The Canadian Mineralogist
Vol. 44, pp. 1403-1429 (2006)

SULFATE MINERALS. I. BOND TOPOLOGY AND CHEMICAL COMPOSITION

Michael SCHINDLER[§], Danielle M.C. HUMINICKI[¶] and Frank C. HAWTHORNE

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

Abstract

The crystal structure of an oxysalt mineral may be divided into two parts: (1) the *structural unit*, an array of high-bond-valence polyhedra that is usually anionic in character, and (2) the *interstitial complex*, an array of large low-valence cations, simple anions, (OH) and (H_2O) groups that is usually cationic in character. The chemical compositions of interstitial complexes in sulfate minerals are explained and predicted using intrinsic properties such as polarity, Lewis acidity, coordination numbers and the average charge of oxygen atoms in the structural unit (average basicity). The interstitial complex can be characterized by its *Lewis acidity*, a measure of the electrophilic character of the complex, and the structural unit can be characterized by its range in *Lewis basicity*. Any complex structural unit $[M^{z+}(H_2O)_n(OH)_m(SO_4)_k]$ can be divided into an acidic component of $(M^{z+}\phi n)$ polyhedra and a basic component of (SO_4) groups. The ligands of the acidic component are primarily bond-valence donors, and the O atoms of the basic component are bond-valence acceptors. Neutral structural units must arrange themselves such that their acidic and basic parts match each other in order to allow linkage *via* hydrogen bonds. Additional (H_2O) groups between structural units are required where hydrogen bonds cannot be accepted directly by a donor atom of the basic part of the structural unit. The Lewis acidities of interstitial complexes in sulfate minerals range from 0.10 to 0.25 *vu* (valence units), with frequency maxima at 0.13, 0.17, 0.20–0.21 and 0.25 *vu*. These maxima correspond to average coordination-numbers of oxygen atoms in the basic component of the structural unit. Using the characteristic range in Lewis basicity of a structural unit and the maximum frequencies of Lewis acidities, the most probable number of bonds from the interstitial complex to the structural unit may be predicted using the valence-matching principle. This number allows prediction of the types of interstitial complexes for a given structural unit.

Keywords: sulfates, bond valence, structural unit, interstitial complex, paragenesis, aqueous species, chemical composition.

SOMMAIRE

On peut diviser la structure cristalline d'un minéral de type oxysel en deux parties, (1) une *unité structurale*, agencement de polyèdres à valence de liaison élevée, généralement à caractère anionique, et (2) un *complexe interstitiel*, agencement de cations relativement gros, à faible valence, ou bien des groupes (OH) and (H_2O), généralement à caractère cationique. Il est possible d'expliquer et de prédire les compositions chimiques des complexes interstitiels des minéraux sulfatés en utilisant des propriétés intrinsèques telles que polarité, acidité de Lewis, coordinence, et charge moyenne sur les atomes d'oxygène de l'unité structurale (basicité moyenne). On peut aussi caractériser le complexe interstitiel par son *acidité de Lewis*, mesure du caractère électrophile du complexe, et l'unité structurale par son intervalle de valeurs de sa *basicité de Lewis*. Toute unité structurale complexe $[M^{z+}(H_2O)_n(OH)_m(SO_4)_k]$ peut être divisée en une composante acidique de polyèdres $(M^{z+}\phi n)$ et une composante basique de groupes (SO_4). Les ligands de la composante acide seraient surtout des donateurs de valences de liaison, tandis que les atomes d'oxygène de la composante basique seraient surtout des accepteurs de valences de liaison. Les unités structurales neutres doivent se disposer de façon à ce que les parties acide et basique concordent l'une avec l'autre pour permettre un couplage grâce à des liaisons hydrogène. Des groupes (H_2O) additionnels entre unités structurales seront nécessaires où les liaisons hydrogène ne peuvent pas être acceptées directement par un atome donateur situé dans la partie basique de l'unité structurale. Les acidités de Lewis des complexes interstitiels des minéraux sulfatés ont une valeur entre 0.10 et 0.25 *vu* (unités de valence), avec des maxima en fréquence à 0.13, 0.17, 0.20–0.21 et 0.25 *vu*. Ces maxima correspondent à la coordinence moyenne des atomes d'oxygène de la composante basique de l'unité structurale. En employant l'intervalle caractéristique de la basicité de Lewis d'une unité structurale et les maxima en fréquence des acidités de Lewis, on peut prédire le nombre probable des liaisons partant du complexe interstitiel vers l'unité structurale en se servant du principe de la concordance des valences. Ce nombre permet la prédiction des types de complexes interstitiels d'une unité structurale quelconque.

(Traduit par la Rédaction)

Mots-clés: sulfates, valences de liaison, unité structurale, complexe interstitiel, paragenèse, espèces aqueuses, composition chimique.

[§] *E-mail address*: schindl0@cc.umanitoba.ca

[¶] *Current address*: Department of Geological Sciences, Virginia Polytechnic and State University, 513 Hunt Club Road 28B, Blacksburg, Virginia 24060, USA.

INTRODUCTION

In dealing with hydroxy-hydrated oxysalt minerals [*e.g.*, copiapite, $[Fe^{3+}_2(OH)(H_2O)_4(SO_4)_3]_2\{Fe^{2+}(H_2O)_6(H_2O)_6\}$; metavoltine, $K_2Na_6[Fe^{3+}_3O(SO_4)_6(H_2O)_3]_2\{Fe^{2+}(H_2O)_6(H_2O)_6\}$], structural complexity and the difficulty in dealing with (OH) and (H_2O) groups preclude standard theoretical approaches to mineral stability. Moreover, additional issues arise in structurally and chemically complex minerals:

(1) What controls their chemical composition? For example, in metavoltine, why are the interstitial cations K_2 *and* Na_6 instead of K_8 or Na_8? Why are there six (H_2O) groups bonded to interstitial cations and six interstitial (H_2O) groups not bonded to interstitial cations, rather than any other number of (H_2O) groups?

(2) Most sulfate minerals are normally stable over a small range of external conditions (*e.g.,* Eh, pH, T, P) and are commonly associated with many (*e.g.*, > 20) other complex minerals of similar composition in some parageneses. What factors control their relative stabilities? Secondary sulfate minerals generally arise from the oxidation of sulfide minerals associated with mine waste. In this type of environment, such oxidation processes release toxic elements such as As, Pb and Cd, and these can be incorporated in the secondary sulfates (Dutrizac & Jambor 2000). Can the factors affecting the incorporation of such elements into the associated sulfate minerals be understood sufficiently so that it can be predicted?

The ideas developed by Hawthorne (1983, 1985a, 1990, 1994, 1997) and Schindler & Hawthorne (2001a) provide a (non-variational) atomistic approach to these questions from a structural perspective, based on the bond topology of structures. This work has evolved into an attempt to provide a unified treatment of the structure, chemical composition and stability of oxysalt minerals crystallizing from low-temperature aqueous solutions. Hawthorne (1985a, 1990), Schindler & Hawthorne (2001b, c, 2004, 2005) and Schindler *et al.* (2000) have applied various aspects of this approach to vanadate, borate, uranyl-oxide-hydrate and uranyl-oxysalt minerals. Here, we will examine the sulfate minerals from this perspective, and compare them to the borate minerals that we have examined previously. We emphasize that we are trying to understand the structural and environmental factors that control the stability and composition of these minerals. We do not intend this to be a predictive method at the present time; predictions are made in order to test the efficacy of this approach, which is currently the only method by which such structural and compositional features of complex minerals can be addressed (or predicted). Readers unfamiliar with this approach are referred to the papers of Hawthorne and Schindler & Hawthorne quoted above. A glossary of terms is given in the Appendix.

GENERAL PHILOSOPHY

Consider the structure of an oxysalt mineral as consisting of a strongly bonded *structural unit* and a weakly bonded *interstitial complex*. The structural unit may be considered as a very complex oxyanion with a characteristic Lewis basicity, and the interstitial complex may be considered as a very complex cation with a characteristic Lewis acidity (Hawthorne 1983, 1985a). The valence-matching principle (Brown 1981, 2002) may then be used to examine the interaction between these two units, allowing qualitative insight into the weak bonding interactions that control the stability of the mineral.

A generalized interstitial complex

A general interstitial complex can be written as

$$\{^{[m]}M^{+}_{a}\ ^{[n]}M^{2+}_{b}\ ^{[l]}M^{3+}_{c}\ (H_2O)_d\ (H_2O)_e\ ^{[q]}(OH)_f\ (H_2O)_g\}^{(a+2b+3c-f)+} \qquad (1)$$

where *M* is any type of interstitial monovalent, divalent and trivalent cation, *d* denotes the number of transformer (H_2O) groups, *e* denotes the number of non-transformer (H_2O) groups bonded to two interstitial cations or bonded to one interstitial cation and receiving one hydrogen bond from another interstitial (H_2O) group, *f* denotes the number of interstitial (OH) groups, [*M*…] denotes coordination number, and *g* denotes the number of (H_2O) groups not bonded to any interstitial cations. Note that the inclusion of trivalent cations in the interstitial complex might seem to conflict with the definition of an interstitial complex as containing only weak bonds. However, some minerals contain higher-valence cations coordinated by several transformer (H_2O) groups. In this case, the valences of the bonds from this *compound cation* are small: *e.g.,* the compound cation $Al(H_2O)_6$ has a mean bond-valence (= Lewis acidity) of $3/(6 \times 2) = 0.25$ valence units (*vu*), and hence qualifies as part of an interstitial complex. We can represent the variation in Lewis acidity of an interstitial complex graphically. Figure 1a shows the variation in the Lewis acidity of the general interstitial complex written above as (1) for a range of values of formal charge and coordination number of the interstitial cations and for a range of transformer (H_2O) content [see Appendix I for a definition of transformer (H_2O)]. The Lewis acidity of the interstitial complex decreases as the number of transformer (H_2O) groups increases, as the cation-coordination numbers increase, and as the charge on the interstitial cation decreases.

Binary structural representation and the valence-matching principle

We may plot the range of basicity of a specific structural unit on a graph that shows the variation in Lewis acidity of cation complexes (Fig. 1b). Where the properties of the structural unit (the yellow-shaded area) and the interstitial complexes (curved lines) intersect, the valence-matching principle is satisfied, and structures of those specific compositions are stable. Where the properties of the structural unit and interstitial complexes do not overlap, the valence-matching principle is not satisfied, and structures of those compositions are not stable.

SULFATE MINERALS

There are several schemes of structural classification for sulfate minerals based on heteropolyhedral structural units (Bokii & Gorogotskaya 1969, Sabelli & Trosti-Ferroni 1985, Pushcharovsky *et al.* 1998, Hawthorne *et al.* 2000). These classifications are based on polymerization of sulfate tetrahedra with ($M\phi_6$) polyhedra (M: divalent or trivalent cations, *i.e.,* Mg^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+}, *etc.*; ϕ: unspecified anion). Hawthorne *et al.* (2000) also considered sulfate minerals that do not contain octahedrally coordinated divalent or trivalent cations. Here, we focus on sulfate minerals with (SO_4) as the only oxyanion. The minerals considered here are listed in Tables 1 and 2.

Definition of the structural unit in sulfate minerals

Hawthorne *et al.* (1996), Schindler *et al.* (2000), Schindler & Hawthorne (2001b, c, 2004, 2007) considered structural units in borate, vanadate and uranyl minerals as consisting of polymerized ($B\phi_3$), ($B\phi_4$), ($V^{5+}\phi_n$), ($V^{4+}\phi_n$) and ($UO_2\phi_n$) polyhedra, respectively. The corresponding average bond-valences in those polyhedra are between 0.66 and 1.25 *vu*, and are higher than the maximum bond-valence for interstitial cations (*i.e.,* a trivalent octahedrally coordinated cation, 0.50 *vu*). This clear distinction cannot be made in sulfate minerals, where bonds with the highest bond-valence are $^{[4]}S^{6+}$–O bonds at 1.50 *vu*. The next highest bond-valences are 0.50 and 0.33 *vu* for $^{[6]}M^{3+}$ and $^{[6]}M^{2+}$ cations, respectively. The crystal-chemical arguments of Hawthorne (1985a) suggest that we consider structural units as polymerized anion complexes of (SO_4) and ($M\phi_n$) polyhedra, with the minimum *average* bond-valence between a linking O atom of a sulfate tetrahedron and a ($M\phi_n$) polyhedron equal to 0.30 *vu*. However, it is more effective to introduce a more flexible definition of the structural unit. A crystal structure tends to break down by breaking the weaker chemical bonds in the structure, and hence we do not wish to classify such bonds as occurring *within* the structural unit. Thus we define the structural unit as being formed by polymerization of (SO_4) tetrahedra with ($M\phi_n$) polyhedra involving the M cations of higher valence. Thus a structural unit can be $[M^{3+}(SO_4)_k\,\phi_n]$ or $[M^{2+}{}_n\,(SO_4)_k\,\phi_n]$, but not $[M^{2+}{}_l\,M^{3+}{}_n\,(SO_4)_k\,\phi_m]$. In the latter case, the higher-valence M^{3+} cations are part of the structural unit, but the lower-valence M^{2+} cations are not. The one exception to this latter rule arises where M^{2+} and M^{3+} cations occupy the same site: $[(M^{2+},M^{3+})_n\,(SO_4)_k\,\phi_M]$. Below, we consider two (somewhat tricky) examples.

(1) Botryogen, $Mg(H_2O)_5Fe^{3+}(OH)(H_2O)(SO_4)_2(H_2O)$, consists of $[Fe^{3+}(SO_4)_2(OH)(H_2O)]^{2-}$ chains cross-linked by ($Mg\phi_6$) polyhedra. Following the definition of Hawthorne (1985a), ($Mg\phi_n$) polyhedra, with an average bond-valence of 0.33 *vu*, belong to the structural unit. However, following the above definition gives the following interstitial complex and structural unit: $\{Mg(H_2O)_5(H_2O)\}[Fe^{3+}(SO_4)_2(OH)(H_2O)]$.

(2) Octahedrally coordinated M cations of different valence occur in voltaite, $\{K_2(Al(H_2O)_6)\}[Fe^{2+}{}_5Fe^{3+}{}_3(SO_4)_{12}(H_2O)_{12}]$, at the same crystallographic site. Here, both M^{2+} and M^{3+} are considered as part of the structural unit. The $Al(H_2O)_6$ octahedra are not considered part of the structural unit, as the average bond-valence from this polyhedron to the rest of the structure is transformed by the presence of six transformer (H_2O) groups $[3 / (6 \times 2) = 0.25\ vu]$ such that it is below the cutoff value of 0.30 *vu*.

THE POLAR CHARACTER OF THE STRUCTURAL UNIT

The development of a binary representation of crystal structure (Hawthorne 1990, 1994, 1997) has led to a great simplification in the examination of structural interactions within complex structures. However, until now, there has been one aspect that was somewhat unsatisfactory: non-framework structural units of neutral charge had no formal interaction, and hence could not hold together and form crystal structures within the context of this approach. Obviously, there are many structures that fall into this category, and this problem needs to be addressed if the bond-valence approach is to be of general utility. The first step toward the solution of this problem was taken by Schindler & Hawthorne (2001a, b). They considered hydrogen bonds from a structural unit to the interstitial complex as modifying the effective charges (and hence, effective Lewis basicity and acidity) of these components. However, this approach is not sufficient to characterize how neutral structural units link together, as there is also a spatial characteristic of such hydrogen bonding that must be incorporated into the mechanism.

The structural unit

Consider the structure of lizardite, $[Mg_3Si_2O_5(OH)_4]$ (Fig. 2). The composite T–O sheets in lizardite are held together by hydrogen bonds between the (OH) groups of the octahedron layer and the bridging O-atoms of the tetrahedron layer in the adjacent T–O sheet. Thus the structural unit (*i.e.*, the T–O sheet) has an effective positive charge on the (OH) side and an effective negative charge on the O(bridging) side. The T–O sheet has a *polar* character that promotes linkage between the

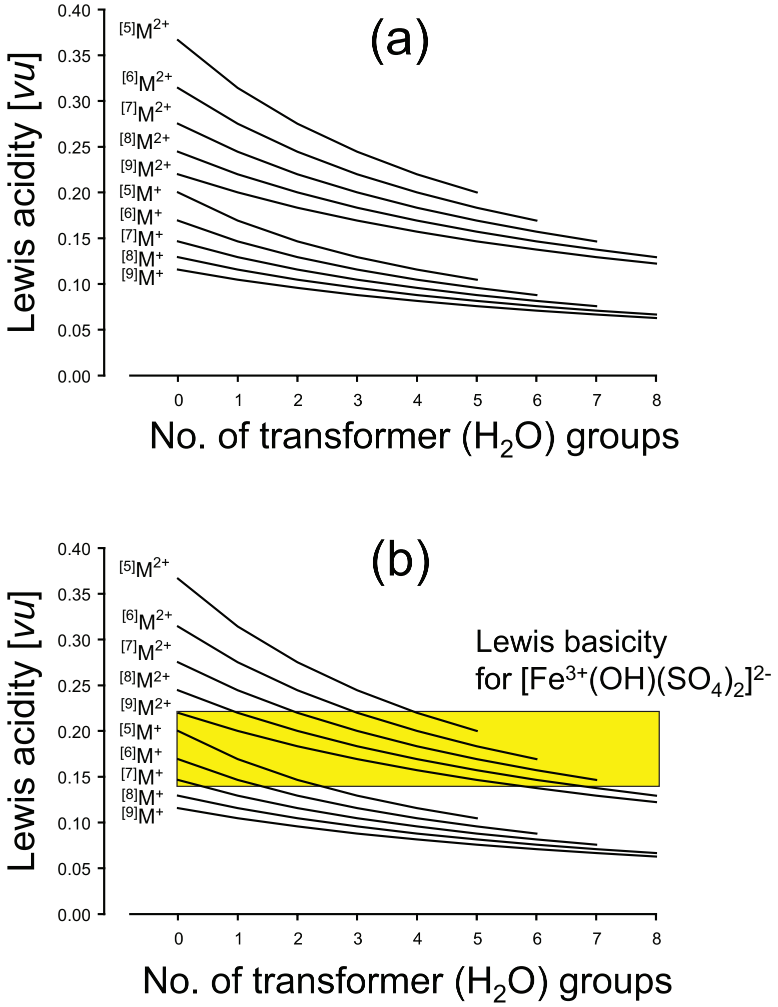

FIG. 1. (a) Variation in Lewis acidity of a general interstitial complex as a function of the number of transformer (H_2O) groups for monovalent, divalent and trivalent cations in [5], [6] and [8] coordination; (b) as (a), with the range in Lewis basicity of the structural unit $[^{[6]}Fe^{3+}(SO_4)_2(OH)]^{2-}$ shown in yellow.

formally neutral structural units. This idea of *structural polarity* will prove important in our treatment of sulfate minerals.

In a sulfate mineral, the general formula of the structural unit may be written as $[M^{z+}(SO_4)_k(OH)_m(H_2O)_n]$. Figures 3a, b and c show fragments of typical structural units for divalent and trivalent *M*-cations and for brucite-like sheets with Jahn–Teller-distorted ($Cu^{2+}\phi_6$) polyhedra. In all three fragments, we observe a polarity similar to that in the lizardite structure: there is an effective positive charge on the $[(M(OH)_m)(H_2O)_n]^{a+}$ component and an effective negative charge on the O atoms of the $(SO_4)^{2-}$ group. In the $[M(OH)_m(H_2O)_n]^{a+}$ component of the structural unit, the constituent (H_2O) and (OH) groups donate hydrogen bonds to the $(SO_4)^{2-}$ component of the structural unit, either directly, or (more commonly) *via* the interstitial complex. Conversely, the $(SO_4)^{2-}$ component of the structural unit accepts bonds only from the interstitial complex. The $[M^{z+}(OH)_m(H_2O)_n]$ component of the structural unit is *acidic*, and the $(SO_4)^{2-}$ component of the structural unit is *basic*. The Lewis acidity of an interstitial complex depends on the average bond-valence of hydrogen bonds emanating from the acidic component of the structural unit. In order to calculate those average bond-valences, we must examine the bonding geometry in the acidic components of structural units.

Structural units with $^{[6]}M^{2+}$ *cations*

Divalent cations in the acidic component of the structural unit commonly occur in octahedral coordination and contribute 0.33 *vu* to the linking O-atoms of the (SO_4) group. Such an O atom receives 1.50 *vu* from the S–O bond and requires an additional 2 – 1.5 – 0.33 = 0.17 *vu* from the interstitial complex. An O atom of an $(M^{2+}\phi_6)$ octahedron that does not link to an (SO_4) group requires an additional 2 – 0.33 = 1.67 *vu*. This large additional bond-valence can be supplied either (1) by attaching two H atoms to form an (H_2O) group, or (2) by attaching one H atom to form an (OH) group, combined with polymerization of $(M^{2+}\phi_6)$ octahedra. Detailed inspection of sulfate structures shows that many of those (H_2O) groups are transformer (H_2O) groups (Table 2). Their constituent O-atoms thus do not receive any bonds from the interstitial complex. Hence, the characteristic bond-valence of the hydrogen bonds emanating from the structural unit in these sulfate minerals is 0.33 / 2 = 0.17 *vu* (Fig. 3a).

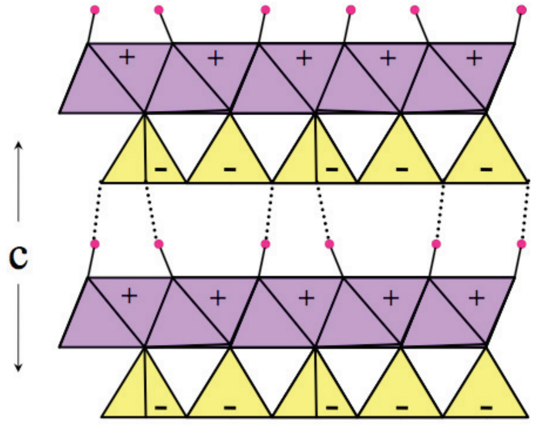

FIG. 2. Diagrammatic representation of the structure of lizardite, showing the polar nature of the structural unit; octahedra: mauve; tetrahedra: yellow; H atoms: red circles; hydrogen bonds: broken lines. The acidic (+) and basic (–) parts of the structural unit are so indicated.

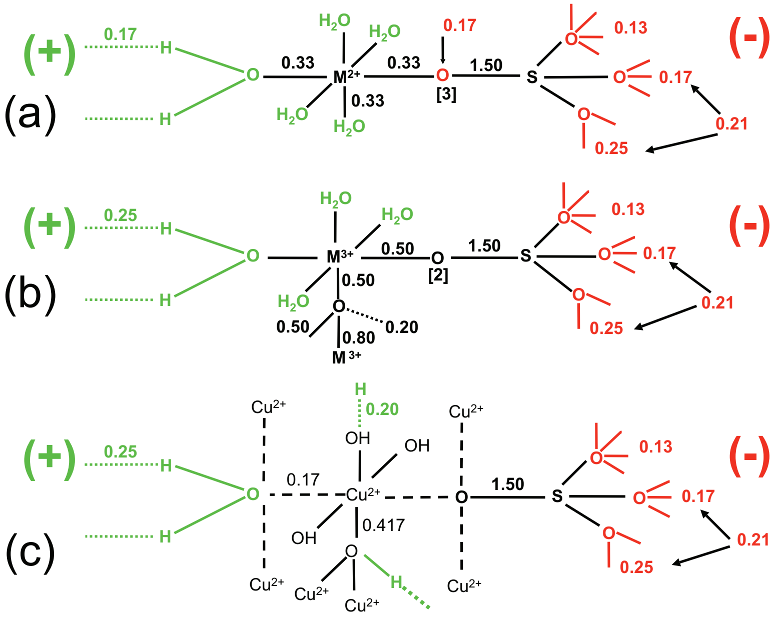

FIG. 3. Bond-valence structure of idealized structural units in sulfate minerals, showing the acidic and basic components of the structural unit, (a) containing [6]-coordinated divalent cations, M^{2+}, (b) containing [6]-coordinated trivalent cations, M^{3+}, (c) containing divalent copper, Cu^{2+}, with its typical Jahn–Teller-distorted octahedral coordination indicated by dashed lines in the figure.

TABLE 1. SELECTED SULFATE MINERALS WITH ISOLATED (SO_4) STRUCTURAL UNITS: CHEMICAL COMPOSITION, INTERSTITIAL COMPLEX AND LEWIS ACIDITY (LA)

Name	Formula	Interstitial complex[1]	LA [*vu*]	Ref.
Hexahydrite	$Mg[SO_4](H_2O)_6$	$\{Mg(H_2O)_6\}^{2+}$	0.17	[1]
Bianchite	$Zn[SO_4](H_2O)_6$	$\{Zn(H_2O)_6\}^{2+}$	0.17	(2)
Chvaleticeite	$Mn^{2+}[SO_4](H_2O)_6$	$\{Mn^{2+}(H_2O)_6\}^{2+}$	0.17	(2)
Ferrohexahydrite	$Fe^{2+}[SO_4](H_2O)_6$	$\{Fe^{2+}(H_2O)_6\}^{2+}$	0.17	(2)
Moorhouseite	$Co[SO_4](H_2O)_6$	$\{Co(H_2O)_6\}^{2+}$	0.17	(2)
Nickel-hexahydrite	$Ni[SO_4](H_2O)_6$	$\{Ni(H_2O)_6\}^{2+}$	0.17	[3]
Retgersite	$Ni[SO_4](H_2O)_6$	$\{Ni(H_2O)_6\}^{2+}$	0.17	[4]
Epsomite	$Mg[SO_4](H_2O)_6(H_2O)$	$\{Mg(H_2O)_6(H_2O)_0(H_2O)_1\}^{2+}$	0.17	[5]
Goslarite	$Zn[SO_4](H_2O)_6(H_2O)$	$\{Zn(H_2O)_6(H_2O)_0(H_2O)_1\}^{2+}$	0.17	(2)
Morenosite	$Ni[SO_4](H_2O)_6(H_2O)$	$\{Ni(H_2O)_6(H_2O)_0(H_2O)_1\}^{2+}$	0.17	[6]
Melanterite	$Fe^{2+}[SO_4](H_2O)_6(H_2O)$	$\{Fe^{2+}(H_2O)_6(H_2O)_0(H_2O)_1\}^{2+}$	0.17	[7]
Bieberite	$Co[SO_4](H_2O)_6(H_2O)$	$\{Co(H_2O)_6(H_2O)_0(H_2O)_1\}^{2+}$	0.17	[8]
Mallardite	$Mn^{2+}[SO_4](H_2O)_6(H_2O)$	$\{Mn^{2+}(H_2O)_6(H_2O)_0(H_2O)_1\}^{2+}$	0.17	(2)
Boothite	$Cu^{2+}[SO_4](H_2O)_6(H_2O)$	$\{Cu^{2+}(H_2O)_6(H_2O)_0(H_2O)_1\}^{2+}$	0.17	(2)
Zinc-melanterite	$Zn[SO_4](H_2O)_6(H_2O)$	$\{Zn(H_2O)_6(H_2O)_0(H_2O)_1\}^{2+}$	0.17	(2)
Alunogen	$Al_2[SO_4]_3(H_2O)_6(H_2O)_{4.4}$	$\{(Al(H_2O)_6)_2(H_2O)_{4.4}\}^{2+}$	0.25	[9]
Picromerite	$K_2Mg[SO_4]_2(H_2O)_6$	$\{^{[8]}K_2Mg(H_2O)_2(H_2O)_4\}^{4+}$	0.17	[10]
Boussingaultite	$(NH_4)_2Mg[SO_4]_2(H_2O)_6$	$\{^{[4]}(NH_4)_2Mg(H_2O)_6\}^{4+}$	0.20	[11]
Cyanochroite	$K_2Cu^{2+}[SO_4]_2(H_2O)_6$	$\{^{[8]}K_2Cu^{2+}(H_2O)_6\}^{4+}$	0.17	[12]
Mohrite	$(NH_4)_2Fe^{2+}[SO_4]_2(H_2O)_6$	$\{^{[4]}(NH_4)_2Fe^{2+}(H_2O)_6\}^{4+}$	0.20	[13]
Nickel-boussingaultite	$(NH_4)_2Ni[SO_4]_2(H_2O)_6$	$\{^{[4]}(NH_4)_2Ni(H_2O)_6\}^{4+}$	0.20	[14]
Lonecreekite	$(NH_4)Fe^{3+}[SO_4]_2(H_2O)_6$	$\{^{[4]}(NH_4)Fe^{3+}(H_2O)_6\}^{4+}$	0.25	(2)
Potassium alum	$KAl[SO_4]_2(H_2O)_6$	$\{^{[8]}KAl(H_2O)_6(H_2O)_6\}^{4+}$	0.20	[15]
Sodium alum	$NaAl[SO_4]_2(H_2O)_6$	$\{^{[6]}NaAl(H_2O)_6(H_2O)_6\}^{4+}$	0.22	[16]
Tschermigite	$(NH_4)Al[SO_4]_2(H_2O)_6$	$\{^{[4]}(NH_4)Al(H_2O)_6(H_2O)_6\}^{4+}$	0.25	[17]
Tamarugite	$NaAl[SO_4]_2(H_2O)_6$	$\{^{[6]}NaAl(H_2O)_6\}^{4+}$	0.22	[18]
Amarillite	$NaFe^{3+}[SO_4]_2(H_2O)_6$	$\{^{[6]}NaFe^{3+}(H_2O)_6\}^{4+}$	0.22	[19]
Mendozite	$NaAl[SO_4]_2(H_2O)_6(H_2O)_5$	$\{^{[6]}NaAl(H_2O)_6(H_2O)_5\}^{4+}$	0.22	[20]
Chalcanthite	$^{[4+2]}Cu^{2+}[SO_4](H_2O)_4(H_2O)$	$\{^{[4+2]}Cu^{2+}(H_2O)_4\}^{2+}$	0.20	[21]
Linarite	$Pb^{2+}\,^{[4+2]}Cu^{2+}[SO_4](OH)_2$	$\{^{[8]}Pb^{[4+2]}Cu^{2+}\,^{[2]}(OH)^{[3]}(OH)\}^{2+}$	0.18	[22]
Chenite	$Pb^{2+}_4(OH)_2\,^{[4+2]}Cu(OH)_4[(SO_4)_2]$	$\{^{[7]}Pb_4^{[4+2]}Cu^{2+}\,^{[3]}(OH)_6\}^{4+}$	0.18	[23]
		Calcium sulfate minerals		
Anhydrite	$Ca[SO_4]$	$\{^{[8]}Ca\}^{2+}$	0.25	[24]
Gypsum	$Ca[SO_4](H_2O)_2$	$\{^{[8]}Ca(H_2O)_2\}^{2+}$	0.20	[25]
Bassanite	$Ca[SO_4](H_2O)_{0.5}$	$\{^{[8]}Ca(H_2O)_{0.5}\}^{2+}$	0.18	[26]
Syngenite	$K_2Ca[SO_4]_2(H_2O)$	$\{^{[8]}K_2\,^{[8]}Ca(H_2O)_0(H_2O)_1\}^{4+}$	0.16	[27]
Görgeyite	$K_2Ca_5[SO_4]_6(H_2O)$	$\{^{[8]}K_2\,^{[8]}Ca_5(H_2O)_0(H_2O)_1\}^{12+}$	0.16	[28]
Glauberite	$CaNa_2[SO_4]_2$	$\{^{[8]}Ca^{[8]}Na_2\}^{4+}$	0.20	[29]
		Alkali metal and NH_4 sulfate minerals		
Glaserite	$K_3Na[SO_4]_2$	$\{^{[10,10,12]}K_3\,^{[6]}Na\}^{4+}$	0.11	[30]
Arcanite	α-$K_2[SO_4]$	$\{^{[9,10]}K_2\}^{2+}$	0.11	[31]
Mascagnite	$(NH_4)_2[SO_4]$	$\{(NH_4)_2\}^{2+}$	0.25	[32]
Palmierite	$K_2Pb[SO_4]_2$	$\{^{[10]}K_2\,^{[12]}Pb\}^{4+}$	0.13	[33]
Kalistrontite	$K_2Sr[SO_4]_2$	$\{^{[10]}K_2\,^{[12]}Sr\}^{4+}$	0.13	(2)
Lecontite	$Na(NH_4)[SO_4](H_2O)_2$	$\{^{[6]}Na(NH_4)(H_2O)_0(H_2O)_2\}^{4+}$	0.20	[34]
Thenardite	$Na_2[SO_4]$	$\{^{[6]}Na_2\}^{2+}$	0.17	[35]
Mirabilite	$Na_2[SO_4](H_2O)_{10}$	$\{^{[6]}Na_2(H_2O)_0(H_2O)_8(H_2O)_2\}^{2+}$	0.17	[36]
		Sulfate minerals with the apatite structure-type		
Barite	$Ba[SO_4]$	$\{^{[10]}Ba\}^{2+}$	0.20	[37]
Celestine	$Sr[SO_4]$	$\{^{[10]}Sr\}^{2+}$	0.20	
[37,35]				
Anglesite	$Pb^{2+}[SO_4]$	$\{^{[10]}Pb\}^{2+}$	0.20	[37]
		Selected sulfate minerals with brucite-like sheets of octahedra $[M\varphi_2]$		
Langite	$Cu^{2+}_4[SO_4](OH)_6(H_2O)_2$	$\{Cu^{2+}_4(OH)_6(H_2O)_2\}^{2+}$	0.23	[38]
Posnjakite	$Cu^{2+}_4[SO_4](OH)_6(H_2O)_2$	$\{Cu^{2+}_4(OH)_6(H_2O)_2\}^{2+}$	0.23	[39]
Wroewolfeite	$Cu^{2+}_4[SO_4](OH)_6(H_2O)_2$	$\{Cu^{2+}_4(OH)_6(H_2O)_2\}^{2+}$	0.23	[40]
Campigliaite	$MnCu^{2+}_4[(SO_4)_2](OH)_6(H_2O)_4$	$\{Cu^{2+}_4(OH)_6Mn(H_2O)_2(H_2O)_2\}^{4+}$	0.20	[41]
Ktenasite	$ZnCu^{2+}_4[(SO_4)_2](OH)_6(H_2O)_6$	$\{Cu^{2+}_4(OH)_6Zn(H_2O)_2(H_2O)_4\}^{4+}$	0.20	[42]
Niedermayrite	$CdCu^{2+}_4[(SO_4)_2](OH)_6(H_2O)_4$	$\{Cu^{2+}_4(OH)_6Cd(H_2O)_2(H_2O)_2\}^{4+}$	0.20	[43]
Christelite	$ZnZn_2Cu^{2+}_2[(SO_4)_2](OH)_6(H_2O)_4$	$\{Zn_2Cu^{2+}_2(OH)_6Zn(H_2O)_2(H_2O)_2\}^{4+}$	0.20	[44]

Structural units with $^{[6]}M^{3+}$ cations

Trivalent *M*-cations in the acidic component of a structural unit commonly occur in octahedral coordination (Fig. 3b). Here, the average bond-valence of an *M*–O bond is 0.50 *vu*, and the corresponding hydrogen bond of an associated transformer (H_2O) group has a bond valence of 0.25 *vu.* The coordination number of an O atom shared between an ($M^{3+}\phi_6$) octahedron and an (SO_4) group is usually [2], because its incident bond-valence sum is 1.50 + 0.50 = 2.00 *vu.* In many structural units in sulfate minerals, ($M^{3+}\phi_6$) octahedra are polymerized, and the linking anions are either an (OH) group or an O atom. An (OH) group commonly links two ($M^{3+}\phi_6$) octahedra and receives one additional bond from the interstitial complex; it also forms one hydrogen bond with an average bond-valence of 0.20 *vu* (Fig. 3b). An O atom commonly links three ($M^{3+}\phi_6$) octahedra and receives two additional bonds from the interstitial complex.

An example: Zincobotryogen, $Zn(H_2O)_5Fe^{3+}(OH)(H_2O)_1(SO_4)_2(H_2O)$, has the structural unit $[Fe^{3+}(SO_4)_2(OH)(H_2O)_1]^{2-}$. There is one transformer (H_2O) group and one (OH) group in the acidic component of the structural unit. The hydrogen bonds from the (H_2O) and (OH) groups have, on average, bond valences of 0.25 and 0.20 *vu*, respectively. The formal charge of the structural unit is 2^-, and the effective charge of the structural unit is $2 \times 0.25 + 0.2 + 2 = 2.70^-$. The composition of the interstitial complex is $\{^{[6]}Zn(H_2O)_4(H_2O)_1\}^{2+}$, and there are $2 + 4 \times 2 = 10$ bonds emanating from the interstitial complex. Moreover, there are three hydrogen bonds emanating from the acidic component of the structural unit. Thus, there are thirteen bonds involving primarily the O atoms of the basic component of the structural unit. The resulting effective Lewis acidity is $2.7 / (2 + 4 \times 2 + 3) = 0.21$ *vu.*

Brucite-like sheets with Jahn–Teller-distorted ($Cu^{2+}\phi_6$) polyhedra

Sulfate minerals with Jahn–Teller-distorted ($Cu^{2+}\phi_6$) octahedra occur in langite, posnjakite, wroewolfeite, campigliaite, ktenasite, niedermayrite and christelite (Table 1). These minerals contain brucite-like sheets of edge-sharing ($Cu^{2+}\phi_6$) octahedra. A key feature of their structures is the local bond-valence requirement that three apical Cu^{2+}–ϕ bonds must meet at a single O-atom of an attached (SO_4) tetrahedron (Hawthorne & Schindler 2000). The linking O-atom of the (SO_4) group receives 1.50 *vu* from the S–O bond, and thus each apical Cu^{2+}–O bond contributes, on average, 0.167 *vu* to the linking O-atom, which is below the cutoff of 0.30 *vu* (Fig. 3c). Hence, these minerals contain an isolated [SO_4] structural unit (Table 1), which is attached to a sheet of polymerized ($Cu^{2+}\phi_6$) polyhedra. These polyhedra are linked *via* equatorial Cu^{2+}–O bonds

---

[1] Both types of (H_2O) groups must be included in the interstitial complex, even if one is not present, as the order indicates which are transformer (H_2O) groups and which are non-transformer H_2O groups.

A reference in square brackets ([1]) indicates that a structure has been refined; a reference in round brackets [(2)] indicates a structure has not been refined.

[1] Zalkin *et al.* (1964), (2) Gaines *et al.* (1997), [3] Ptasiewicz-Bak *et al.* (1983), [4] Stadnicka *et al.* (1987), [5] Calleri *et al.* (1984), [6] Iskhakova *et al.* (1991), [7] Baur (1964), [8] Kellersohn *et al.* (1991), [9] Menchetti & Sabelli (1974), [10] Kannan & Viswamitra (1965), [11] Maslen *et al.* (1988), [12] Robinson & Kennard (1972), [13] Figgis *et al.* (1992), [14] Tahirov *et al.* (1994), [15] Larson & Cromer (1967), [16] Cromer *et al.* (1967), [17] Abdeen *et al.* (1981), [18] Robinson & Fang (1969), [19] Li *et al.* (1990), [20] Fang & Robinson (1972), [21] Bacon & Titterton (1975), [22] Effenberger (1987), [23] Hess *et al.* (1988), [24] Hawthorne & Ferguson (1975c), [25] Pedersen & Semmingsen (1982), [26] Abriel & Nesper (1993), [27] Bokii *et al.* (1978), [28] Mukhtarova *et al.* (1980), Smith & Walls (1980), [29] Araki & Zoltai (1967), [30] Okada & Ossaka (1980), [31] McGinnety (1972), [32] Hasebe (1981), [33] Bachmann (1953), [34] Corazza *et al.* (1967), [35] Hawthorne & Ferguson (1975b), [36] Levy & Lisensky (1978), [37] Jacobsen *et al.* (1998), [38] Galy *et al.* (1984), [39] Menchetti & Sabelli (1979), [40] Hawthorne & Groat (1985), [41] Menchetti & Sabelli (1982), [42] Menchetti & Sabelli (1978), [43] Giester *et al.* (1998), [43] Adiwidjaja *et al.* (1996).

TABLE 2. SELECTED SULFATE MINERALS WITH COMPLEX STRUCTURAL UNITS, SHOWING LEWIS ACIDITY (LA), AVERAGE BASICITY (AB) AND COORDINATION NUMBER OF THE INTERSTITIAL COMPLEX [CN_{in}]

Name	Formula	Interstitial complex	LA [vu]	AB [vu]	[CN_{in}]	Ref.
Minasragrite	$[V^{4+}O(SO_4)(H_2O)_4](H_2O)$	$\{(H_2O)_0(H_2O)_0(H_2O)_1\}$	0.25	0.17	0.88	[1]
Xitieshanite	$[Fe^{3+}(SO_4)Cl(H_2O)_4](H_2O)_2$	$\{(H_2O)_0(H_2O)_0(H_2O)_2\}$	0.25	0.18	0.88	[2]
Blödite	$Na_2[Mg(SO_4)_2(H_2O)_4]$	$\{{}^{[6]}Na_2\}^{2+}$	0.21	0.30	1.67	[3]
Nickelblödite	$Na_2\,[Ni(SO_4)_2(H_2O)_4]$	$\{{}^{[6]}Na_2\}^{2+}$	0.21	0.30	1.67	(4)
Changoite	$Na_2\,[Zn(SO_4)_2(H_2O)_4]$	$\{{}^{[6]}Na_2\}^{2+}$	0.21	0.30	1.67	(5)
Leonite	$K_2\,[Mg(SO_4)_2(H_2O)_4]$	$\{{}^{[11]}K_2\}^{2+}$	0.13	0.30	2.50	[6]
Mereiterite	$K_2\,[Fe(SO_4)_2(H_2O)_4]$	$\{{}^{[11]}K_2\}^{2+}$	0.13	0.30	2.50	[7]
Römerite	$Fe^{2+}(H_2O)_6\,[Fe^{3+}{}_2(SO_4)_4(H_2O)_8]$	$\{{}^{[6]}Fe^{2+}(H_2O)_6\}^{2+}$	0.23	0.22	1.17	[8]
Polyhalite	$K_2Ca_2\,[Mg(SO_4)_4(H_2O)_2]$	$\{{}^{[11]}K_2\,{}^{[8]}Ca\}^{6+}$	0.17	0.38	2.33	[9]
Leightonite	$K_2Ca_2[Cu^{2+}(SO_4)_4(H_2O)_2]$	$\{{}^{[11]}K_2\,{}^{[8]}Ca\}^{6+}$	0.17	0.38	2.33	(4)
Rozenite	$[Fe^{2+}(SO_4)(H_2O)_4]$	–	0.17	0.20	1.00	[10]
Starkeyite	$[Mg(SO_4)(H_2O)_4]$	–	0.17	0.20	1.00	[11]
Ilesite	$[Mn^{2+}(SO_4)(H_2O)_4]$	–	0.17	0.20	1.00	(4)
Aplowite	$[Co^{2+}(SO_4)(H_2O)_4]$	–	0.17	0.20	1.00	[12]
Boyleite	$[Zn(SO_4)(H_2O)_4]$	–	0.17	0.20	1.00	(4)
Bonattite	$[Cu^{2+}(SO_4)(H_2O)_3]$	–	0.17	0.17	0.86	[13]
Kröhnkite	$Na_2\,[Cu^{2+}(SO_4)_2(H_2O)_2]$	$\{{}^{[7]}Na_2\}^{2+}$	0.17	0.28	1.80	[14]
Coquimbite	$Al(H_2O)_6\,[Fe^{3+}{}_3(SO_4)_6(H_2O)_6](H_2O)_6$	$\{{}^{[6]}Al(H_2O)_6\}^{3+}$	0.25	0.18	0.80	[15]
Paracoquimbite	$Fe^{3+}(H_2O)_6\,[Fe^{3+}{}_3(SO_4)_6(H_2O)_6](H_2O)_6$	$\{{}^{[6]}Fe^{3+}(H_2O)_6\}^{3+}$	0.25	0.18	0.80	[16]
Metavoltine	$K_2Na_6Fe^{2+}(H_2O)_6\,[Fe^{3+}{}_3O(SO_4)_6(H_2O)_3]_2(H_2O)_6$	$\{{}^{[9]}K_2\,{}^{[6]}Na_6Fe^{2+}(H_2O)_6\}^{10+}$	0.17	0.22	1.39	[17]
Pentahydrite	$[Mg(SO_4)(H_2O)_4](H_2O)$	$\{(H_2O)_0(H_2O)_0(H_2O)_1\}$	0.17	0.20	1.00	[18]
Siderotil	$[Fe^{2+}(SO_4)(H_2O)_4](H_2O)$	$\{(H_2O)_0(H_2O)_0(H_2O)_1\}$	0.17	0.20	1.00	(4)
Jokokuite	$[Mn^{2+}(SO_4)(H_2O)_4](H_2O)$	$\{(H_2O)_0(H_2O)_0(H_2O)_1\}$	0.17	0.20	1.00	(4)
Butlerite	$[Fe^{3+}(SO_4)(OH)(H_2O)_2]$	–	0.25	0.14	0.71	[19]
Parabutlerite	$[Fe^{3+}(SO_4)(OH)(H_2O)_2]$	–	0.25	0.14	0.71	[20]
Uklonskovite	$Na[Mg(SO_4)F(H_2O)_2]$	$\{{}^{[6]}Na\}^{+}$	0.17	0.26	1.43	[21]
Fibroferrite	$[Fe^{3+}(SO_4)(OH)(H_2O)_2]$	–	0.25	0.14	0.71	[22]
Botryogen	$Mg(H_2O)_5\,[Fe^{3+}(SO_4)_2(OH)(H_2O)_1](H_2O)$	$\{Mg(H_2O)_4(H_2O)_1\}^{2+}$	0.21	0.26	1.30	[23]
Zincobotryogen	$Zn(H_2O)_5\,[Fe^{3+}(SO_4)_2(OH)(H_2O)_1](H_2O)$	$\{Zn(H_2O)_4(H_2O)_1\}^{2+}$	0.21	0.26	1.30	[24]
Krausite	$K[Fe^{3+}(SO_4)_2(H_2O)_2]$	$\{{}^{[10]}K\}^{+}$	0.13	0.16	1.33	[25]
Sideronatrite	$Na_2\,[Fe^{3+}(SO_4)_2(OH)](H_2O)_3$	$\{{}^{[6]}Na_2\}^{2+}$	0.17	0.24	1.44	[26]
Metasideronatrite	$Na_4\,[Fe^{3+}{}_2(SO_4)_4(OH)_2](H_2O)_3$	$\{{}^{[6]}Na_4\}^{4+}$	0.17	0.24	1.44	(27)
Guildite	$Cu^{2+}(H_2O)_4\,[Fe^{3+}(SO_4)_2(OH)]$	$\{{}^{[4+2]}Cu^{2+}(H_2O)_4\}^{2+}$	0.2	0.24	1.22	[28]
Natrochalcite	$Na[Cu^{2+}{}_2(SO_4)_2(OH)(H_2O)]$	$\{{}^{[8]}Na\}^{+}$	0.15	0.16	1.10	[28]
Ferrinatrite	$Na_3(H_2O)_3\,[Fe^{3+}(SO_4)_3]$	$\{{}^{[6]}Na_2\,{}^{[7]}Na(H_2O)_0(H_2O)_3\}^{3+}$	0.16	0.25	1.75	[29]
Copiapite	$Fe^{2+}(H_2O)_6\,[Fe^{3+}{}_2(SO_4)_3(OH)(H_2O)_4]_2(H_2O)_6$	$\{Fe^{2+}(H_2O)_6(H_2O)_0(H_2O)_6\}^{2+}$	0.21	0.16	0.88	[30]
Magnesiocopiapite	$Mg(H_2O)_6\,[Fe^{3+}{}_2(SO_4)_3(OH)(H_2O)_4]_2(H_2O)_6$	$\{Mg(H_2O)_6(H_2O)_0(H_2O)_6\}^{2+}$	0.21	0.16	0.88	[31]
Cuprocopiapite	$Cu^{2+}(H_2O)_6\,[Fe^{3+}{}_2(SO_4)_3(OH)(H_2O)_4]_2(H_2O)_6$	$\{Cu^{2+}(H_2O)_6(H_2O)_0(H_2O)_6\}^{2+}$	0.21	0.16	0.88	(4)
Ferricopiapite	$(Fe^{3+}{}_{0.67}\square_{0.33})(H_2O)_6\,[Fe^{3+}{}_4(SO_4)_6(OH)_2(H_2O)_8](H_2O)_6$	$(Fe^{3+}{}_{0.67}\square_{0.33})\,\{(H_2O)_6(H_2O)_0(H_2O)_6\}^{2+}$	0.21	0.16	0.88	[32]
Calciocopiapite	$Ca(H_2O)_6\,[Fe^{3+}{}_2(SO_4)_3(OH)(H_2O)_4]_2(H_2O)_6$	$\{Ca(H_2O)_6(H_2O)_0(H_2O)_6\}^{2+}$	0.21	0.16	0.88	(4)
Zincocopiapite	$Zn(H_2O)_6\,[Fe^{3+}{}_2(SO_4)_3(OH)(H_2O)_4]_2(H_2O)_6$	$\{Zn(H_2O)_6(H_2O)_0(H_2O)_6\}^{2+}$	0.21	0.16	0.88	(4)
Aluminocopiapite	$(Al_{0.67}\square_{0.33})[Fe^{3+}{}_2(SO_4)_3(OH)(H_2O)_4]_2(H_2O)_6$	$(Al_{0.67}\square_{0.33})\,(H_2O)_6(H_2O)_0(H_2O)_6\}^{2+}$	0.21	0.16	0.88	(33)
Ransomite	$[Cu^{2+}(H_2O)_4][Fe^{3+}{}_2(SO_4)_4(H_2O)_2]$	$\{{}^{[6]}Cu^{2+}(H_2O)_4\}^{2+}$	0.21	0.16	0.78	[34]
Amarantite	$[Fe^{3+}{}_2O(SO_4)_2(H_2O)_4](H_2O)_3$	$\{(H_2O)_0(H_2O)(H_2O)_3\}$	0.25	0.12	0.62	[35]
Hohmannite	$[Fe^{3+}{}_2O(SO_4)_2(H_2O)_4](H_2O)_4$	$\{(H_2O)_0(H_2O)_0(H_2O)_4\}$	0.25	0.12	0.62	[36]

with an average bond-valence of [2 – (2 × 0.167)] / 4 = 0.417 *vu*.

Attachment of the isolated [SO_4] group to the sheet of polymerized ($Cu^{2+}\phi_6$) polyhedra results in a unit with a strong polarity between its acidic and basic parts (Fig. 3c). The acidic component of the unit contains (OH) groups that link three adjacent ($Cu\phi_6$) octahedra. The bond-valence sum incident at each O-atom is 3 × 0.417 = 1.25 *vu*; thus, each O-atom requires an additional bond-valence of 0.75 *vu* from the O–H bond,

TABLE 2 (continued). SELECTED SULFATE MINERALS WITH COMPLEX STRUCTURAL UNITS, SHOWING LEWIS ACIDITY (LA), AVERAGE BASICITY (AB) AND COORDINATION NUMBER OF THE INTERSTITIAL COMPLEX [CN_{in}]

Name	Formula	Interstitial complex	LA [vu]	AB [vu]	[CN_{in}]	Ref.
Kornelite	$[Fe^{3+}{}_2(SO_4)_3(H_2O)_6](H_2O)_{1.25}$	$\{(H_2O)_0(H_2O)_0(H_2O)_{1.25}\}$	0.25	0.13	0.66	[37]
Rhomboclase	$(H_5O_2)[Fe^{3+}(SO_4)_2(H_2O)_2]$	$\{H_5O_2\}^+$	0.2	0.18	0.90	[38]
Vanthoffite	$Na_6\,[Mg(SO_4)_4]$	$\{^{[6]}Na_6\}^{6+}$	0.17	0.375	2.25	[39]
Goldichite	$K[Fe^{3+}(SO_4)_2(H_2O)_2](H_2O)_2$	$\{^{[9]}K(H_2O)_0(H_2O)_2\}^+$	0.18	0.18	1.30	[40]
Millosevichite	$[Al_2(SO_4)_3]$	–	0	0.00	0.00	[41]
Mikasaite	$[Fe^{3+}{}_2(SO_4)_3]$	–	0	0.00	0.00	(4)
Chalcocyanite	$[Cu^{2+}(SO_4)]$	–	0	0.00	0.00	[42]
Zincosite	$[Zn(SO_4)]$	–	0	0.00	0.00	[42]
Voltaite	$K_2[Al(H_2O)_6][Fe^{2+}{}_5Fe^{3+}{}_3(SO_4)_{12}(H_2O)_{12}]$	$\{^{[12]}K_2{}^{[6]}Al(H_2O)_6\}^{5+}$	0.16	0.16	1.00	[43]
Zincovoltaite	$K_2[Al(H_2O)_6][Zn_5Fe^{3+}{}_3(SO_4)_{12}(H_2O)_{12}]$	$\{^{[12]}K_2{}^{[6]}Al(H_2O)_6\}^{5+}$	0.16	0.16	1.00	(4)
Antlerite	$[Cu_3(SO_4)(OH)_4]$	-	0.2	0.10	0.50	[44]
Caminite	$[Mg_3(SO_4)_2(OH)_2]$	-	0.2	0.04	0.20	[45]
Euchlorine	$NaK[^{[6]}Cu^{2+}\,{}^{[5]}Cu^{2+}{}_2O(SO_4)_3]$	$\{^{[7]}Na^{[7]}K\}^{2+}$	0.14	0.15	1.08	[46]
Fedotovite	$K_2\,[^{[5]}Cu^{2+}{}_3O(SO_4)_3]$	$\{^{[7]}K_2\}^{2+}$	0.14	0.15	1.08	[47]
Klyuchevskite	$K_3\,[^{[5]}Cu^{2+}{}_3(Fe,Al)O_2(SO_4)_4]$	$\{^{[8]}K_2{}^{[7]}K\}^{3+}$	0.13	0.17	1.28	[48]
Alumo-klyuchevskite	$K_3\,[Cu^{2+}{}_3AlO_2(SO_4)_4]$	$\{^{[8]}K_2{}^{[7]}K\}^{3+}$	0.13	0.17	1.28	(4)
Dolerophanite	$[^{[6]}Cu^{[5]}CuO(SO_4)]$	-	0	0.00	0.00	[49]
Zircosulfate	$[^{[8]}Zr(SO_4)_2(H_2O)_4]$	-	0.25	0.13	0.67	[50]
Sodium-zippeite	$Na_5(H_2O)_{12}[(^{[7]}UO_2)_8(SO_4)_4O_5(OH)_3]$	$\{^{[7]}Na_3{}^{[6]}Na_2(H_2O)_0(H_2O)_{12}\}^+$	0.17	0.14	0.90	[51]
Synthetic *M*-zippeite, *M* = Mg, Zn, Co	$M(H_2O)_{3.5}[(UO_2)_2(SO_4)O_2]$	$\{^{[6]}M(H_2O)_3(H_2O)_{0.5}\}^{2+}$	0.22	0.20	0.90	[51]
Jarosite	$^{[12]}K[Fe_3(SO_4)_2(OH)_6]$	$^{[12]}K$	0.12	0.16	1.28	[52]
Kieserite	$[Mg(SO_4)(H_2O)]$	-	0.17	0.08	0.40	[53]
Dwornikite	$[Ni(SO_4)(H_2O)]$	-	0.17	0.08	0.40	[54]
Szmikite	$[Mn^{2+}(SO_4)(H_2O)]$	-	0.17	0.08	0.40	[54]
Gunningite	$[Zn(SO_4)(H_2O)]$	-	0.17	0.08	0.40	[54]
Szomolnokite	$[Fe^{2+}(SO_4)(H_2O)]$	-	0.17	0.08	0.40	[54]
Poitevinite	$[Cu^{2+}(SO_4)(H_2O)]$	-	0.17	0.08	0.40	[55]
Metahohmannite	$[Fe^{3+}{}_2O(SO_4)_2(H_2O)_4]$	-	0.25	0.12	0.62	[56]

References: [1] Tachez *et al.* (1979), [2] Zhou *et al.* (1988), [3] Rumanova & Malitskaya (1959), Hawthorne (1985b), (4) Gaines *et al.* (1997), (5) Schluter *et al.* (1999), [6] Jarosch (1985), [7] Giester & Rieck (1995), [8] Fanfani *et al.* (1970), [9] Schlatti *et al.* (1970), [10] Baur (1960), [11] Baur (1962), [12] Kellersohn (1992), [13] Zahrobsky & Baur (1968), [14] Hawthorne & Ferguson (1975a), [15] Fang & Robinson (1970), [16] Robinson & Fang (1971), [17] Giacovazzo *et al.* (1976), [18] Baur & Rolin (1972), [19] Fanfani *et al.* (1971), [20] Borène (1970), [21] Sabelli (1985), [22] Scordari (1981a), [23] Süsse (1968), [24] Yang & Fang (1988), [25] Effenberger *et al.* (1986), [26] Scordari (1981b), (27) Scordari *et al.* (1982), [28] Chevrier *et al.* (1993), [29] Scordari (1977), Mereiter (1976), [30] Fanfani *et al.* (1973), [31] Süsse (1970), (32) Fanfani *et al.* (1973), (33) Jolly & Foster (1967), [34] Wood (1970), [35] Süsse (1967), Giacovazzo & Menchetti (1969), [36] Scordari (1978), [37] Robinson & Fang (1973), [38] Mereiter (1974), [39] Fischer & Hellner (1964), [40] Graeber & Rosenzweig (1971), [41] Dahmen & Gruehn (1993), [42] Wildner & Giester (1988), [43] Mereiter (1972), [44] Hawthorne *et al.* (1989), [45] Keefer *et al.* (1981), Hochella *et al.* (1983), [46] Scordari & Stasi (1990), [47] Starova *et al.* (1991), [48] Gorskaya *et al.* (1992), [49] Effenberger (1985), [50] Singer & Cromer (1959), [51] Burns *et al.* (2003), [52] Menchetti & Sabelli (1976), [53] Hawthorne *et al.* (1987), [54] Wildner & Giester (1991), [55] Giester *et al.* (1994), [56] Scordari *et al.* (2004).

and each H-atom requires an additional 0.25 *vu* from its hydrogen bond. The acidic component of the unit can also contain (H_2O) groups, which are attached to the brucite-like sheets in the same way as the $(SO_4)^{2-}$ groups. Assuming a similar average bond-valence sum from the three apical (Cu–ϕ) bonds ($3 \times 0.17 = 0.50$ *vu*), the bond valence of the two resulting hydrogen bonds is 0.50 / 2 = 0.25 *vu* (Fig. 3c).

Example: In wroewolfeite, $\{Cu^{2+}{}_4(OH)_6(H_2O)\}$ $[SO_4]\{H_2O\}$ (Hawthorne & Groat 1985), the acidic parts of the polar structure are the $\{Cu_4(OH)_6\}$ sheet and the attached (H_2O) group, and the basic part is the attached (SO_4) group. In the $\{Cu_4(OH)_6\}$ sheet, four (OH)-groups accept three equatorial Cu–O bonds with an average bond-valence of 0.417 *vu*, and two (OH) groups accept two equatorial Cu–O bonds and one apical Cu–O bond (0.17 *vu*). Hence, O atoms of the latter two (OH) groups accept $2 \times 0.417 + 0.17 = 1.0$ *vu* and require an additional 1.0 *vu* from the O–H bond. The bond valence of the hydrogen bond is the difference between the formal charge of the H (1^+) and the bond valence of the O–H bond; thus its bond valence is formally $1.0 - 1.0 = 0.0$ *vu*. Hence, the O atoms of the (SO_4) group accept 2×0.0 and 4×0.25 *vu* from hydrogen bonds of the six (OH) groups, $2 \times 0.25 = 0.5$ *vu* from two hydrogen bonds of the (H_2O) group and $3 \times 0.17 = 0.5$ *vu* from three apical Cu–O bonds. The corresponding Lewis basicity of the (SO_4) group is its charge divided by the number of bonds accepted by the (SO_4) group: $2 / 11 = 0.18$ *vu*.

POLAR CHARACTER AND NUMBER OF INTERSTITIAL (H_2O) GROUPS

In a sulfate mineral with a neutral (non-framework) structural unit, hydrogen bonds emanating from the acidic part of the structural unit can be accepted either by O atoms of the basic part of an adjacent structural unit or by O atoms of an interstitial (H_2O) group. In the latter case, the (H_2O) groups distribute the bond valence of an accepted hydrogen bond to O atoms of adjacent structural units. In the absence of interstitial (H_2O) groups, adjacent structural units must link directly through hydrogen bonds from the acidic part of one structural unit to the basic part of the adjacent structural unit. Thus adjacent structural units must arrange themselves such that their acidic and basic parts match each other and promote this linkage. If such an arrangement is not possible, interstitial (H_2O) groups must be present in order to link the acidic and basic part of adjacent structural units. Thus, the number of interstitial (H_2O) groups between neutral structural units depends on the number of hydrogen bonds that cannot be accepted directly by a donor atom of the basic part of the structural unit.

Examples

Rozenite: The structural unit $[M^{2+}(SO_4)(H_2O)_4]$ occurs as a cluster in rozenite, $[Fe^{2+}(SO_4)(H_2O)_4]$, starkeyite, $[Mg(SO_4)(H_2O)_4]$, ilesite, $[Mn^{2+}(SO_4)(H_2O)_4]$, aplowite, $[Co^{2+}(SO_4)(H_2O)_4]$, and boyleite, $[Zn(SO_4)(H_2O)_4]$, and as chains in pentahydrite, $[Mg(SO_4)(H_2O)_4](H_2O)$, siderotil, $[Fe^{2+}(SO_4)(H_2O)_4](H_2O)$, and jokokuite, $[Mn^{2+}(SO_4)(H_2O)_4](H_2O)$. Why is there an interstitial (H_2O) group between the chain structural-units and not between the cluster structural-units? In order to answer this question, we examine the arrangements of the structural units and the hydrogen bonding between their acidic and basic components.

Figures 4a and c show the arrangement of cluster structural units in rozenite (Baur 1960). We may emphasize aspects of their polarity more clearly if we represent each cluster by a square with the polarity indicated by + (acid) and – (basic) symbols, respectively (Figs. 4b, d). In the (100) plane (Fig. 4b), squares adjacent in the *b* direction have opposite polarities. In Figure 4b, the squares to the left have their ++ signs arranged NW–SE, whereas the next (central) square has its ++ signs arranged NE–SW. Hence squares adjacent in the *b* direction can match their polarities only if adjacent squares are shifted half the repeat distance in the *c* direction. Hydrogen bonds link octahedra with tetrahedra (indicated with dashed lines in Fig. 4a). The arrangement of clusters differs in the (010) plane (Figs. 4c, d). Here, the polarity of squares adjacent in the *a* direction is the same (they both have their ++ signs arranged NW–SE), and hence squares adjacent in the *a* direction match with no shift in the *c* direction (Fig. 4d). The clusters are slightly tilted along the *c* axis, which allows formation of a hydrogen bond parallel to the *c* axis. Hence, each hydrogen bond emanating from the acidic part can be accepted by an O atom of the basic part (Figs. 4c, d).

Pentahydrite: Figure 5 shows the arrangement of chain structural units in pentahydrite, $Fe^{2+}(SO_4)(H_2O)_4]$ (H_2O) (Baur & Rolin 1972). In the *ab* plane, the acidic part of the structural unit opposes the basic parts of adjacent structural units (Figs. 5a, b). The tetrahedra (the basic part of the chain) alternately point up and down (in the *a* direction) along the length of the chain. Thus, a hydrogen bond between adjacent chains is possible only where an apex of a tetrahedron points toward the upper (or lower) adjacent chain of polyhedra; the hydrogen bonds are shown in black in Figure 5. At those parts of the structure where the tetrahedra point in the wrong direction to form a hydrogen bond to an adjacent chain, the distance between the acidic and basic parts of the chain is too great for direct hydrogen-bonds to form (Figs. 5a, c) and "bridging" interstitial (H_2O) groups occur here. Thus the acidic part of the chain hydrogen-bonds to an interstitial (H_2O) group, which then hydrogen-bonds to the basic part of the adjacent chain (Figs. 5b, d).

Inspection of these two examples (Figs. 4, 5) shows that acidic and basic parts of adjacent neutral structural units oppose each other. However, the arrangement and the size of the structural units do not always allow direct hydrogen bonding. In this case, interstitial (H_2O) are required to bridge the "gap" between hydrogen-bond acceptors and hydrogen-bond donors. Polarity affects (1) the relative positioning of adjacent structural units, and (2) the presence of interstitial (H_2O) groups.

OXYGEN-COORDINATION NUMBERS IN SULFATE MINERALS WITH $[M^{z+}(SO_4)_K(OH)_M(H_2O)_N]$ STRUCTURAL UNITS

Schindler & Hawthorne (2001a, b) showed that there is a correlation between average basicity and average coordination number of O for structural units in borate minerals. The coordination number of O is a critical issue in the crystal chemistry of oxide and oxysalt minerals. The behavior of these two broad classes of minerals is somewhat different, and we examine this issue next.

Average basicity of a structural unit

Schindler *et al.* (2000) defined the *average basicity* of a structural unit as the average bond-valence sum per O atom contributed by the interstitial species and other structural units. This is the *effective charge* of the structural unit divided by the number of oxygen atoms in the structural unit, where the effective charge is the formal charge of the structural unit as modified by transfer of charge involved in the hydrogen bonds emanating from the structural unit (*i.e.*, 0.20 *vu* for an average hydrogen bond). For example, consider the structural unit of sideronatrite: $[Fe^{3+}(SO_4)_2(OH)]^{2-}$. The effective charge is $(2 + 0.2 \times 1)^- = 2.2^-$, and the number of O atoms in the structural unit is 9; the resulting average basicity = 2.2 / 9 = 0.24 *vu*.

Average coordination number of O versus average basicity

Figure 6a shows the variation of average coordination-number of O and as a function of average basicity. In this plot, data for sulfate structural units with only higher-valent *M*-cations (M^{3+}, M^{4+}) are indicated with red squares, and with M^{2+} cations, by red triangles. The distribution of data shows that O atoms in structural units containing M^{3+} and M^{4+} cations have, on average, lower coordination numbers than those in structural units with M^{2+} cations. Details of the stereochemistry in $[M^{z+}(SO_4)_k(OH)_m(H_2O)_n]$ structural units (Figs. 3a, b) give the reasons for this:

(1) O atoms linking ($M^{3+}\phi_6$) polyhedra, and linking ($M^{3+}\phi_6$) polyhedra and (SO_4) groups (Fig. 3b), have lower coordination numbers than the corresponding O-atoms linking ($M^{2+}\phi_6$) polyhedra and linking ($M^{2+}\phi_6$) and (SO_4) groups (Fig. 3a).

(2) The bond valence of hydrogen bonds involving transformer (H_2O) groups is larger for structural units with M^{3+} cations than for structural units with M^{2+} cations. This reduces the number of bonds at the acceptor O-atoms of the (SO_4) group in structural units containing M^{3+} cations. Hence, the higher the ratio of ($M^{3+}\phi_6$) polyhedra to (SO_4) groups, the lower the average coordination-number of O in structural units containing trivalent cations.

These differences in the average coordination number of O in structural units containing trivalent and divalent cations, respectively, can be better visualized by showing the average basicity of the structural unit as a function of the average coordination-number of O involving bonds *inside* the structural unit, CN_{str} (Fig. 6b). For structural units of similar average basicity, those containing M^{3+} cations have lower average coordination-numbers than those containing M^{2+} cations.

Figure 6c shows the average basicity as a function of the average coordination-number of O in the structural unit calculated from the interstitial bonds (CN_{in}), *i.e.*, the number of bonds to the structural unit divided by the number of O atoms in the structural unit (note that $CN = CN_{str} + CN_{in}$). This correlation shows that the number of incident bonds depends on the average basicity and not on the degree of polymerization of the ($M^{z+}\phi_6$) polyhedra. This is to be expected, as the O atoms of the (SO_4) groups [and not of the ($M^{z+}\phi_6$) groups] are the principal bond-valence acceptors in $[M^{z+}(SO_4)_k(OH)_m(H_2O)_n]$ structural units (Figs. 3a, b).

The positive correlation between average basicity and [CN_{in}] defines a band rather than a single line, in accord with the observation that a specific structural unit usually exhibits a range of mean coordination-numbers for its constituent O atoms. As well as predicting a specific average coordination-number for O atoms in a given structural unit, Figure 6c also predicts the *range of possible average coordination-numbers of O atoms* in a structural unit. Where a specific structural unit occurs in a series of minerals, the O atoms of the structural unit show a range of mean coordination-numbers. Moreover, Figure 6c allows calculation of the range of possible Lewis base-strengths for a specific structural unit.

Structural units in borate minerals

In trying to understand the factors affecting the structure topology and chemical composition of oxysalt minerals that crystallize (predominantly) from aqueous solution, it is of interest to compare groups of structures based on different oxyanions (*e.g.*, sulfates and borates), as these groups exhibit different mechanisms of dealing with variations in chemical and physical conditions. Here, we will briefly compare borate and sulfate minerals (1) because borates can show differences in coordination number ([3] or [4]) of the principal oxyanion, whereas sulfates do not, and (2) borates have been examined previously using the same approach (Schindler & Hawthorne 2001a, b, c).

In borate minerals, the structural units contain only B cations; these are isovalent but can adopt two coordination numbers, [3] and [4]. This difference in coordination of B causes differences in the average B–O bond-valence: 1.0 to 0.75 *vu*. The variation in *average basicity* as a function of CN_{str} and CN_{in} in borate structural units are shown in Figures 7b and c, respectively. The value CN_{str} does not change with

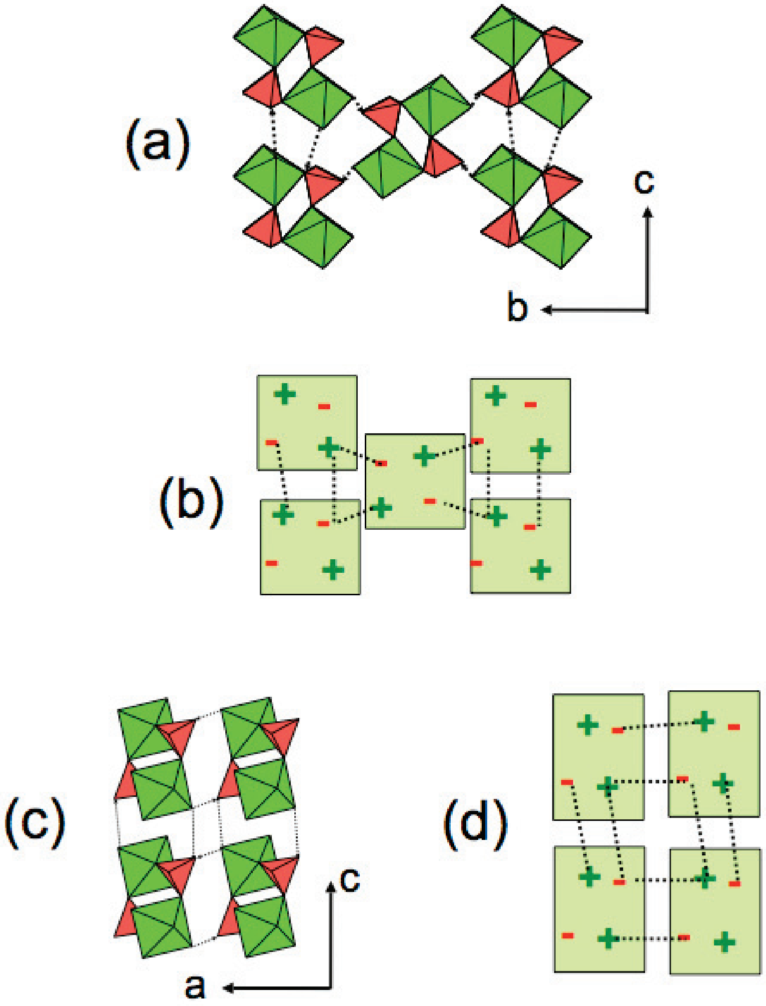

FIG. 4. Arrangement of the [$M^{2+}(SO_4)(H_2O)_4$] cluster structural unit in the mineral rozenite in (a) the *bc* plane, and (b) in the *ac* plane; on the left side, the arrangement of the cluster is indicated with a model of the polyhedra in which the *M* octahedra and sulfate tetrahedra are colored in green and red, respectively; on the right side, the arrangement of the cluster is indicated in the form of a polarity model, at which the position of the (H_2O) groups and O atoms of the sulfate tetrahedra are indicated by green plus and red minus signs. The hydrogen bonds in both models are indicated as dashed lines.

average basicity in borate structural units; it is almost always [2]. This is surprising, as one might expect that O atoms in structural units with a higher proportion of $^{[3]}$B to have lower CN_{str} values than those with a higher proportion of $^{[4]}$B. However, Schindler & Hawthorne (2001b) showed that $^{[4]}$B : $^{[3]}$B correlates with the average basicity; thus, increasing the average bond-valence of B–O bonds by increasing the proportion of $^{[3]}$B is balanced by decreasing average basicity. This can be expressed by the following equation:

$$[B(OH)_4]^- \ (0.45\ vu) + H^+ \\ \rightarrow [B(OH)_3]\ (0.20\ vu) + H_2O \qquad [1]$$

In both structural units, CN_{str} is [2], but the increase of the average bond-valence from 0.75 to 1.0 *vu* is

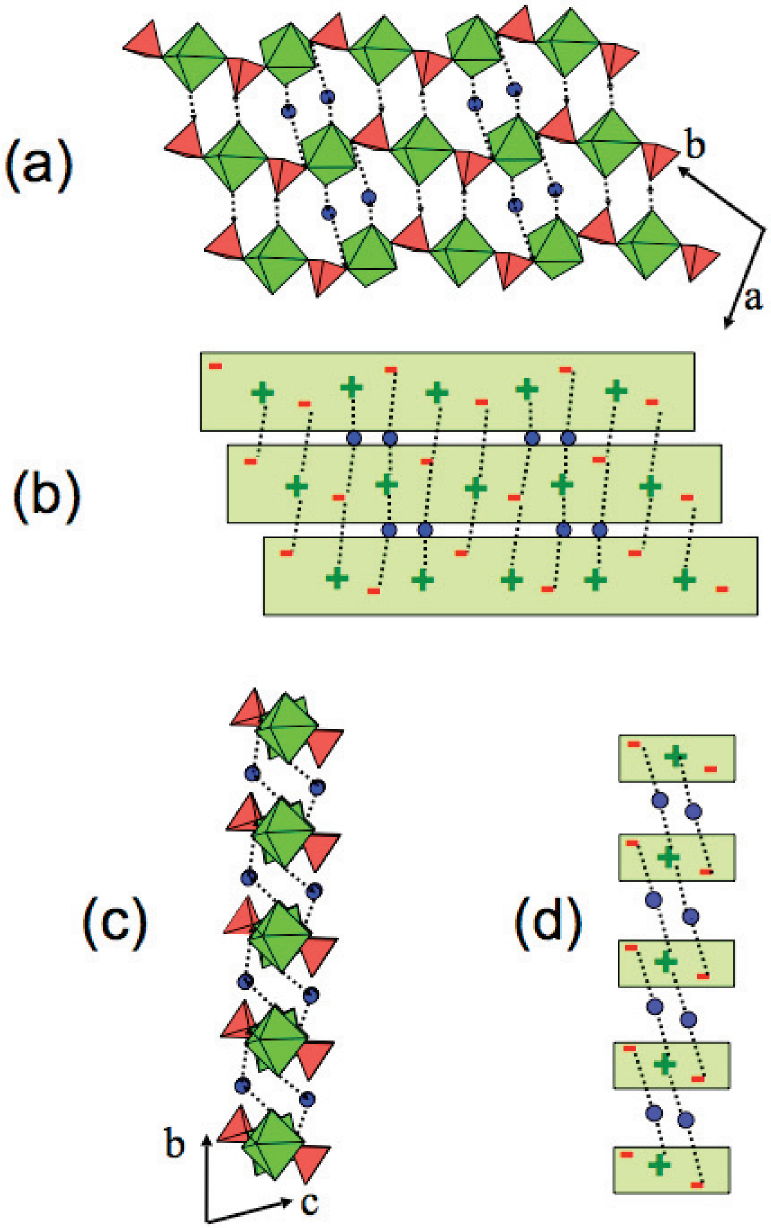

FIG. 5. Arrangement of the [$M^{2+}(SO_4)(H_2O)_4$] chain structural unit in the mineral pentahydrite in (a) the *ab* plane, and (b) in *bc* plane. The color of the polyhedra and plus and negative signs in the polyhedral (left) and polarity model (right) are the same as in Figure 4. The interstitial (H_2O) groups are drawn as blue circles, and the hydrogen bonds are indicated as dashed lines.

balanced by the decrease in average basicity from 0.45 to 0.20 *vu*.

Figure 7c shows the algebraic difference between Figures 7a and b (*cf.* Figs. 6a, b and c):

$$CN - CN_{str} = CN_{in} \qquad (5)$$

Because CN correlates with average basicity and CN_{str} is approximately constant, CN_{in} varies in a similar way to CN as a function of average basicity (*cf.* Figs. 7a and c). In both correlations, the bands of data approach the maximum O-coordination numbers [2] and [4], respectively.

Average basicity versus CN_{in} in sulfate and borate structural units

Comparison of Figures 6c and 7c shows that the bands of data have similar slopes at lower average basicity but different slopes at higher average basicity. Unlike the relation for borate structural units (Fig. 7c), the band of data points for sulfate structural units (Fig. 6c) does not approach any maximum value of CN_{in}. The reason for this is simple: structural units of sulfate and borate minerals with high average basicity have similar average coordination-numbers of O, CN; however, CN_{str} is lower in sulfate minerals than in borate minerals. Hence, more interstitial cations bond to O atoms of structural units in sulfate minerals than is the case in borate minerals.

An example: Polyhalite, $\{K_2Ca_2\}[Mg(SO_4)_4(H_2O)_2]$, contains the structural unit $[Mg(SO_4)_4(H_2O)_2]^{6-}$; the effective charge of the structural unit is $4 \times 0.2 + 6 = 6.8^-$, and the corresponding average basicity is 6.8 / 18 = 0.38 *vu* [based on a bond valence of 0.20 *vu* for the hydrogen bond]. The coordination number of O referred to bonds in the structural unit (CN_{str}) is [1.45], and the overall coordination-number of O is [3.8]; thus CN_{in} is equal to [3.8] – [1.45] = [2.35].

The structural unit $[B_3O_3(OH)_5]^{2-}$ has an average basicity 0.38 *vu* and occurs in minerals such as inyoite, $\{Ca(H_2O)_3(H_2O)\}[B_3O_3(OH)_5]$. The coordination numbers of O in inyoite are [3.8] for CN and [2] for CN_{str} , and hence CN_{in} = [3.8] – [2.0] = [1.80], as compared with [2.35] for a structural unit of identical average basicity in polyhalite.

Lewis Acidities of Interstitial Complexes in Sulfate Minerals

Sulfate minerals can be divided into two major groups: (1) those having isolated (SO_4) groups as structural units, and (2) those having complex $[M^{z+}(SO_4)_k(OH)_m(H_2O)_n]$ groups as structural units (Hawthorne *et al.* 2000). Tables 1 and 2 list compositions and Lewis acidities (LA) of interstitial complexes in selected sulfate minerals with structural units $[(SO_4)]$ and $[M^{z+}(SO_4)_k(OH)_m(H_2O)_n]$, respectively. The chemical compositions of the minerals are given as $M_a(H_2O)_{d+e}[MO(SO_4)(OH)(H_2O](H_2O)_g$, whereas $d + e$ are the number of (H_2O) groups bonded, and g is the number of (H_2O) groups not bonded, to the interstitial M cation [d are transformer and e are non-transformer (H_2O) groups]. The interstitial complex is written in the form $\{M_a(H_2O)_d(H_2O)_e(H_2O)_g\}$, where the different types of (H_2O) groups are given only if necessary. For example, if there are only transformer (H_2O) groups, the interstitial complex is written $\{M(H_2O)_d\}$; if there is one $(H_2O)_g$ group but no $(H_2O)_d$ and $(H_2O)_e$ groups, the interstitial complex is written as $\{(H_2O)_0(H_2O)_0(H_2O)_1\}$.

There are only a few sulfate minerals in which the interstitial hydrogen bonding is not resolved. In these cases, we used stereochemical constraints to determine the probable interstitial hydrogen bonding. We do not consider structural data of minerals in which cations occur at Wyckoff positions of high symmetry; this is the case for some minerals of the alunite supergroup, $(M^+, M^{2+})[M^{3+}{}_3(TO_4)_2(OH)_6]$, M^+ = K, Na, Ag^+,Tl^+, $(NH_4)^+$, $(H_3O)^+$; M^{2+} = Ca, Pb^{2+}, Sr, Ba; M^{3+} = Al, Fe^{3+}, $T = S^{6+}$. In this group, all M^+ and M^{2+} cations occur, at least in principle, at the Wyckoff position 3*a* of space group $R\bar{3}m$. This results in formal [12]-coordination of cations such as $(H_3O)^+$, $(NH_4)^+$, Ag^+, and Na^+, which normally occur in [3], [4] and [6] coordination, respectively. It is possible that the formal coordination-number of [12] is effectively reduced by either static or dynamic displacement.

Lewis acidity of interstitial complexes associated with $[SO_4]$ structural units

When developing this bond-valence approach for borate minerals, Schindler & Hawthorne (2001a, b), following Brown (1981), assigned an average bond-valence of 0.20 *vu* to a hydrogen bond, used this value to calculate the effective charge of a structural unit and, in turn, the average basicity and range in Lewis basicity of a structural unit. Considering the transformer effect of (H_2O) groups bonded to divalent and trivalent cations in the structural unit, the bond valences of these hydrogen bonds are 0.17 and 0.25 *vu*, respectively (Fig. 3). These values are more exact than the previous estimate of 0.20 *vu* and also better represent the difference in polarity between structural units containing divalent and trivalent M-cations. Furthermore, the hydrogen bonds emanating from the $M^{3+}(H_2O)_n$ and $M^{2+}(H_2O)_n$ parts of the structural unit affect the Lewis acidity of the interstitial complex because two hydrogen bonds of 0.25 *vu* have the same aggregate bond-valence as three hydrogen bonds of 0.17 *vu*. Hence, we should use these values (0.17 and 0.25 *vu*) for calculation of the Lewis acidity. However, the dilemma is that we cannot use these values for calculation of the range in Lewis basicity, because the degree of correlation between average basicity and $[CN_{in}]$ is much less than the correlation shown in Figure 6c. This means that we have to work with two types of Lewis acidity: one based on an average hydrogen-bond-valence of 0.20 *vu* (to be compared with the calculated range in Lewis basicity), and the other based on hydrogen bonds of 0.17 and 0.25 *vu* (to be used to examine the distribution of Lewis acidities of interstitial complexes in sulfate minerals).

In order to calculate the latter type of Lewis acidity, we have to determine the number of transformer (H_2O) groups in $M^{3+}(H_2O)_n$ and $M^{2+}(H_2O)_n$, because each constituent (H_2O) group is not necessarily a transformer (H_2O) group. Inspection of the structures of complex sulfate minerals (Table 2) shows that in some cases, interstitial cations bond to O atoms of (H_2O) groups in the structural unit, changing the bond valence of the hydrogen bond emanating from the (H_2O) group of the structural unit and, in turn, the Lewis acidities of the acidic part of the structural unit and the interstitial complex. A simple way to calculate this "modified" Lewis acidity is shown in Figure 8. Consider the complex sulfate ${}^{[z]}A^{+}_{2}\,[M^{2+}(SO_4)(H_2O)]$. In the ideal case, the interstitial cations ${}^{[z]}A^{+}$ bond only to O atoms of the sulfate group. The Lewis acidity of the interstitial complex and acidic part of the structural unit is $(2 + 2 \times 0.17) / (z + 2)$ (Fig. 8a).

Next, let us consider the case where one of the A cations bonds also to an (H_2O) group of the structural unit. In this case, the bond valence of the hydrogen bond emanating from the (H_2O) group is $0.17 + 0.5s$, whereas s is the unknown bond-valence of the A–(OH_2) bond. The bond valence of the hydrogen bond emanating from the (H_2O) group is $0.17 + 0.5 \times 1/Z$. Inspection of Figure 8b shows that knowledge of the exact value of s is not necessary to calculate the Lewis acidity because only Z, the formal charge of the interstitial cation, appears in the expression for it (Figs. 8a, b). Thus, we can calculate the Lewis acidity of the interstitial complex and the acidic part of the structural unit if we subtract the number of those bonds from the number of bonds emanating from the interstitial cation and the acidic part of the structural unit.

The Lewis basicity of the (SO_4) oxyanion is 0.17 *vu*. Following the valence-matching principle, the interstitial complexes should have Lewis acidities close to 0.17 *vu*. Figure 9b shows the frequency of Lewis acidities of interstitial complexes in sulfate minerals with isolated (SO_4) groups (Fig. 9a) as their structural unit (Table 1). Here, the Lewis acidities range from 0.11 to 0.25 *vu*, with maxima at 0.17 and 0.20 *vu*. The highest Lewis acidity (0.25 *vu*) occurs where each O-atom of the (SO_4) group receives, on average, two additional bonds from the interstitial complex (Fig. 9a). The minimum Lewis acidity of an interstitial complex (0.11 *vu*) occurs, on average, where two atoms of O of the (SO_4) group receive five additional bonds and two atoms of O receive four additional bonds from the interstitial complex. Interstitial complexes with Lewis acidities of 0.25 and 0.17 *vu* result in average coordination-numbers for O of [3] and [4], respectively (Fig. 9b). If Lewis acidities occur between 0.17 and 0.25 *vu*, the corresponding average coordination-number of O in the (SO_4) group is between [3] and [4]. Consider an interstitial complex with a Lewis acidity of 0.20 *vu*: there are ten interstitial bonds to four O-atoms of one (SO_4) group, which results in an average coordination of $(10 + 4) / 4 = [3.5]$ (Fig. 9b) for O.

The high frequency of interstitial complexes with a Lewis acidity of 0.17 *vu* corresponds to that expected from the valence-matching principle. However, we did not expect a high frequency of interstitial complexes with a Lewis acidity of 0.20 *vu* (Fig. 9b). This maximum may be an indication of a particularly stable configuration in sulfate minerals, which is supported by the fact that geologically widespread minerals such as anglesite, $\{Pb\}[SO_4]$, barite, $\{Ba\}[SO_4]$, celestine, $\{Sr\}[SO_4]$, and gypsum, $\{Ca(H_2O)_2\}[SO_4]$, contain interstitial complexes with Lewis acidities of 0.20 *vu* (Table 1). Furthermore, anglesite, barite and celestine are less soluble than many other sulfate minerals, and gypsum is formed by the reaction of anhydrite, $\{Ca\}[SO_4]$ (0.25 *vu*), and bassanite, $\{Ca(H_2O)_{0.5}\}[SO_4]$ (0.22 *vu*), with water. These systematics suggest a relation between the type of coordination of the anions of the sulfate group and relative solubility.

Lewis acidities of interstitial complexes associated with $[M^{z+}(SO_4)_k(OH)_m(H_2O)_n]$ structural units

Figure 10a shows the frequency of Lewis acidities in selected sulfate minerals of this type (Table 2). The Lewis acidities extend from 0.10 to 0.25 *vu*, with maxima at 0.13, 0.17, 0.20–0.21 and 0.25 *vu*. The occurrence of these maxima can be explained in light of the coordination number of O in the (SO_4) group. Lewis acidities of 0.25, 0.17 and 0.13 *vu* correspond to average coordination-numbers of [3], [4] and [5], respectively (Fig. 3). A Lewis acidity of 0.20–0.21 *vu* occurs if two atoms of O of a sulfate group (which do not bond to an M^{z+} atom) are [3]- and [4]-coordinated, respectively (Fig. 3). In which way the Lewis acidity corresponds to 0.17 and 0.20–0.21 *vu* depends on the number of acceptor O-atoms between the acidic and basic components of the structural unit [*i.e.*, O atoms that are shared between $(M^{z+}\phi_6)$ octahedra and (SO_4) tetrahedra]. The distribution of Lewis-acidity values (Fig. 10a) indicates that the coordination numbers of O atoms in (SO_4) groups determines the Lewis acidity of the interstitial complex and the acidic part of the structural unit in sulfate minerals.

Lewis acidities in all sulfate minerals with $[SO_4]$ structural units

One can also calculate the Lewis acidities of interstitial complexes in minerals in which only (SO_4) groups are considered as the structural unit and all $(M^{z+}\phi_6)$

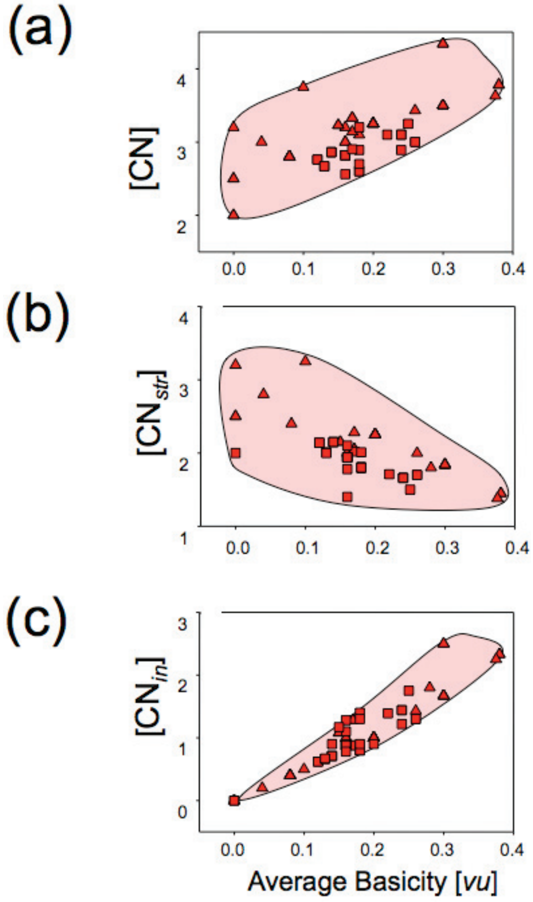

FIG. 6. Variation in various types of coordination numbers of O atoms as a function of average basicity in sulfate minerals: (a) all bonds in the structure [*CN*], (b) bonds in the structural unit [*CN$_{str}$*], and (c) bonds from the interstitial complex [*CN$_{in}$*]. Red squares: structural units containing only trivalent or tetravalent *M*-cations; red triangles: structural units containing divalent *M*-cations.

polyhedra are considered as part of the interstitial complex. Figure 10b shows their distribution, together with the Lewis acidities of sulfate minerals with isolated (SO_4) groups (Table 1). Here, the Lewis acidities range from 0.10 to 0.50 *vu*; note that the two minerals with Lewis acidities of 0.50 *vu* are not included in Figure 10b. Maxima occur at 0.17, 0.20 and 0.25 *vu*, and subsidiary maxima occur at 0.18, 0.22, 0.28, 0.30 and 0.33 *vu*. The Lewis acidities 0.28 (more exactly 0.286), 0.30 and 0.33 *vu* occur if the (SO_4) group receives 7, 6.5 and 6 bonds from the interstitial cations, respectively, with corresponding average coordination-numbers of [2.75], [2.625] and [2.50] for the O atoms.

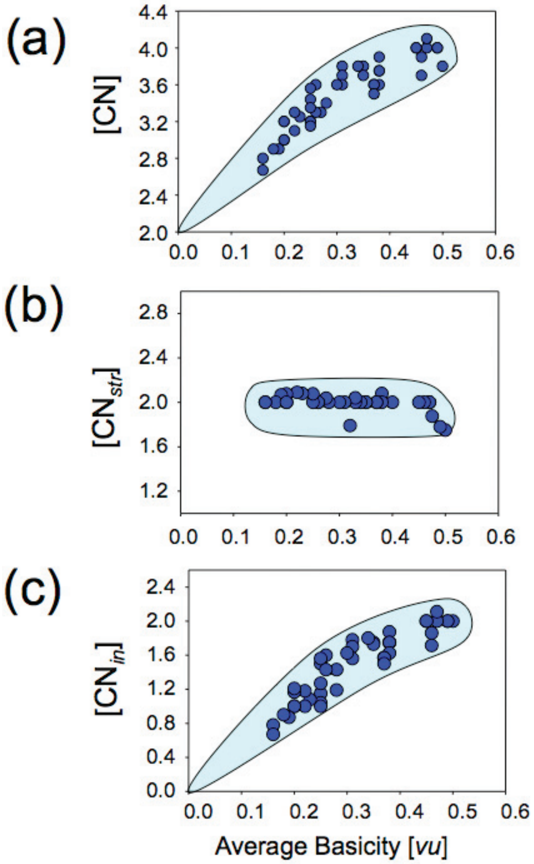

FIG. 7. Variation in various types of coordination numbers of O atoms as a function of average basicity in borate minerals: (a) all bonds in the structure [*CN*], (b) bonds in the structural unit [CN$_{str}$], and (c) bonds in the interstitial complex [*CN$_{in}$*].

PREDICTION OF INTERSTITIAL COMPLEXES IN SULFATE MINERALS

Figure 6c shows the variation in average basicity as a function of [*CN$_{in}$*] for the sulfate minerals of Table 2. This relation can be used to calculate the range in Lewis basicity of a specific structural unit, and Figure 1 can then be used to predict the interstitial complexes compatible with that specific structural unit. Let us consider sulfate minerals that have the following two structural units in common: $[M^{2+}(SO_4)_2(H_2O)_4]^{2-}$ (M = Mg, Ni, Zn, Fe^{2+}) and $[M^{3+}(SO_4)_2(OH)]^{2-}$ ($M = Fe^{3+}$).

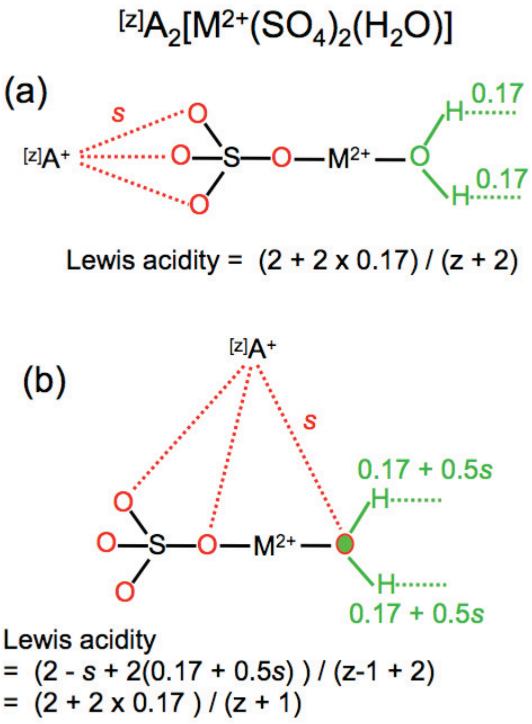

FIG. 8. Bond-valence structure of the idealized structure of $^{[7]}A^{+}[^{[6]}M^{2+}(SO_4)_2(H_2O)]$; the acidic and basic components of the structural units are colored green and red, respectively. (a) The interstitial cation *A* bonds exclusively to O atoms of the basic part; (b) the interstitial cation *A* bonds to O atoms of the basic and acidic parts (see text for details).

The structural unit $[M^{2+}(SO_4)_2(H_2O)_4]^{2-}$ *(M = Mg, Ni, Zn,* Fe^{2+}*)*

This structural unit occurs in blödite, $\{Na_2\}[Mg(SO_4)_2(H_2O)_4]$, nickelblödite, $\{Na_2\}[Ni(SO_4)_2(H_2O)_4]$, changoite, $\{Na_2\}[Zn(SO_4)_2(H_2O)_4]$, leonite, $\{K_2\}[Mg(SO_4)_2(H_2O)_4]$, mereiterite, $\{K_2\}[Fe(SO_4)_2(H_2O)_4]$, and römerite, $\{Fe^{2+}(H_2O)_6\}[Fe^{2+}(SO_4)_2(H_2O)_4]$. The effective charge of the structural unit is $(2 + 0.2 \times 8)^{-} = 3.6^{-}$, and the number of O atoms in the structural unit is 12; hence the average basicity is 3.6 / 12 = 0.30 *vu* (based on a hydrogen bond-valence of 0.20 *vu*).

The maximum and minimum numbers of bonds to the structural unit are the numbers of O atoms in the structural unit times the minimum and maximum values of $[CN_{in}]$, respectively. Inspection of Figure 6c shows that the corresponding range in $[CN_{in}]$ for the structural unit $[M^{2+}(SO_4)_2(H_2O)_4]^{2-}$ is [1.65]–[2.50] (for an average basicity of 0.30 *vu*). Thus there are a maximum of 12 × [2.50] = 30 and a minimum of 12 × [1.65] = 20 bonds. This results in a maximum Lewis basicity of (8 × 0.20 + 2) / 20 = 0.18 *vu* and a minimum Lewis basicity of (8 × 0.20 + 2) / 30 = 0.12 *vu*.

Figure 11a shows the variation in Lewis acidity of a general interstitial complex as a function of cation charge, cation coordination-number, and the number of transformer (H_2O) groups, with the range of Lewis basicity of the $[M^{2+}(SO_4)_2(H_2O)_4]^{2-}$ structural unit marked by a yellow box. Where the Lewis-acidity curves intersect the range of Lewis basicity of the structural unit, the valence-matching principle is satisfied, and a stable structure can form. First, consider interstitial monovalent cations. For coordination numbers [12] and above, the curves do not intersect the range of Lewis basicity of the structural unit, and monovalent cations cannot occur. For coordination numbers [11] and [9] to [5], a monovalent cation can occur with 0, 0–2, 0–3, 0–4, 0–5 and 1–4 transformer (H_2O) groups present, respectively (Table 3). For divalent interstitial

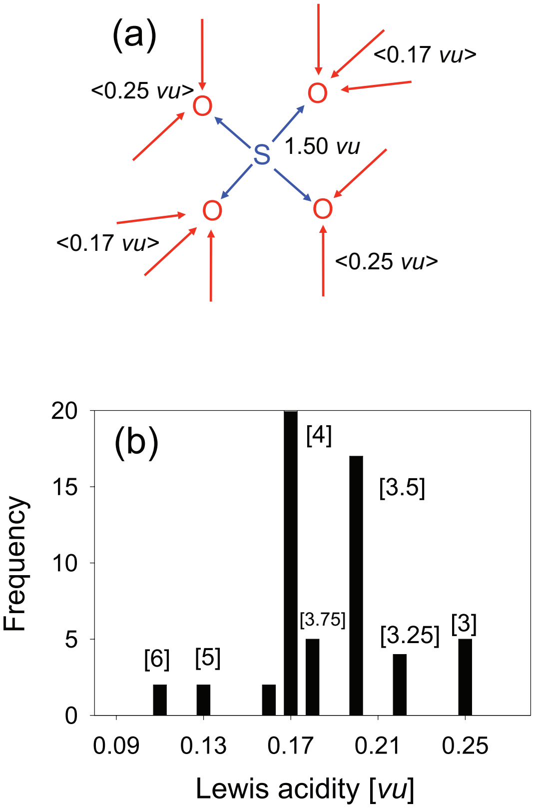

FIG. 9. (a) Possible bond-valence arrangements around an $(SO_4)^{2-}$ group. (b) Variation in Lewis acidity of interstitial complexes in selected sulfate minerals with isolated $(SO_4)^{2-}$ groups as their structural unit; the corresponding mean coordination-numbers of the O atoms of the $(SO_4)^{2-}$ group also are shown.

cations, $^{[6]}M^{2+}$ is only possible if it does not bond to any anion of the structural unit (*e.g.*, if it occurs as isolated $[^{[6]}M^{2+}(H_2O)_6]$ or $[^{[6]}M^{2+}(OH)_m(H_2O)_n]^{(2-m)+}$ groups), and hence it is possible with 5–6 transformer (H_2O) groups, $^{[7]}M^{2+}$ is possible with 5–7 transformer (H_2O) groups, $^{[8]}M^{2+}$ is possible with 4–8 transformer (H_2O) groups, and $^{[9]}M^{2+}$ is possible with 3–5 transformer (H_2O) groups.

As discussed above, one can calculate an exact value of the Lewis acidity for the interstitial complex and the acidic part of the structural unit if one considers the transformer effect of the (H_2O) groups in the acidic part of the structural unit. For the structural unit $[M^{2+}(SO_4)_2(H_2O)_4]^{2-}$, the average bond-valence of each hydrogen bond is 0.17 *vu*; on the basis of this value, the effective charge of the interstitial complex and the acidic part of the structural unit is $2 + 8 \times 0.17 = 3.36$ *vu*. The Lewis acidity is the effective charge divided by the number of emanating bonds. In the case of the observed maxima in Lewis acidity, 0.13, 0.17, 0.21 and 0.25 *vu*, the corresponding numbers of bonds are $3.36 / 0.13 = 26$, $3.36 / 0.17 = 20$, $3.36 / 0.21 = 16$ and $3.36 / 0.25 = 13.5$, respectively. There are eight hydrogen bonds emanating from the acidic part of the structural unit, and thus the most probable numbers of bonds from the interstitial complex to the O atoms of the basic part of the structural units are $26 - 8 = 18$, $20 - 8 = 12$, $16 - 8 = 8$ and $13.5 - 8 = 5.5$. The average bond-valence in the latter case is $2 / 5.5 = 0.36$ *vu*, which is above the "cut-off" between the interstitial complex and the structural unit (see above). The numbers 12 and 8 would occur for two monovalent cations in [6]-coordination, where either the O atoms of the basic part accept all 12 bonds or only eight bonds, and the remaining four bonds are accepted by the O groups of the acidic part of the structural unit. This is, for example, the case in blödite, nickelblödite and changoite, where the two $^{[6]}$Na in the interstitial complex $\{^{[6]}Na_2(H_2O)_0\}$ bond to eight atoms of O of the basic part and to four atoms of O of the acidic part of the structural unit. Eighteen bonds will occur for two monovalent cations in [11]-coordination, where the O atoms of the basic and acidic parts accept 18 and 4 bonds, respectively. This is, for example, the case in leonite and mereiterite, both of which have the interstitial complex $\{^{[11]}K(H_2O)_0\}$. For divalent cations, probable interstitial complexes are those with $^{[6]}M^{2+}$ and six transformer (H_2O) groups. Here, the O atoms of the basic and acidic parts accept either 12 and 0 or 8 and 4 hydrogen bonds, respectively.

The structural unit $[Fe^{3+}(OH)(SO_4)_2]^{2-}$

This structural unit occurs in sideronatrite, $\{Na_2(H_2O)_3\}[Fe^{3+}(SO_4)_2(OH)]$, metasideronatrite, $\{Na_4(H_2O)_3\}[Fe^{3+}(SO_4)_2(OH)]_2(H_2O)_3$, guildite, $\{^{[4+2]}Cu^{2+}(H_2O)_4\}$ $[Fe^{3+}(SO_4)_2(OH)]$, and chaidamuite, $\{^{[6]}Zn(H_2O)_4\}[Fe^{3+}(SO_4)_2(OH)]$. The effective charge of this structural unit is $(2 + 0.2 \times 1)^- = 2.2^-$, and the number of O atoms in the structural unit is 9; hence the average basicity is $2.2 / 9 = 0.24$ *vu*. Using this value in combination with Figure 6c, we may derive the minimum and maximum possible values of CN_{in}: [1.10] – [1.75]. For CN_{in} = [1.10], there are $1.1 \times 9 = 10$ interstitial bonds. The structural unit does not contain any transformer (H_2O) groups, and the corresponding Lewis basicity is $2.2 / 10 = 0.22$ *vu*. Following the same calculation for the upper limit of CN_{int} gives the range in Lewis basicity of the $[M^{3+}(SO_4)_2(OH)]$ structural unit: 0.14–0.22 *vu*.

Using Figure 1, we can predict the range in chemical composition for possible interstitial complexes. Two interstitial monovalent cations are possible for coordination numbers [5] to [7] with 0–2.5, 0–1.5 and 0–0.5 transformer (H_2O) groups per cation, respectively (Table 3). For divalent interstitial cations, $^{[6]}M^{2+}$ is possible with 3–6 transformer (H_2O) groups, $^{[7]}M^{2+}$ is possible with 2–7 transformer (H_2O) groups, $^{[8]}M^{2+}$ is possible with 1–7 transformer (H_2O) groups, and $^{[9]}M^{2+}$ is possible with 0–6 transformer (H_2O) groups. Examination of the minerals listed in Table 2 shows that almost

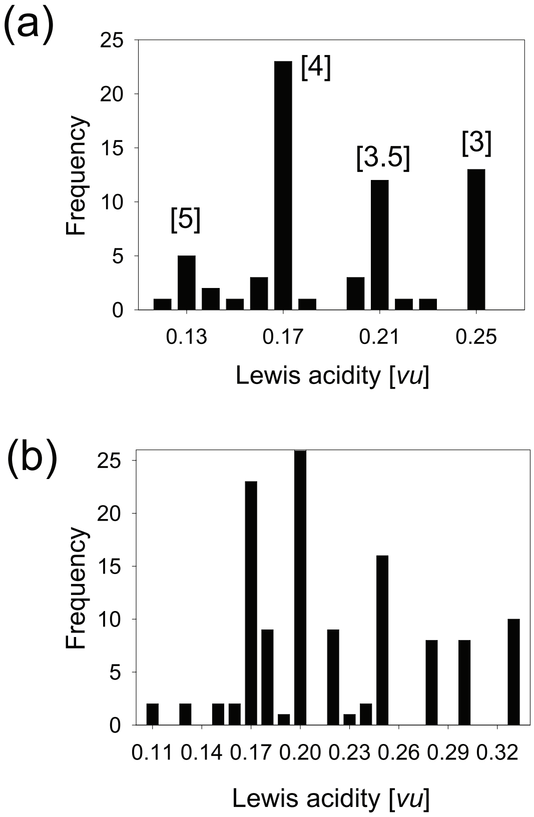

FIG. 10. Variation in Lewis acidity of interstitial complexes in sulfate minerals with (a) $[M^{z+}(SO_4)_k(OH)_m(H_2O)_n]$ structural units, and (b) $[SO_4]$ structural units.

TABLE 3. AVERAGE BASICITY, PREDICTED COORDINATION-NUMBER OF OXYGEN [CN_{in}], RANGE IN LEWIS BASICITY , AND PREDICTED AND MOST PROBABLE INTERSTITIAL COMPLEXES FOR THE STRUCTURAL UNITS [$M^{2+}(H_2O)_4(SO_4)_2]^{2-}$ and [$M^{3+}(OH)(SO_4)_2]^{2-}$

Structural unit	Average basicity [*vu*]	Predicted [CN_{in}]	Range in Lewis basicity [*vu*]	Predicted interstitial complexes*	Most probable interstitial complexes*	Observed interstitial complexes in minerals
$[M^{2+}(SO_4)_2(H_2O)_4]^{2-}$	0.3	1.65–2.50	0.12–0.18	$\{^{[5]}M^{+}_{2}(H_2O)_{2-8}\}^{2+}$	$\{^{[5]}M^{+}_{2}(H_2O)_{1}\}^{2+}$	
				$\{^{[6]}M^{+}_{2}(H_2O)_{0-10}\}^{2+}$	$\{^{[6]}M^{+}_{2}(H_2O)_{0}\}^{2+}$	$\{^{[6]}Na_2\}^{2+}$; blödite, nickelblödite, changoite
				$\{^{[8]}M^{+}_{2}(H_2O)_{0-6}\}^{2+}$	$\{^{[8]}M^{+}_{2}(H_2O)_{2}\}^{2+}$	
				$\{^{[11]}M^{+}_{2}(H_2O)_{0}\}^{2+}$	$\{^{[11]}M^{+}_{2}(H_2O)_{0}\}$	$\{^{[11]}K_2\}^{2+}$; leonite mereiterite
				$\{^{[6]}M^{2+}(H_2O)_{6}\}^{2+}$	$\{^{[6]}M^{2+}(H_2O)_{6}\}^{2+}$	
				$\{^{[7]}M^{2+}(H_2O)_{5-7}\}^{2+}$	$\{^{[7]}M^{2+}(H_2O)_{5}\}^{2+}$	
				$\{^{[8]}M^{2+}(H_2O)_{4-8}\}^{2+}$	$\{^{[8]}M^{2+}(H_2O)_{4}\}^{2+}$	
				$\{^{[9]}M^{2+}(H_2O)_{3-9}\}^{2+}$	$\{^{[9]}M^{2+}(H_2O)_{3}\}^{2+}$	
$[M^{3+}(SO_4)_2(OH)]^{2-}$	0.24	1.10–1.75	0.14–0.22	$\{^{[5]}M^{+}_{2}(H_2O)_{0-5}\}^{2+}$	$\{^{[5]}M^{+}_{2}(H_2O)_{0-1}\}^{2+}$	
				$\{^{[6]}M^{+}_{2}(H_2O)_{0-3}\}^{2+}$	$\{^{[6]}M^{+}_{2}(H_2O)_{0}\}^{2+}$	$\{^{[6]}Na_2\}^{2+}$; sideronatrite, metasideronatrite
				$\{^{[8]}M^{+}_{2}\}^{2+}$: not possible		
				$\{^{[9]}M^{+}_{2}\}^{2+}$: not possible		
				$\{^{[6]}M^{2+}(H_2O)_{3-6}\}^{2+}$	$\{^{[6]}M^{2+}(H_2O)_{4-6}\}^{2+}$	$\{^{[4+2]}Cu^{2+}(H_2O)_4\}^{2+}$; guildite $\{^{[6]}Zn(H_2O)_4\}^{2+}$; chaidamuite
				$\{^{[8]}M^{2+}(H_2O)_{1-7}\}^{2+}$	$\{^{[8]}M^{2+}(H_2O)_{2-4}\}^{2+}$	
				$\{^{[9]}M^{2+}(H_2O)_{0-6}\}^{2+}$	$\{^{[9]}M^{2+}(H_2O)_{1-3}\}^{2+}$	

* With the number of transformer (H_2O) groups.

all O atoms of the acidic part of the Fe^{3+} structural units are transformer (H_2O) groups. Hence, the frequency of Lewis acidities can be used more effectively than in the case of structural units containing M^{2+} cations, because we do not have to consider bonding between the interstitial complex and the O atoms of the acidic part. Using the range in Lewis basicity of the structural unit and the frequency of Lewis acidities, probable Lewis acidities of the interstitial complexes are 0.17, 0.20–0.21 and (perhaps) 0.13 *vu*. The corresponding chemical compositions for the interstitial complexes are as follows: $^{[5]}M^{+}$ cations with one transformer (H_2O) group, $^{[6]}M^{+}$ cations with no transformer (H_2O) groups, $^{[6]}M^{2+}$ cations with either 2, 4 or 6 transformer (H_2O) groups, $^{[7]}M^{2+}$ cations with 1, 3 or 5 transformer (H_2O) groups, $^{[8]}M^{2+}$ cations with 0, 2 or 4 transformer (H_2O) groups, and $^{[9]}M^{2+}$ cations with 1 or 3 transformer (H_2O) groups. As indicated in Table 3, all minerals of this group conform to these predictions: both sideronatrite and metasideronatrite have an interstitial complex $\{^{[6]}Na_2(H_2O)_0....\}$, guildite has an interstitial complex $\{^{[6]}Cu^{2+}(H_2O)_4\}$, and chaidamuite has an interstitial complex $\{^{[6]}Zn(H_2O)_4\}$.

The generalized structural unit $[^{[m]}M_a(SO_4)_b(OH)_c(H_2O)_d]$

The above calculations for the structural units $[M^{2+}(SO_4)_2(H_2O)_4]^{2-}$ (M = Mg, Ni, Zn, Fe^{2+}) and $[Fe^{3+}(SO_4)_2(OH)]^{2-}$ illustrate how we can explain aspects of the interstitial complex of a mineral, given its structural unit. The results of calculations for all sulfate minerals with $[^{[m]}M_a(SO_4)_b(OH)_c(H_2O)_d]^{z-}$ structural units are shown in Table 4, where they are compared with the observed interstitial complexes.

For some structural units, the predicted interstitial complexes vary over a wide range of cations or transformer (H_2O) groups. In order to predict more exact compositions of interstitial complexes, we can use the frequency of Lewis acidities to calculate the most probable number of interstitial bonds. As mentioned above, the most probable number of bonds to O atoms of the basic part of structural units containing M^{2+} cations is not necessarily equal to the number of bonds emanating from the interstitial complex, because O atoms in the acidic part of these structural units are also potential acceptors of bonds from the interstitial complex. In

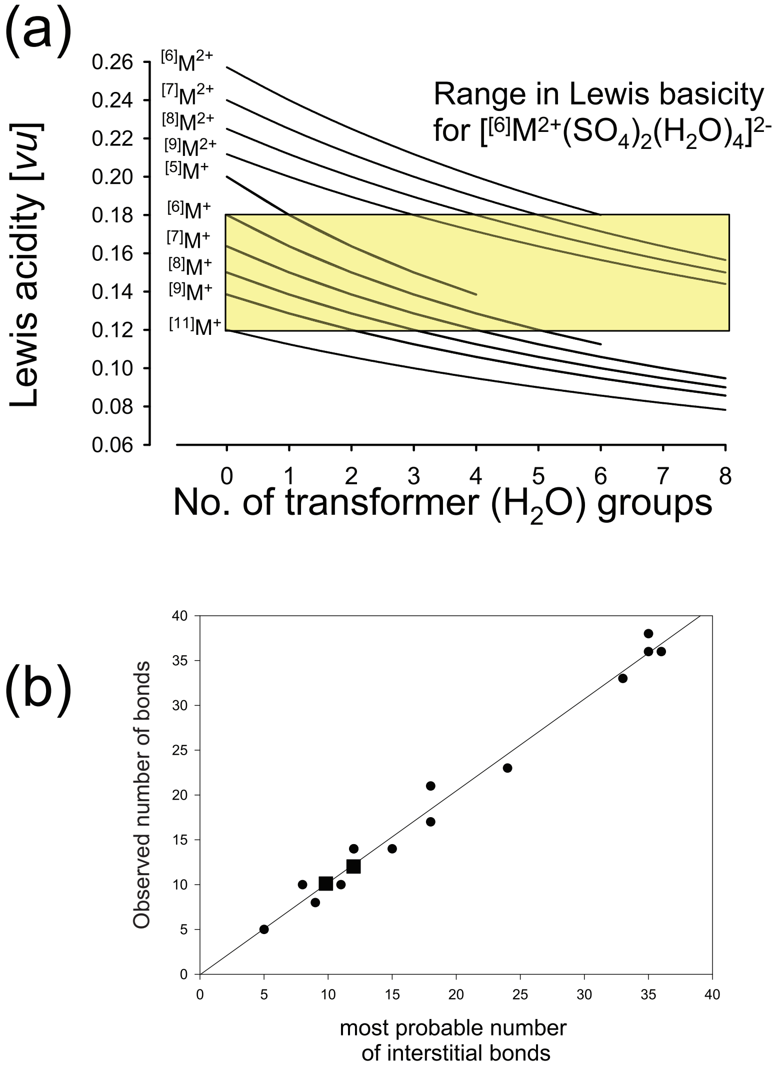

FIG. 11. (a) Variation in Lewis acidity of a generalized interstitial complex with the number of transformer (H_2O) groups for monovalent, divalent and trivalent cations in selected coordinations, and showing the range in Lewis basicity for $[^{[6]}M^{2+}(SO_4)_2(H_2O)_4]^{2-}$. (b) Comparison of the predicted and observed number of bonds from the interstitial complex to the structural unit in sulfate minerals with structural units of the form $[M_a(SO_4)_b(OH)_c(H_2O)_d]^{e-}$.

the case of structural units containing M^{3+}, M^{4+}, M^{5+} and M^{6+} cations, the most probable number of bonds can be seen as the most likely number of bonds emanating from the interstitial complex, because the O atoms in the acidic part of these structural units are almost always transformer (H_2O) groups. For example, minerals of the copiapite group have the structural unit $[M^{3+}{}_2(SO_4)_3(OH)(H_2O)_4]_2{}^{2-}$ (Table 2). Maximum frequencies of Lewis acidity occur at 0.17, 0.20–0.21 and 0.25 *vu*. The corresponding numbers of interstitial bonds are 6.4 / 0.17 = 38, 6.4 / 0.21 = 30 and 6.4 / 0.25 = 26, respectively. There are 18 interstitial hydrogen bonds from the structural unit, and the most probable numbers of bonds from the interstitial complex to the structural unit are 38 – 18 = 20, 30 – 18 = 12 and 26 – 18 = 8, which are in accord with the observed number of 12 interstitial bonds in copiapite.

For each structural unit, the most probable and the observed numbers of bonds from the interstitial complex to the structural unit are listed in Table 4. In Figure 11b, we compare these values, and show that, using the frequency of Lewis-acidity values, one can predict the number of interstitial bonds quite closely.

The largest deviations between predicted and observed number of bonds occur for structural units in which the central *M*-cations are not in regular octahedral coordination, *e.g.*, structural units with Jahn–Teller-distorted $(Cu^{2+}\phi_6)$ polyhedra. Eby & Hawthorne (1993) showed that virtually all $(Cu^{2+}\phi_6)$ octahedra in Cu^{2+} oxysalt minerals have a [4 + 2] arrangement: the mean Cu^{2+}–O(equatorial) bond-length is 1.97 Å, and the corresponding mean bond-valence is 0.40 *vu*; the mean Cu^{2+}–O(apical) bond-length is 2.45 Å, and the corresponding mean bond-valence is 0.10 *vu*. In sulfate structural units, the apical bonds link either to (SO_4) groups or to oxyanion-centered O-atoms (see Hawthorne *et al.* 2000). Depending on local bond-valence requirements in the structure, their individual bond-valences vary

TABLE 4. PREDICTED RANGE IN COORDINATION NUMBER OF OXYGEN, LEWIS BASICITY (*vu*), PREDICTED AND OBSERVED INTERSTITIAL COMPLEXES, AND PREDICTED AND OBSERVED NUMBER OF BONDS TO STRUCTURAL UNITS IN SULFATE MINERALS

Structural unit	Average basicity	Predicted CN_{int}	Range in Lewis basicity	Predicted interstitial complexes	Observed interstitial complexes*	Probable	Obs.
						number of bonds	
$[M^{3+}{}_3(SO_4)_6(H_2O)_6]^{3-}$	0.18	0.80–1.45	0.14–0.25	$\{M^{3+}(H_2O)_6\}^{3+}$	$\{^{[6]}Fe^{3+}(H_2O)_6\}^{3+}$	12, 17, 24	12
$[M^{3+}{}_3O(SO_4)_6(H_2O)_3]^{5-}$	0.22	0.90–1.55	0.15–0.26	$\{^{[9]}M^{+}{}_5\}^{5+}$: not possible $\{^{[6]}M^{+}(H_2O)_{0-8}(H_2O)_{0-30}\}^{5+}$ $\{^{[6]}M^{2+}{}_{2.5}(H_2O)_{4-15}(H_2O)_{0-11}\}^{5+}$	$\{^{[9]}K_2{}^{[6]}Na_6Fe^{2+}(H_2O)_6\}^{10+}$	20, 25, 33	33
$[^{[4+2]}Cu^{2+}(SO_4)_2(H_2O)_2]^{2-}$	0.28	1.45–1.90	0.16–0.20	$\{^{[7]}M^{+}{}_2(H_2O)_{0-1}(H_2O)_{0-14}\}^{2+}$	$\{^{[7]}Na_2\}^{2+}$	14, 19	14
$[M^{3+}(SO_4)_2(H_2O)_2]^{-}$	0.18	0.80–1.45	0.14–0.25	$\{^{[10]}M^{+}(H_2O)_0(H_2O)_{0-10}\}^{+}$ $\{^{[6]}M^{2+}(H_2O)_{2-6}(H_2O)_{0-4}\}^{2+}$	$\{^{[10]}K\}^{+}$ $\{^{[4+2]}Cu^{2+}(H_2O)_4\}^{2+}$	6, 8, 11	10, 10
$[M^{3+}(SO_4)_2(OH)]^{2-}$	0.24	1.10–1.75	0.14–0.22	$\{^{[6]}M^{+}(H_2O)_{0-3}(H_2O)_{0-12}\}^{+}$ $\{^{[6]}M^{2+}(H_2O)_{3-6}(H_2O)_{0-4}\}^{2+}$	$\{^{[6]}Na_2\}^{2+}$ $\{^{[4+2]}Cu^{2+}(H_2O)_4\}^{2+}$	10, 12	10, 12
$[M^{3+}(SO_4)_3]^{3-}$	0.25	1.15–1.80	0.14–0.22	$\{^{[7]}M^{+}{}_3(H_2O)_0(H_2O)_{0-21}\}^{3+}$	$\{^{[7]}Na_3\}^{3+}$	15, 18, 24	21
$[M^{3+}{}_2(SO_4)_3(OH)(H_2O)_4]_2{}^{2-}$	0.16	0.70–1.30	0.15–0.27	$\{^{[6]}M^{2+}(H_2O)_{0-6}(H_2O)_{0-6}\}^{2+}$	$\{Fe^{2+}(H_2O)_6\}^{2+}$ $\{Mg(H_2O)_6\}^{2+}$ $\{Ca(H_2O)_6\}^{2+}$ $\{Cu^{2+}(H_2O)_6\}^{2+}$ $\{Zn(H_2O)_6\}^{2+}$	8, 12, 20	12
$[M^{3+}(SO_4)_2(OH)(H_2O)]^{2-}$	0.26	1.20–1.80	0.15–0.23	$\{^{[6]}M^{2+}(H_2O)_{3-6}(H_2O)_{0-4}\}^{2+}$	$\{Mg(H_2O)_4(H_2O)_1\}^{2+}$ $\{Zn(H_2O)_4(H_2O)_1\}^{2+}$	8, 10, 13	10
$[^{[4+2]}Cu^{2+}{}_2(SO_4)_2(OH)(H_2O)]^{-}$	0.16	0.70–1.30	0.13–0.24	$\{^{[8]}M^{+}(H_2O)_{0-2}(H_2O)_{0-8}\}^{+}$	$\{^{[8]}Na\}^{+}$	3, 6, 9	8
$[M^{3+}(SO_4)_2(H_2O)_2]^{-}$	0.18	0.80–1.45	0.14–0.25	$\{^{[5]}M^{+}(H_2O)_{0-5}(H_2O)_0\}^{+}$	$\{H_5O_2\}^{+}$	4, 5, 8	5
$[M^{2+}{}_5Fe^{3+}{}_3(SO_4)_{12}(H_2O)_{12}]^{5-}$	0.16	0.70–1.30	0.13–0.23	$\{^{[12]}M^{+}{}_5\}^{5+}$: not possible $\{^{[6]}M^{3+}(H_2O)_6\}_{1.67}$	$\{^{[12]}K_2{}^{[6]}Al(H_2O)_6\}^{5+}$	15, 23, 35	36
$[^{[4+2]}Cu^{[4+1]}Cu_2O(SO_4)_3]^{2-}$	0.15	0.65–1.20	0.13–0.24	$\{^{[7]}M^{+}{}_2(H_2O)_{0-1}(H_2O)_{0-14}\}^{2+}$	$\{^{[7]}Na^{[7]}K\}^{2+}$	8, 10, 12, 15	14
$[^{[4+1]}Cu_3O(SO_4)_3]^{2-}$	0.17	0.75–1.40	0.11–0.21	$\{^{[7]}M^{+}{}_2(H_2O)_{0-4}(H_2O)_{0-14}\}^{2+}$	$\{^{[7]}K_2\}^{2+}$	10, 12, 16	14
$[^{[4+1]}Cu_3M^{3+}O_2(SO_4)_4]^{3-}$	0.17	0.75–1.40	0.12–0.22	$\{^{[8]}M^{+}{}_3(H_2O)_{0-1}(H_2O)_{0-24}\}^{3+}$ $\{^{[7]}M^{+}{}_3(H_2O)_{0-4}(H_2O)_{0-21}\}^{3+}$	$\{^{[8]}K_2{}^{[7]}K\}^{3+}$	15, 18, 24	23

* Non-transformer and non-bonding (H_2O) groups are not listed here because they cannot be predicted.

from 0.03 to 0.21 *vu* (Eby & Hawthorne 1993); thus in Cu^{2+}-bearing sulfate structural units, bond valences between ($Cu\phi_6$) and (SO_4) groups (Fig. 3c) vary over a much larger range than in structural units with other octahedrally coordinated M^{2+} cations (Fig. 3b).

SUMMARY

Sulfate minerals are divided into two classes on the basis of the bond-valence of the *M*–O(S) bond. (1) Where the latter bond-valence exceeds 0.30 *vu*, the corresponding *M* cation and the (SO_4) groups are considered as part of a complex [$MO(SO_4)(OH)(H_2O)$] structural unit. (2) Where the *M*–O(S) bond-valence is less than 0.30 *vu*, the [SO_4] group is considered as the structural unit, and the *M* cation is considered as part of the interstitial complex. The following structural parameters may be used to understand the chemical compositions of interstitial complexes in sulfate minerals:

Polarity

(1) Complex [$MO(SO_4)(OH)(H_2O)$] structural units have an acidic part involving (H_2O) groups bonded to *M* cations, and a basic part involving O atoms of the (SO_4) group.

(2) The relative arrangement of structural units in a mineral is strongly controlled by the requirement that the acidic and basic parts of adjacent structural units should be spatially adjacent.

(3) Where acidic and basic parts of adjacent structural units are too far apart to link through a hydrogen bond from one structural unit to another, additional interstitial (H_2O) groups must occur to bridge the gap.

Lewis acidity

(4) The distribution of Lewis acidity of interstitial complexes in sulfate minerals with [SO_4] structural units has distinct maxima at 0.17 and 0.20 *vu*. As the Lewis basicity of the $(SO_4)^{2-}$ group is 0.17 *vu*, the maximum in Lewis acidity at 0.17 *vu* is in accord with the valence-matching principle. The maximum at 0.20 *vu* may be an indication of a particularly stable configuration in sulfate minerals, which is supported by the fact that geologically widespread minerals such as anglesite, barite, celestine and gypsum contain interstitial complexes with a Lewis acidity of 0.20 *vu*.

Average basicity

(5) The coordination number [*CN*] of O atoms in complex structural units may be factored into the number of bonds per O atom involved in the structural unit [CN_{str}] and the number of bonds per O atom involved in the interstitial complex [CN_{in}]: [CN] = [CN_{str}] + [CN_{in}]. There is a strong correlation between [CN_{in}] and the average basicity of the structural unit, with which one can calculate the maximum and minimum possible number of bonds from the interstitial complex and the acidic part of the structural unit to all O atoms of the structural unit, and in turn, the possible range in Lewis basicity of the structural unit.

(6) The overlap of the possible range in Lewis basicity of the structural unit with the Lewis acidity calculated for a general interstitial complex allows prediction of (1) the interstitial cations and their coordination numbers, and (2) the number of transformer (H_2O) groups in interstitial complexes that obey the valence-matching principle. There is good agreement between the observed structural units and those predicted to be stable for a wide variety of sulfate minerals.

ACKNOWLEDGEMENTS

We thank Fernando Scordari, an anonymous reviewer and our returning Editor Bob Martin for their comments, and Charlie Alpers for his comments on an earlier version of this manuscript. FCH was supported by a Canada Research Chair in Crystallography and Mineralogy and by Major Facilities Access, Research Tools and Equipment, and Discovery Grants from the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

ABDEEN, A.M., WILL, G., SCHÄFER, W., KIRFEL, A., BARGOUTH, M.O., RECKER, K. & WEISS, A. (1981): X-ray and neutron diffraction study of alums. III. The crystal structure of ammonium aluminium alum. *Z. Kristallogr.* **157**, 147-166.

ABRIEL, W. & NESPER, R. (1993): Bestimmung der Kristallstruktur von $CaSO_4(H_2O)_{0.5}$ mit Röntgenbeugungsmethoden und mit Potentialprofil-Rechnungen. *Z. Kristallogr.* **205**, 99-113.

ADIWIDJAJA, G., FRIESE, K., KLASKA, K.-H. & SCHLÜTER J. (1996): The crystal structure of christelite $Zn_3Cu_2(SO_4)_2(OH)_6 \bullet 4(H_2O)$. *Z. Kristallogr.* **211**, 518-521.

ARAKI, T. & ZOLTAI, T. (1967): Refinement of the crystal structure of a glauberite. *Am. Mineral.* **52**, 1272-1277.

BACHMANN, H.G. (1953): Beiträge zur Kristallchemie natürlicher und künstlicher Schwermetallvanadate. III. Das Bleiorthovanadat, seine Darstellung, Kristallstruktur und Isotypiebeziehungen. *Neues Jahrb. Mineral., Monatsh.*, 209-223.

BACON, G.E. & TITTERTON, D.H. (1975): Neutron-diffraction studies of $CuSO_4 \bullet 5H_2O$ and $CuSO_4 \bullet 5D_2O$. *Z. Kristallogr.* **141**, 330-341.

BAUR, W.H. (1960): Die Kristallstruktur von $FeSO_4 \bullet 4H_2O$. *Naturwiss.* **47**, 467.

BAUR, W.H. (1962): Zur Kristallchemie der Salzhydrate. Die Kristallstrukturen von $MgSO_4•4H_2O$ (Leonhardtit) und $FeSO_4•4H_2O$ (Rozenit). *Acta Crystallogr.* **15**, 815-826.

BAUR, W.H. (1964): On the crystal chemistry of salt hydrates. III. The determination of the crystal structure of $FeSO_4•7H_2O$ (melanterite). *Acta Crystallogr.* **17**, 1167-1174.

BAUR, W.H. & ROLIN, J.L. (1972): Salt hydrates. IX. The comparison of the crystal structure of magnesium sulfate pentahydrate with copper sulfate pentahydrate and magnesium chromate pentahydrate. *Acta Crystallogr.* **B28**, 1448-1455.

BOKII, G.B. & GOROGOTSKAYA, L.I. (1969): Crystal chemical classification of sulfates. *Zh. Strukt. Khim.* **10**, 624-632 (in Russ.).

BOKII, G.B., PAL'CHIK, N.A. & ANTIPIN, M.YU. (1978): More precise determination of the syngenite crystal structure. *Trudy Inst. Geol. Geofiz., Akad. Nauk SSSR, Sibir. Otd.* **385**, 3-7 (in Russ.).

BORÈNE, J. (1970): Structure cristalline de la parabutlerite. *Bull. Soc. fr. Minéral. Cristallogr.* **93**, 185-189.

BROWN, I.D. (1981): The bond-valence method: an empirical approach to chemical structure and bonding. *In* Structure and Bonding in Crystals **2** (M. O'Keeffe & A. Navrotsky, eds.). Academic Press, New York, N.Y. (1-30).

BROWN, I.D. (2002): *The Chemical Bond in Inorganic Chemistry. The Bond Valence Model.* Oxford University Press, Oxford, U.K.

BURNS, P.C., DEELY, K.M. & HAYDEN, L.A. (2003): The crystal chemistry of the zippeite group. *Can. Mineral.* **41**, 687-706.

CALLERI, M., GAVETTI, A., IVALDI, G. & RUBBO, M. (1984): Synthetic epsomite, $MgSO_4•7H_2O$: absolute configuration and surface features of the complementary {111} forms. *Acta Crystallogr.* **B40**, 218-222.

CHEVRIER, G., GIESTER, G. & ZEMANN, J. (1993): Neutron refinements of $NaCu_2(H_3O_2)(SO_4)_2$ and $RbCu_2(H_3O_2)(SeO_4)_2$: variation of the hydrogen bond system in the natrochalcite-type series. *Z. Kristallogr.* **206**, 7-14.

CORAZZA, E., SABELLI, C. & GIUSEPPETTI, G. (1967): The crystal structure of lecontite, $NaNH_4SO_4•2(H_2O)$. *Acta Crystallogr.* **22**, 683-687.

CROMER, D.T., KAY, M.I. & LARSON, A.C. (1967): Refinement of the alum structures. II. X-ray and neutron diffraction of $NaAl(SO_4)_2•12H_2O$, γ-alum. *Acta Crystallogr.* **22**, 182-187.

DAHMEN, T. & GRUEHN, R. (1993): Beitrage zum thermischen Verhalten von Sulfaten. IX. Einkristallstrukturverfeinerung der Metall(III)-sulfate $Cr_2(SO_4)_3$ und $Al_2(SO_4)_3$. *Z. Kristallogr.* **204**, 57-65.

DUTRIZAC, J.E. & JAMBOR, J.L. (2000): Jarosites and their application in hydrometallurgy. *In* Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance (C.N. Alpers, J.L. Jambor & D.K. Nordstrom, eds.). *Rev. Mineral. Geochem.* **40**, 405-452.

EBY, R.K. & HAWTHORNE, F.C. (1993): Structural relations in copper oxysalt minerals. I. Structural hierarchy. *Acta Crystallogr.* **B49**, 28-56.

EFFENBERGER, H. (1985): $Cu_2O(SO_4)$, dolerophanite: refinement of the crystal structure with a comparison of $OCu(II)_4$ tetrahedra in inorganic compounds. *Monatsh. Chem.* **116**, 927-931.

EFFENBERGER, H. (1987): Crystal structure and chemical formula of schmiederite, $Pb_2Cu_2(OH)_4(SeO_3)(SeO_4)$, with a comparison to linarite, $PbCu(OH)_2(SO_4)$. *Mineral. Petrol.* **36**, 3-12.

EFFENBERGER, H., PERTLIK, F. & ZEMANN, J. (1986): Refinement of the crystal structure of krausite: a mineral with an interpolyhedral oxygen–oxygen contact shorter than the hydrogen bond. *Am. Mineral.* **71**, 202-205.

FANFANI, L., NUNZI, A. & ZANAZZI, P.F. (1970): The crystal structure of roemerite. *Am. Mineral.* **55**, 78-89.

FANFANI, L., NUNZI, A. & ZANAZZI, P.F. (1971): The crystal structure of butlerite. *Am. Mineral.* **56**, 751-757.

FANFANI, L., NUNZI, A., ZANAZZI, P.F. & ZANZARI, A.R. (1973): The copiapite problem: the crystal structure of a ferrian copiapite. *Am. Mineral.* **58**, 314-322.

FANG, J.H. & ROBINSON, P.D. (1970): Crystal structures and mineral chemistry of hydrated ferric sulfates. I. The crystal structure of coquimbite. *Am. Mineral.* **55**, 1534-1540.

FANG, J.H. & ROBINSON, P.D. (1972): Crystal structures and mineral chemistry of double-salt hydrates. II. The crystal structure of mendozite, $NaAl(SO_4)_2•11H_2O$. *Am. Mineral.* **57**, 1081-1088.

FIGGIS, B.N., KEPERT, C.J., KUCHARSKI, E.S. & REYNOLDS, P.A. (1992): Charge-density study of deuterated ammonium ferrous Tutton salt at 85 K and comparison with Cr^{II} and Cu^{II} salts. *Acta Crystallogr.* **B48**, 753-761.

FISCHER, W. & HELLNER, E. (1964): Über die Struktur des Vanthoffits. *Acta Crystallogr.* **17**, 1613.

GAINES, R.V., SKINNER, H.C.W., FOORD, E.E., MASON, B. & ROSENZWEIG, A. (1997): *Dana's New Mineralogy* (8th ed.). John Wiley & Sons, New York, N.Y.

GALY, J., JAUD, J., PULOU, R. & SEMPÉRE, R. (1984): Structure cristalline de la langite, $Cu_4[SO_4(OH)_6H_2O]H_2O$. *Bull. Minéral.* **107**, 641-648.

GIACOVAZZO, G. & MENCHETTI, S. (1969): Sulla struttura della amarantite. *Rend. Soc. Ital. Mineral. Petrol.* **25**, 399-406.

Giacovazzo, G., Scordari, F., Todisco, A. & Menchetti, S. (1976): Crystal structure model for metavoltine from Sierra Gorda. *Tschermaks Mineral. Petrogr. Mitt.* **23**, 155-166.

Giester, G., Lengauer, C.L. & Redhammer, G. (1994): Characterization of the $FeSO_4 \bullet H_2O$ – $CuSO_4 \bullet H_2O$ solid-solution series, and the nature of poitevinite, $(Cu,Fe)SO_4 \bullet H_2O$. *Can. Mineral.* **32**, 873-884.

Giester, G. & Rieck, B. (1995): Mereiterite, $K_2Fe(SO_4)_2 \bullet 4(H_2O)$, a new leonite-type mineral from the Lavrion mining district, Greece. *Eur. J. Mineral.* **7**, 559-566.

Giester, G., Rieck, B. & Brandstatter, F. (1998): Niedermayrite, $Cu_4Cd(SO_4)_2(OH)_6 \bullet 4H_2O$, a new mineral from the Lavrion mining district, Greece. *Mineral. Petrol.* **63**, 19-34.

Gorskaya, M.G., Filatov, S.K., Rozhdestvenskaya, I.V. & Vergasova, L.P. (1992): The crystal structure of klyuchevskite, $K_3Cu_3(Fe,Al)O_2(SO_4)_4$, a new mineral from Kamchatka volcanic sublimates. *Mineral. Mag.* **56**, 411-416.

Graeber, E.J. & Rosenzweig, A. (1971): The crystal structures of yavapaiite, $KFe(SO_4)_2$, and goldichite, $KFe(SO_4)_2 \bullet 4H_2O$. *Am. Mineral.* **56**, 1917-1933.

Hasebe, K. (1981): Studies of the crystal structure of ammonium sulfate in connection with its ferroelectric phase transition. *J. Phys. Soc. Japan* **50**, 1266-1274.

Hawthorne, F.C. (1983): Graphical enumeration of polyhedral clusters. *Acta Crystallogr.* **A39**, 724-736.

Hawthorne, F.C. (1985a): Towards a structural classification of minerals: the $^{VI}M^{IV}T_2\Phi_n$ minerals. *Am. Mineral.* **70**, 455-473.

Hawthorne, F.C. (1985b): Refinement of the crystal structure of bloedite: structural similarities in the $[^{VI}M(^{IV}T\phi_4)_2\phi_n]$ finite-cluster minerals. *Can. Mineral.* **23**, 669-674.

Hawthorne, F.C. (1990): Structural hierarchy in $M^{[6]}T^{[4]}\phi_n$ minerals. *Z. Kristallogr.* **192**, 1-52.

Hawthorne, F.C. (1994): Structural aspects of oxide and oxysalt crystals. *Acta Crystallogr.* **B50**, 481-510.

Hawthorne, F.C. (1997): Structural aspects of oxide and oxysalt minerals. *In* Modular Aspects of Minerals (S. Merlino, ed.). *Eur. Mineral. Union, Notes in Mineral.* **1**, 373-429.

Hawthorne, F.C., Burns, P.C. & Grice, J.D. (1996): The crystal chemistry of boron. *In* Boron: Mineralogy, Petrology and Geochemistry (E.S. Grew & L.M. Anovitz, eds.). *Rev. Mineral.* **33**, 41-115.

Hawthorne, F.C. & Ferguson, R.B. (1975a): Refinement of the crystal structure of kröhnkite. *Acta Crystallogr.* **B31**, 1753-1755.

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

Hawthorne, F.C. & Ferguson, R.B. (1975c): Anhydrous sulfates. II. Refinement of the crystal structure of anhydrite. *Can. Mineral.* **13**, 289-292.

Hawthorne, F.C. & Groat, L.A. (1985): The crystal structure of wroewolfeite, a mineral with $[Cu_4(OH)_6(SO_4)(H_2O)]$ sheets. *Am. Mineral.* **70**, 1050-1055.

Hawthorne, F.C., Groat, L.A. & Eby, R.K. (1989): Antlerite, $Cu_3SO_4\ (OH)_4$, a heteropolyhedral wallpaper structure. *Can. Mineral.* **27**, 205-209.

Hawthorne, F.C., Groat, L.A., Raudsepp, M. & Ercit, T.S. (1987): Kieserite, $MgSO_4(H_2O)$, a titanite-group mineral. *Neues Jahrb. Mineral., Abh.* **157**, 121-132.

Hawthorne, F.C., Krivovichev, S.V. & Burns, P.C. (2000): The crystal chemistry of sulfate minerals. *In* Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance (C.N. Alpers, J.L. Jambor & D.K. Nordstrom, eds.). *Rev. Mineral. Geochem.* **40**, 1-112.

Hawthorne, F.C. & Schindler, M.S. (2000): Topological enumeration of decorated $[Cu^{2+}\phi_2]_N$ sheets in hydroxy-hydrated copper oxysalt minerals. *Can. Mineral.* **38**, 751-761.

Hess, H., Keller, P. & Riffel, H. (1988): The crystal structure of chenite, $Pb_4Cu(OH)_6(SO_4)_2$. *Neues Jahrb. Mineral., Monatsh.*, 259-264.

Hochella, M.F., Jr., Keefer, K.D. & de Jong, B.H.W.S. (1983): The crystal chemistry of a naturally occurring magnesium hydroxide sulfate hydrate, a precipitate of heated seawater. *Geochim. Cosmochim. Acta* **47**, 2053-2058.

Iskhakova, L.D., Dubrovinskii, L.S. & Charushnikova, I.A. (1991): Crystal structure, calculation of parameters of atomic interaction potential and thermochemical properties of $NiSO_4 \bullet nH_2O$ (n = 7,6). *Kristallografiya* **36**, 650-655. (in Russ.)

Jacobsen, S.D., Smyth, J.R., Swope, R.J. & Downs, R.T. (1998): Rigid-body character of the SO_4 groups in celestine, anglesite and barite. *Can. Mineral.* **36**, 1053-1060.

Jarosch, D. (1985): Kristallstruktur des Leonits, $K_2Mg(SO_4)_2 \bullet 4H_2O$. *Z. Kristallogr.* **173**, 75-79.

Jolly, J.H. & Foster, H.L. (1967): X-ray diffraction data of aluminocopiapite. *Am. Mineral.* **52**, 1220-1223.

Kannan, K.K. & Viswamitra, M.A. (1965): Crystal structure of magnesium potassium sulfate hexahydrate $MgK_2(SO_4)_2 \bullet 6H_2O$. *Z. Kristallogr.* **122**, 161-174.

Keefer, K.D., Hochella, M.F., Jr. & de Jong, B.H.W.S. (1981): The structure of magnesium hydroxide sulfate hydrate $MgSO_4 \bullet 1/3Mg(OH)_2 \bullet 1/3H_2O$. *Acta Crystallogr.* **B37**, 1003-1006.

Kellersohn, T. (1992): Structure of cobalt sulfate tetrahydrate. *Acta Crystallogr.* **C48**, 776-779.

Kellersohn, T., Delaplane, R.G. & Olovsson, I. (1991): Disorder of a trigonally planar coordinated water molecule in cobalt sulfate heptahydrate, $CoSO_4 \bullet 7D_2O$ (bieberite). *Z. Naturforsch.* **B46**, 1635-1640.

Larson, A.C. & Cromer, D.T. (1967): Refinement of the alum structures. III. X-ray study of the α-alums, K, Rb and $NH_4Al(SO_4)_2 \bullet 12H_2O$. *Acta Crystallogr.* **22**, 793-800.

Levy, A.H. & Lisensky, G.C. (1978): Crystal structures of sodium sulfate decahydrate (Glauber's salt) and sodium tetraborate decahydrate (borax). Redetermination by neutron diffraction. *Acta Crystallogr.* **B34**, 3502-3510.

Li, J.J., Zhou, J.L. & Dong, W. (1990): The structure of amarillite. *Chinese Sci. Bull.* **35**, 2073-2075.

Maslen, E.N., Ridout, S.C., Watson K.J. & Moore, F.H. (1988): The structures of Tuttons's salts. I. Diammonium hexaaqua magnesium(II) sulfate. *Acta Crystallogr.* **C44**, 409-412.

McGinnety, J.A. (1972): Redetermination of the structures of potassium sulphate and potassium chromate: the effect of electrostatic crystal forces upon observed bond lengths. *Acta Crystallogr.* **B28**, 2845-2852.

Mellini, M. & Merlino, S. (1978): Ktenasite, another mineral with $[(Cu,Zn)_2(OH)_3O]^-$ octahedral sheets. *Z. Kristallogr.* **147**, 129-140.

Mellini, M. & Merlino, S. (1979): Posnjakite. $[Cu_4(OH)_6(H_2O)O]$ octahedral sheets in its structure. *Z. Kristallogr.* **149**, 249-257.

Menchetti, S. & Sabelli, C. (1974): Alunogen. Its structure and twinning. *Tschermaks Mineral. Petrogr. Mitt.* **21**, 164-178.

Menchetti, S. & Sabelli, C. (1976): Crystal chemistry of the alunite series: crystal structure refinement of alunite and synthetic jarosite. *Neues Jahrb. Mineral., Monatsh.*, 406-417.

Menchetti, S. & Sabelli, C. (1982): Campigliaite, $Cu_4Mn(SO_4)_2(OH)_6 \bullet 4H_2O$, a new mineral from Campiglia Marittima, Tuscany, Italy. I. Occurrence and description. *Am. Mineral.* **67**, 385-393.

Mereiter, K. (1972): Die Kristallstruktur des Voltaits, $K_2Fe^{2+}{}_5Fe^{3+}{}_3Al(SO_4)_{12} \bullet 18H_2O$. *Tschermaks Mineral. Petrogr. Mitt.* **18**, 185-202.

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

Mereiter, K. (1976): Die Kristallstruktur des Ferrinatrits, $Na_3Fe[SO_4]_3 \bullet 3H_2O$. *Tschermaks Mineral. Petrogr. Mitt.* **23**, 317-327.

Mukhtarova, N.N., Kalinin, V.R., Rastsvetaeva, R.K., Ilyukhin, V.V. & Belov, N.V. (1980): The crystal structure of görgeyite $K_2Ca_5(SO_4)_6H_2O$. *Dokl. Akad. Nauk SSSR* **252**, 102-105 (in Russ.).

Okada, K. & Ossaka, J. (1980): Structures of potassium sodium sulphate and tripotassium sodium disulphate. *Acta Crystallogr.* **B36**, 919-921.

Pedersen, B.F. & Semmingsen, D. (1982): Neutron diffraction refinement of the structure of gypsum, $CaSO_4 \bullet 2H_2O$. *Acta Crystallogr.* **B38**, 1074-1077.

Ptasiewicz-Bak, H., McIntyre, G.J. & Olovsson, I. (1983): Structure of monoclinic nickel sulphate hexadeuterate, $NiSO_4 \bullet 6D_2O$. *Acta Crystallogr.* **C39**, 966-968.

Pushcharovsky. D.Yu., Lima-de-Faria, J. & Rastsvetaeva, R.K. (1998): Main structural subdivisions and structural formulas of sulphate minerals. *Z. Kristallogr.* **213**, 141-150.

Robinson, D.J. & Kennard, C.H.L. (1972): Potassium hexaaquacopper(II) sulfate, $CuH_{12}K_2O_{14}S_2$. *Cryst. Struct. Commun.* **1**, 185-188.

Robinson, P.D. & Fang, J.H. (1969): Crystal structures and mineral chemistry of double-salt hydrates. I. Direct determination of the crystal structure of tamarugite. *Am. Mineral.* **54**, 19-30.

Robinson, P.D. & Fang, J.H. (1971): Crystal structures and mineral chemistry of hydrated ferric sulphates. II. The crystal structure of paracoquimbite. *Am. Mineral.* **56**, 1567-1571.

Robinson, P.D. & Fang, J.H. (1973): Crystal structures and mineral chemistry of hydrated ferric sulphates. III. The crystal structure of kornelite. *Am. Mineral.* **58**, 535-539.

Rumanova, I.M. & Malitskaya, G.I. (1959): Revision of the structure of astrakhanite by weighted phase projection methods. *Kristallografiya* **4**, 510-525 (in Russ.).

Sabelli, C. (1985): Uklonskovite, $NaMg(SO_4)F \bullet 2H_2O$: new mineralogical data and structure refinement. *Bull. Minéral.* **108**, 133-138.

Sabelli, C. & Trosti-Ferroni, R. (1985): A structural classification of sulfate minerals. *Per. Mineral.* **54**, 1-46.

Schindler, M. & Hawthorne, F.C. (2001a): A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals. I. Theory. *Can. Mineral.* **39**, 1225-1242.

Schindler, M. & Hawthorne, F.C. (2001b): A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals. II. Crystal structure and chemical composition of borate minerals. *Can. Mineral.* **39**, 1243-1256.

Schindler, M. & Hawthorne, F.C. (2001c): A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals. III. Paragenesis of borate minerals. *Can. Mineral.* **39**, 1257-1274.

Schindler, M. & Hawthorne, F.C. (2004): A bond-valence approach to the uranyl-oxide hydroxy-hydrate minerals: chemical composition and occurrence. *Can. Mineral.* **42**, 1601-1627.

Schindler, M. & Hawthorne, F.C. (2007): The stereochemistry and chemical composition of interstitial complexes in uranyl-oxysalt minerals. *Can. Mineral.* **45** (in press).

Schindler, M., Hawthorne, F.C. & Baur, W.H. (2000): A crystal-chemical approach to the composition and occurrence of vanadium minerals. *Can. Mineral.* **38**, 1443-1456.

Schlatti, M., Sahl, K., Zemann, A. & Zemann, J. (1970): Die Kristallstruktur des Polyhalits, $K_2Ca_2Mg[SO_4]_4•2H_2O$. *Tschermaks Mineral. Petrogr. Mitt.* **14**, 75-86.

Schlüter, J., Klaska, K-H. & Gebhard, G. (1999): Changoite, $Na_2Zn(SO_4)_2•4H_2O$, the zinc analogue of blödite, a new mineral from Sierra Gorda, Antofagasta, Chile. *Neues Jahrb. Mineral., Monatsh.*, 97-103.

Scordari, F. (1977): The crystal structure of ferrinatrite, $Na_3(H_2O)_3[Fe(SO_4)_3]$ and its relationship to Maus's salt, $(H_3O)_2K_2\{K_{0.5}(H_2O)_{0.5}\}_6[Fe_3O(H_2O)_3(SO_4)_6](OH)_2$. *Mineral. Mag.* **41**, 375-383.

Scordari, F. (1978): The crystal structure of hohmannite, $Fe_2(H_2O)_4[(SO_4)_2]•4H_2O$ and its relationship to amaranite, $Fe_2(H_2O)_4[(SO_4)_2O]•3H_2O$. *Mineral. Mag.* **42**, 144-146.

Scordari, F. (1981a): 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**, 17-29.

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

Scordari, F. & Stasi, F. (1990): The crystal structure of euchlorine, $NaKCu_3O(SO_4)_3$. *Neues Jahrb. Mineral., Abh.* **161**, 241-253.

Scordari, F., Stasi, F. & Milella, G. (1982): Concerning metasideronatrite. *Neues Jahrb. Mineral., Monatsh.*, 341-347.

Scordari, F., Ventruti, G. & Gualtieri, A.F. (2004): The structure of metahohmannite, $Fe^{3+}{}_2[O(SO_4)_2]•4H_2O$, by in situ synchrotron powder diffraction. *Am. Mineral.* **89**, 365-370.

Singer, J.& Cromer, D.T. (1959): The crystal structure analysis of zirconium sulphate tetrahydrate. *Acta Crystallogr.* **12**, 719-723.

Smith, G.W. & Walls, R. (1980): The crystal structure of görgeyite $K_2SO_4•5CaSO_4•H_2O$. *Z. Kristallogr.* **151**, 49-60.

Stadnicka, K., Glazer, A.M. & Koralewski, M. (1987): Structure, absolute configuration and optical activity of α-nickel sulfate hexahydrate. *Acta Crystallogr.* **B43**, 319-325.

Starova, G.L., Filatov, S.K., Fundamensky, V.S. & Vergasova, L.P. (1991): The crystal structure of fedotovite, $K_2Cu_3O(SO_4)_3$. *Mineral. Mag.* **55**, 613-616.

Süsse, P. (1967): Crystal structure of amarantite. *Naturwiss.* **54**, 642-643.

Süsse, P. (1968): Die Kristallstruktur des Botryogens. *Acta Crystallogr.* **B24**, 760-767.

Süsse, P. (1970): The crystal structure of copiapite. *Neues Jahrb. Mineral., Monatsh.*, 286-287.

Tachez, M., Théobald, F., Watson, K.J. & Mercier, R. (1979): Redétermination de la structure du sulfate de vanadyle pentahydraté $VOSO_4•5H_2O$. *Acta Crystallogr.* **B35**, 1545-1550.

Tahirov, T.H., Lu, T.-H., Huang, C.-C. & Chung, C.-S. (1994): A precise structure redetermination of nickel ammonium sulfate hexahydrate, $Ni(H_2O)_6•2NH_4•2SO_4$. *Acta Crystallogr.* **C50**, 668-669.

Wildner, M. & Giester, G. (1988): Crystal structure refinements of synthetic chalcocyanite ($CuSO_4$) and zincosite ($ZnSO_4$). *Mineral. Petrol.* **39**, 201-209.

Wildner, M. & Giester, G. (1991): The crystal structures of kieserite-type compounds. I. Crystal structures of $Me(II)SO_4•H_2O$ (Me = Mn, Fe, Co, Ni, Zn). *Neues Jahrb. Mineral., Monatsh.*, 296-306.

Wood, M.M. (1970): The crystal structure of ransomite. *Am. Mineral.* **55**, 729-734.

Yang, Hexiong & Fang, Pingqiu (1988): Crystal structure of zincobotryogen. *Kuangwu Xuebao* **8**, 1-12.

Zahrobsky, R.F. & Baur, W.H. (1968): On the crystal chemistry of salt hydrates. V. The determination of the crystal structure of $CuSO_4•3H_2O$ (bonattite). *Acta Crystallogr.* **B24**, 508-513.

Zalkin, A., Ruben, H. & Templeton, D.H. (1964): The crystal structure and hydrogen bonding of magnesium sulfate hexahydrate. *Acta Crystallogr.* **17**, 235-240.

Zhou, J., Li, J. & Dong, W. (1988): The crystal structure of xitieshanite. *Kexue Tongbao* **33**, 502-505 (in Chinese).

Received October 31, 2005, revised manuscript accepted June 1, 2006.

APPENDIX

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

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

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

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

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

Structural unit: the strongly bonded part of the structure; it is usually anionic, but can be neutral or cationic. The components of the structural unit are written in square brackets, and are written in the following order: $M(T\phi_4)\phi$, where M are cations, $(T\phi_4)$ are oxyanions, and ϕ are anions bonded to M cations. This order is used because the linkage between M and $(T\phi_4)$ defines the dimensionality of the structural unit; note that *both* $(T\phi_4)$ and ϕ are anions coordinating M.

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

$$\{{}^{[m]}M^{+}{}_{a}\ {}^{[n]}M^{2+}{}_{b}\ {}^{[1]}M^{3+}{}_{c}\ (H_2O)_d$$
$$(H_2O)_e\ {}^{[q]}(OH)_f\ (H_2O)_g\}^{(a+2b+3c-f)+}$$

Note that the stereochemical roles of (H_2O) are only preserved if all types of (H_2O) and (OH) groups are written down, even if their number is zero; *i.e.*, $(H_2O)_d(H_2O)_e(OH)_f(H_2O)_g = (H_2O)_2(H_2O)_0(OH)_0(H_2O)_1$; $(H_2O)_2(H_2O)_1$ does not preserve all this information.

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

Transformer (H₂O) groups: (H_2O) groups in which the O atoms accept only one bond from a cation (inclusive of hydrogen bonds). Hence, they receive only one bond, but propagate two hydrogen bonds, *i.e.*, they split one bond into two bonds. This effect transforms the higher bond-valence of one cation–(H_2O) bond into the lower bond-valences of two hydrogen bonds.

Non-transformer (H₂O) groups: (H_2O) groups in which the O atoms accept two additional bonds from cations (inclusive of hydrogen bonds). Hence, they receive two bonds and also propagate two bonds (*i.e.*, they do not transform bonds). Non-transformer (H_2O) groups propagate bond valence to acceptor O-atoms of the structural unit.

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

$$\{{}^{[m]}M^{+}{}_{a}\ {}^{[n]}M^{2+}{}_{b}\ {}^{[1]}M^{3+}{}_{c}\ (H_2O)_d\ (H_2O)_e$$
$${}^{[q]}(OH)_f\ (H_2O)_g\}^{(a+2b+3c-f)+}$$
$$[M^{z+}\ (SO_4)_i\ (OH)_j\ (H_2O)_k]^{(a+2b+3c-f)-}$$

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

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

Average basicity of the structural unit: the effective charge of the structural unit divided by the number of O atoms in the structural unit.

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

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