20	1.918
O(2)	$0.393^{\times 2}\downarrow$	$1.456^{\times 2}\downarrow$		0.20			2.050
O(3)W	$0.330^{\times 2}\downarrow$		0.80	0.80			1.930
O(4)W	$0.332^{\times 2}\downarrow$				0.80	0.80	1.932
$\sum$	2.112	5.548	1	1	1	1	

Table 8. Bond-valence (*v.u.*) for pentahydrite.

	Mg(1)	Mg(2)	S	H(51)	H(51)	H(61)	H(62)	H(71)	H(72)	H(81)	H(82)	H(91)	H(92)	$\sum$
O(1)	$0.34^{\times 2}\downarrow$		1.48									0.18		2.00
O(2)		$0.33^{\times 2}\downarrow$	1.49			0.09							0.09	2.00
O(3)			1.54					0.18		0.20				1.92
O(4)			1.27	0.32					0.20		0.20			1.99
O(5)W	$0.37^{\times 2}\downarrow$			0.68	0.95									2.00
O(6)W	$0.38^{\times 2}\downarrow$					0.91	0.71							2.00
O(7)W		$0.38^{\times 2}\downarrow$						0.82	0.80					2.00
O(8)W		$0.39^{\times 2}\downarrow$								0.80	0.80			1.99
O(9)W					0.05		0.29					0.82	0.91	2.07
$\sum$	2.18	2.20	5.78	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	

Table 9. Bond-valence (*v.u.*) for hexahydrite.

	Mg(1)	Mg(2)	S	H(51)	H(51)	H(61)	H(62)	H(71)	H(72)	H(81)	H(82)	H(91)	H(92)	H(101)	H(102)	$\sum$
O(1)			1.49	0.16						0.23				0.16		2.04
O(2)			1.54								0.17	0.29				2.00
O(3)			1.47		0.17	0.17			0.17							1.98
O(4)			1.50				0.17	0.17							0.17	2.01
O(5)W	$0.39^{\times 2}\downarrow$			0.84	0.83											2.06
O(6)W	$0.38^{\times 2}\downarrow$					0.83	0.83									2.04
O(7)W	$0.37^{\times 2}\downarrow$							0.83	0.83							2.03
O(8)W		$0.35^{\times 2}\downarrow$								0.77	0.83		0.07			2.03
O(9)W		$0.39^{\times 2}\downarrow$										0.71	0.93			2.01
O(10)W		$0.38^{\times 2}\downarrow$												0.84	0.83	
$\sum$	2.28	2.24	6.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	

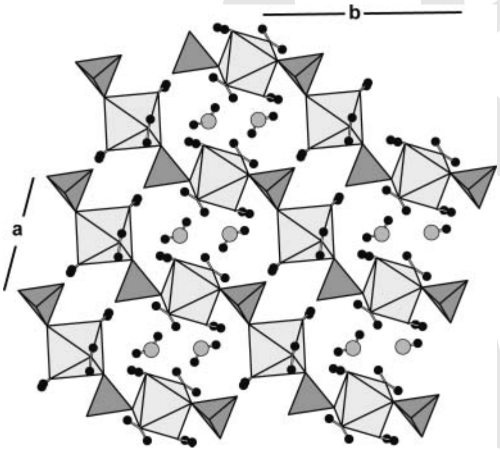

Fig. 7. The crystal structure of pentahydrite projected onto (001); legend as in Fig. 2.

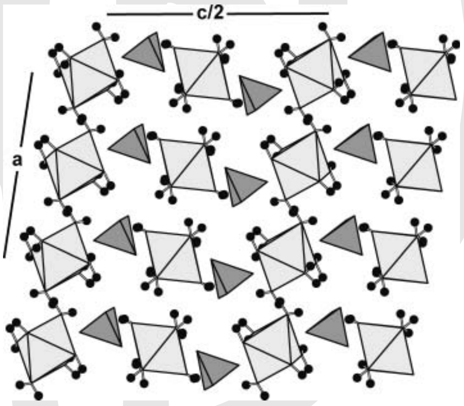

Fig. 8. The crystal structure of hexahydrite projected onto (100); legend as in Fig. 2.

through hydrogen bonds involving (H_2O) groups not bonded to Mg (Table 8).

$n = 6–11$: $^{[6]}Mg(SO_4)(H_2O)_{6–11}$

In the structure of hexahydrite ($n = 6$), $Mg(SO_4)(H_2O)_6$ (Fig. 8), all octahedron vertices are (H_2O) groups and both octahedra and tetrahedra are isolated, linked only by hydrogen bonds (Table 9). In epsomite ($n = 7$) and meridianiite ($n = 11$), both octahedra and tetrahedra are also isolated and linked by hydrogen bonds only, but with additional (H_2O) groups not directly bonded to Mg.

Discussion

Figures 2 to 8 show what we expect: the connectivity of the structures decreases with increasing content of (H_2O) groups. We may put this on a more quantitative basis by showing the numbers of the various structural linkages as a function of (H_2O) content (Fig. 9). The structure of $Mg(SO_4)$ has two linkages between octahedrally coordinated cations ($M–M$) and four linkages between octahedrally and tetrahedrally coordinated cations ($M–T$) (Fig. 9a). As the number of (H_2O) groups in the structure increases, first the number of $M–M$ linkages decreases in a 1 : 1 ratio with the (increasing) number of (H_2O) groups until no $M–M$ linkages are left, and then the number of $M–T$ linkages decreases with the (increasing) number of (H_2O) groups until no $M–T$ linkages are left (at $n = 6$) (Fig. 9a). In this series of structures, (H_2O) is either bonded to octahedrally coordinated Mg or it is held in the structure solely by hydrogen bonds, and the number of bonded and 'free' (H_2O) groups (Fig. 9b) accords with the variation in $M–M$ and $M–T$ linkages.

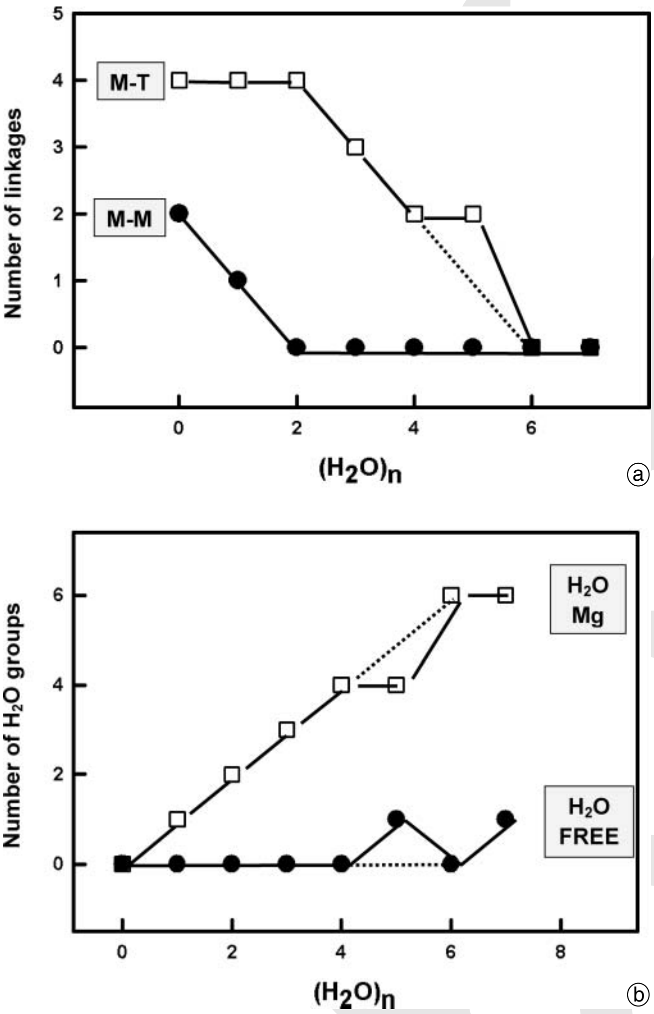

Fig. 9. Linkage variation as a function of H_2O content in $Mg(SO_4)(H_2O)_n$ structures; (**a**) variation in the number of $M–M$ (octahedron–octahedron) and $M–T$ (octahedron–tetrahedron) linkages as a function of (H_2O) content; (**b**) variation in the number of (H_2O) groups linked to Mg and the number of (H_2O) groups not linked to Mg as a function of (H_2O) content.

In general, the change in bond topology is monotonic as a function of (H_2O) content. The exception is for $n = 5$ where, instead of replacing an $M–T$ linkage, the fifth (H_2O) group is held in the structure by hydrogen bonds only; it is not linked to Mg as expected from the systematic behaviour of the previous ($n < 5$) compositions. The reason for this behaviour is unclear. Ma *et al.* (2009a) noted that all octahedrally coordinated Mg atoms in these structures link to an even number of (H_2O) groups, an observation which is in accord with the unusual behaviour of pentahydrite. However, this observation was subsequently vitiated by the structure of synthetic $Mg(SO_4)(H_2O)_{2.5}$ (Ma *et al.*, 2009b) in which one of the two crystallographically distinct Mg atoms links to three (H_2O) groups (Fig. 5a).

Variation in anion-coordination number as a function of (H_2O) content

We wish a more quantitative understanding of how this connectivity varies as a function of (H_2O) content. In order to approach this problem, we need a quantitative representation of the connectivity of a structure. Graph theory (*e.g.*, Wilson, 1979) provides us with such a representation.

A graph is formally defined as a set of points called *vertices* and a set of pairs of vertices called edges (Fig. 10). We may label the vertices and we may colour the vertices to produce a labelled polychromatic graph. We may order the vertices that define each edge, and thus a direction is associated with each edge, and we may associate a weight with each edge. The result is a weighted polychromatic digraph. We may associate atoms with the vertices of the graph, and we may associate chemical bonds with the edges of the graph, where the bonds are considered to be directed from a cation to an anion (here,

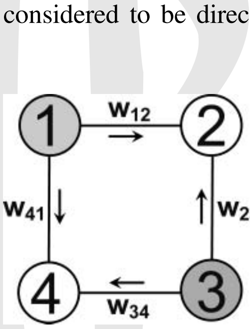

Fig. 10. A labelled weighted chromatic digraph: a set of coloured vertices (circles) numbered 1 to 4, and a set of pairs of vertices (lines) called edges (where the ordering denotes a direction) which are associated with a set of weights, w_{ij}.

we use the words ‘cation’ and ‘anion’ to denote atoms of low and high electronegativity, respectively; they carry no indication of ionic bonding). The *degree* of a vertex of the graph is the number of edges incident and exident at that vertex; the *indegree* of a vertex is the number of edges incident at that vertex, and the *outdegree* of a vertex is the number of edges exident at that vertex. The handshaking lemma (Wilson, 1979) for a digraph requires that the sum of the in-degrees of all vertices is equal to the sum of the out-degrees of all vertices. This theorem is quite obvious when one realizes that every (directed) edge is exident from one vertex and incident at another vertex.

Consider the general formula $M_p(XO_4)_q(H_2O)_n$ where M is a [6]-coordinated cation, X is a [4]-coordinated cation, and H is [2]-coordinated (*i.e.*, there are no bifurcated or trifurcated hydrogen bonds). The number of bonds exident from the cations is $6 \cdot p + 4 \cdot q + 2 \cdot 2n = 4n + 6p + 4q$ and there are $n + 4q$ anions in $M_p(XO_4)_q(H_2O)_n$. The Lewis acidities of the constituent cations are 1.50, 0.33 and 0.20 *v.u.* for S^{6+}, Mg and H, respectively. The valence-sum rule constrains the anion coordination numbers to [2], [3] and [4]. Let there be a, b and c anions of coordination numbers [2], [3] and [4], respectively. The number of bonds incident at the anions is thus $a \cdot 2 + b \cdot 3 + c \cdot 4 = 2a + 3b + (n + 4q - a - b) \cdot 4 = 4(n + 4q) - (2a + b)$. The handshaking lemma requires that the number of bonds exident from the cations is equal to the number of bonds incident at the anions. Hence $4n + 6p + 4q = 4(n + 4q) - (2a + b)$, which reduces to the following:

$$2a + b = 6(2q - p)\,. \tag{1}$$

What is extremely interesting about this equation is that it does not contain n, the number of (H_2O) groups in the structure of $M_p(XO_4)_q(H_2O)_n$. This means that in all $M_p(XO_4)_q(H_2O)_n$ structures with anion-coordination numbers of [2], [3] and [4], the number of anions with coordination numbers [2] and [3] is independent of the number of (H_2O) groups in the structure, a very general and rather unexpected result.

We may solve Eq. (1) for specific values of p and q, as a and b must be positive integers. Here we are interested in the $Mg(SO_4)(H_2O)_n$ structures, *i.e.*, $p = q = 1$, and Eq. (1) reduces to

$$2a + b = 6\,. \tag{2}$$

Integer solutions to Eq. (2) are listed in Table 10 for $n = 1 - 6$. Not all of these solutions are available for all stoichiometries. The number of anions in the $Mg(SO_4)(H_2O)_n$ structures is $(4 + n)$, and the number of [4]-coordinated anions must be positive or zero: $4 + n - a - b \geq 0$. This number is given in Table 10 where it is immediately apparent that solutions (1) and (2) are not available for $Mg(SO_4)$. The bond-valence tables (Tables 2–9) provide us with the anion-coordination numbers of these structures (and it is the anion-coordination numbers that describe their connectivity), and these are summarized in Table 11. A notable systematic behaviour is immediately apparent. For $n = 1 - 2$, the structures are in accord with solution (3) of Eq. (2), whereas for $n > 2$ (except for those structures that do not conform to our initial constraints (n is an integer, $M = $ Mg), the structures are in accord with solution (1) of Eq. (2).

Table 10. Possible integer solutions to the equation $2a + b = 6$.

(1)	(2)	(3)	(4)
[2] · 0	[2] · 1	[2] · 2	[2] · 3
[3] · 6	[3] · 4	[3] · 2	[3] · 0
[4] · ($n - 2$)	[4] · ($n - 1$)	[4] · n	[4] · ($n + 1$)

Table 11. Anion-coordination numbers [N] in minerals and synthetic compounds of the form $Mg(SO_4)(H_2O)_n$ ($n = 1 - 6$).

n	Name	[2]	[3]	[4]	Solution
0	Synthetic	2	2	0	3
1	Kieserite	2	2	1	3
2	Sanderite	0	12	0	1
2.5	Synthetic	0	12	1	–
3	Extrapolated	0	6	1	1
4	Starkeyite	0	6	2	1
4	Cranswickite	0	6	2	1
5	Pentahydrite	0	6	3	1
6	Hexahydrite	0	6	4	1

Bond-topological effects on enthalpy of formation

Where there are systematic changes in bond topology in a series of chemically related structures, it is of interest to try and relate these changes to variations in physical properties. In particular, Burdett *et al.* (1984) has shown that the electronic energy density of states of a crystal can be related to the bond topology of the structure *via* the method of moments, and Hawthorne (1994, 1997) has discussed the crystal-chemical implications of this relation. In the $Mg(SO_4)(H_2O)_n$ structures, there is a systematic change in bond topology with increasing value of n, as described by the changes in anion coordination number (Table 11). How does this change relate to the change in enthalpy of formation? Figure 11 shows that the variation in ΔH (taken from Grevel and Kajzlan, 2011; Pillay *et al.*, 2005) as a function of n, the number of (H_2O) groups in the structure, is linear across the whole range of composition from $n = 0$ to 11. We have shown that (H_2O) groups can enter the structures of these minerals in two different ways: they may attach to the $(Mg\varphi_6)$ octahedra in the structure, depolymerizing the structural unit, or they may enter as an interstitial species, being held in the structure solely by hydrogen bonds. Figure 9 shows that where $n = 1 - 4$ and 6, the (H_2O) groups are entirely linked to $(Mg\varphi_6)$ octahedra, whereas for $n = 5$, 7 and 11, an increasing number of (H_2O) groups are interstitial species, linked in the structure only by hydrogen bonding. Despite these significant bond-topological differences in the character of (H_2O) groups within the $Mg(SO_4)(H_2O)_n$ structures, ΔH of formation is co-linear for both types of structures (Fig. 11), indicating that the heat of formation is independent of the way in which the (H_2O) groups are held in the structure, and is dependent only on the number of (H_2O) groups (*i.e.*, the chemical composition).

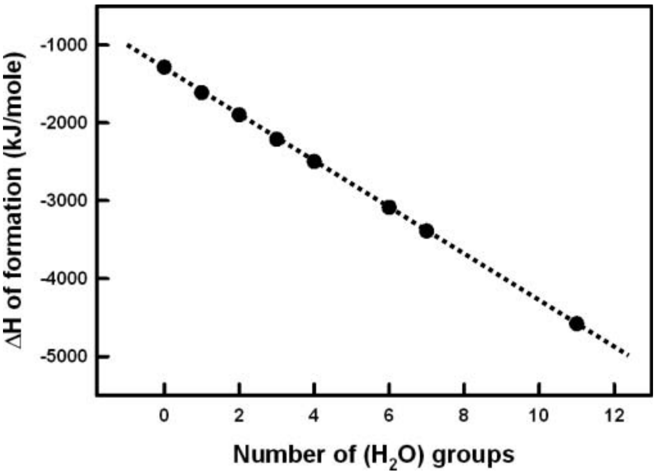

Fig. 11. Variation in enthalpy of formation as a function of the amount of H_2O present in the structure for the $MgSO_4(H_2O)n$ structures.

A possible connectivity for $Mg(SO_4)(H_2O)_3$

The systematic behaviour of these structures suggests a possible structure for the $n = 3$ compound (Table 11). The systematic changes apparent in Table 11 suggest that $Mg(SO_4)(H_2O)_{2.5}$ should have the anion coordinations corresponding to solution 1. In sanderite, there are two crystallographically distinct (SO_4) tetrahedra and each shares vertices with four octahedra. In $Mg(SO_4)(H_2O)_{2.5}$, there are two (SO_4) tetrahedra; one tetrahedra links to four octahedra and the other tetrahedra links to three octahedra. This suggests that in $Mg(SO_4)(H_2O)_3$, (SO_4) tetrahedra will link to three octahedra. The resulting connectivity and bond valences are given in Table 12. There are seven anions, three of which have the coordination number [3] and one of which has the coordination number [4]; inspection of Table 10 shows that these coordination numbers correspond to solution 1 for $n = 3$. We may construct this structure by putting octahedra and tetrahedra at alternate vertices of a plane 6^3 net, joined by their vertices, the other octahedron vertices being occupied by (H_2O) groups (Fig. 12a), forming a layer of composition $[Mg(SO_4)(H_2O)_3]$. The linkage between layers is via hydrogen bonds, particularly those to the tetrahedron vertex that is not shared with an octahedron (Fig. 12b). Alternate tetrahedra face in opposite directions relative to the plane of the sheet, promoting intersheet hydrogen bonding in both directions. Note that in Figure 12b, the dotted lines denoting hydrogen bonds are conceptual rather than specific; each isolated tetrahedron vertex will accept three hydrogen bonds (Table 12), providing the [4]-coordinated vertex that is part of the pattern of coordination numbers expected for this particular stoichiometry. Note too that this stoichiometry ($n = 3$) gives rise to a sheet structure, intermediate between the framework structure of sanderite ($n = 2$) and the chain and ring structures of starkeyite and cranswickite ($n = 4$).

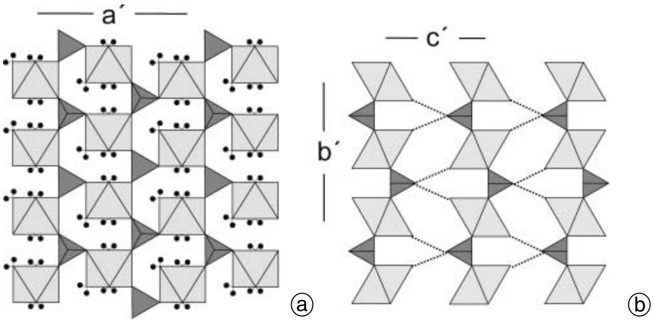

Fig. 12. A proposed bond topology for the structure of $^{[6]}Mg(SO_4)(H_2O)_3$ shown (**a**) orthogonal to the plane of the structural unit, and (**b**) parallel to the plane of the structural unit.

Summary

In the crystal structures of the $^{[6]}Mg(SO_4)(H_2O)_n$ compounds, we have shown the following systematic changes in bond topology as a function of (H_2O) content:

(1) As the number of (H_2O) groups in the structure increases, the number of Mg—Mg linkages decreases in a 1 : 1 ratio with the (increasing) number of (H_2O) groups until no Mg—Mg linkages are left, and then the number of Mg—S linkages decreases with the (increasing) number of (H_2O) groups until no Mg—S linkages are left (at $n = 6$).

(2) The change in bond topology is monotonic as a function of (H_2O) content except for $n = 5$ where, instead of replacing an Mg—S linkage, the fifth (H_2O) group is held in the structure by hydrogen bonds only; it is not linked to Mg as expected from the systematic behaviour of the previous ($n < 5$) compositions. The reason for this is not yet understood.

(3) Representing these structures as polychromatic labelled digraphs, the handshaking lemma allows us to derive a relation between the (known) coordination numbers of the cations (Mg = [6], S^{6+} = [4],

Table 12. Proposed bond-valence structure of $Mg(SO_4)(H_2O)_3$.

	Mg	S	∑	H(11)	H(12)	H(21)	H(22)	H(31)	H(32)	∑
O(1)	0.33	1.50	1.83		0.20					2.03
O(2)	0.33	1.50	1.83				0.20			2.03
O(3)	0.33	1.50	1.83						0.20	2.03
O(4)		1.50	1.50	0.20		0.20		0.20		2.10
O(1)W	0.33			0.80	0.80					1.93
O(2)W	0.33					0.80	0.80			1.93
O(3)W	0.33							0.80	0.80	1.93
∑	2.00	6.00		1	1	1	1	1	1	

$H = [2]$) and the coordination numbers of the anions: $2a + b = 6$, where a and b are the numbers of anions of coordination number [2] and [3], respectively. There are four integer solutions to this equation, and the $Mg(SO_4)(H_2O)_n$ structures correspond to two of these solutions.

(4) Structures are known for $n = 0–2$, $4–7$, 11; considering the variations in connectivity and coordination number as a function of n, a structure is proposed for $Mg(SO_4)(H_2O)_3$.

(5) It is apparent that stoichiometry, the valence-sum rule, and the handshaking lemma strongly constrain the variation in bond topology as a function of (H_2O) content. However, for structures of more complex composition, the effects of variability in cation valence, cation ratio, and the presence of additional interstitial constituents still need to be characterized.

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