

**THE CRYSTAL STRUCTURE OF HUMMERITE, $\text{KMg}(\text{V}_5\text{O}_{14})\cdot 8\text{H}_2\text{O}$:
BONDING BETWEEN THE $[\text{V}_{10}\text{O}_{28}]^{6-}$ STRUCTURAL UNIT
AND THE $\{\text{K}_2\text{Mg}_2(\text{H}_2\text{O})_{16}\}^{6+}$ INTERSTITIAL COMPLEX**

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ABSTRACT

The arrangement of atoms in hummerite, $\text{KMg}(\text{V}_5\text{O}_{14})\cdot 8\text{H}_2\text{O}$, has been redetermined to locate the H-atom positions, essential for analysis of the bonding between the structural unit and the interstitial complex. The mineral crystallizes in space group $P\bar{1}$, with a 8.8178(4), b 10.7236(5), c 11.0707(5) Å, α 65.798(1), β 74.057(1), and γ 71.853(1)°. The structure was solved and the hydrogen atoms located using 20,335 reflections measured on a CCD-detector diffractometer with $\text{MoK}\alpha$ X-radiation; the final refinement converged to an R of 0.021. The structural unit in hummerite is the $[\text{V}_{10}\text{O}_{28}]^{6-}$ decavanadate group, similar to that in synthetic vanadium compounds and in pascoite. The symmetry-equivalent structural units are linked by bonding to potassium and hydrogen atoms in the interstitial complex, $\{\text{K}_2\text{Mg}_2(\text{H}_2\text{O})_{16}\}^{6+}$. The Mg atom occurs in octahedral coordination with six (H_2O) groups in the interstitial complex. The K atom occurs in an irregular [10]-coordination, with five bonds to (H_2O) groups of the interstitial complex and five bonds to oxygen atoms of the decavanadate structural unit. An extensive network of hydrogen bonds further links the structural unit and interstitial unit. Evaluation of the hydrogen bonding between these two components of the structure shows that the valence-matching principle is satisfied, and thus the atom arrangement in hummerite defines a stable structure.

Keywords: hummerite, crystal structure, hydrogen-bonding.

SOMMAIRE

Nous avons établi de nouveau l'agencement des atomes dans la hummerite, $\text{KMg}(\text{V}_5\text{O}_{14})\cdot 8\text{H}_2\text{O}$, afin de déterminer la position des atomes d'hydrogène, données essentielles dans une analyse des liaisons entre l'unité structurale de base et le complexe interstitiel. Le minéral cristallise dans le groupe spatial $P\bar{1}$, avec a 8.8178(4), b 10.7236(5), c 11.0707(5) Å, α 65.798(1), β 74.057(1), et γ 71.853(1)°. Nous en avons affiné la structure et localisé les atomes d'hydrogène au moyen de 20,335 réflexions mesurées avec un diffractomètre muni d'un détecteur de type CCD (rayonnement $\text{MoK}\alpha$). L'affinement final a convergé sur un résidu R de 0.021. L'unité structurale de la hummerite est le groupe décavanadate $[\text{V}_{10}\text{O}_{28}]^{6-}$, semblable à celui des composés synthétiques de vanadium et de la pascoïte. Les unités structurales équivalentes selon la symétrie sont liées au potassium et à l'hydrogène du complexe interstitiel, $\{\text{K}_2\text{Mg}_2(\text{H}_2\text{O})_{16}\}^{6+}$. L'atome de Mg possède une coordinence octaédrique, avec six groupes (H_2O) dans un complexe interstitiel. L'atome K, à coordinence [10], est situé dans un polyèdre irrégulier, avec cinq liaisons à des groupes (H_2O) du complexe interstitiel et cinq liaisons à des atomes d'oxygène du group décavanadate de l'unité structurale. Un réseau important de liaisons hydrogène assure le reste des liaisons entre le complexe structural et le complexe interstitiel. Une évaluation des liaisons hydrogène entre ces deux composantes de la structure montre que le principe de la concordance des valences est satisfait, et que donc l'agencement des atomes dans la hummerite mène à une structure stable.

(Traduit par la Rédaction)

Mots-clés: hummerite, structure cristalline, liaisons hydrogène.

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INTRODUCTION

Interest in synthetic and natural vanadium oxide compounds has recently been rekindled, in part because of their potential use as secondary-cathode materials for advanced Li batteries and their key role in oxidative catalysis (Zavalij & Whittingham 1999). Schindler *et al.* (2000a) provided an excellent summary of the crystal-chemical aspects of vanadium by examining the structural chemistry of natural and synthetic phases. Those authors proffered a crystal-chemical approach to the composition and occurrence of vanadium minerals that describes vanadium minerals by two component parts: the *structural unit*, the anionic part of the structure that consists of polyhedra of higher bond-valence, and the *interstitial complex*, the cationic part of the structure that contains alkali and alkaline-earth cations and (H₂O) and (OH) groups. They also described the role of H₂O groups in vanadium minerals, predicted the range in Lewis basicity for different structural units, and demonstrated the efficacy of the valence-matching principle in evaluating the structures of complex vanadium-hydrate minerals.

Here we use the approach of Schindler *et al.* (2000a) to examine the atom arrangement in hummerite, KMg(V₅O₁₄)•8H₂O. This study was prompted by the recent description of the new mineral dickthomssenite, Mg(V₂O₆)•7H₂O (Hughes *et al.* 2001), a vanadium mineral with magnesium in the interstitial complex. Examination of the extant V minerals with Mg in the interstitial complex showed that the arrangement of atoms in hummerite was not known. Upon determination of the atomic arrangement, we found that the structure was reported in a local publication (Griffen 1990), but the work was not widely disseminated. In addition, the hydrogen-atom positions, essential for evaluation of bonding between the structural unit and interstitial complex, were not determined in the earlier work. We thus report the description of the structure of hummerite and comment on bonding between the decavanadate structural unit and the interstitial complex, including the extensive network of hydrogen bonds that is essential to understanding the atomic arrangement.

TABLE 1. EXPERIMENTAL PARAMETERS FOR HUMMERITE

Crystal size:	0.20 × 0.24 × 0.32 mm		Space group:	P $\bar{1}$	
Unit-cell parameters (refined from 5,571 reflections):					
<i>a</i>	8.8178(4) Å	<i>b</i>	10.7236(5) Å	<i>c</i>	11.0707(5) Å
α	65.798(1)°	β	74.057(1)°	γ	71.853(1)°
Frame width, scan time, number of frames:	0.20°, 20 s, 4800				
Detector distance:	5 cm				
Effective transmission:	0.8118 – 1.000				
R _{int} (before – after SADABS absorption correction):	0.044 – 0.018				
Measured reflections, full sphere:	20,335				
Unique reflections, refined parameters:	6,402, 326				
R ₁ :	0.021 for 5,674 unique data, I > 4σ; 0.026 for 6,402 unique data				
Difference peaks:	+0.40, -0.32 e ⁻ Å ⁻³		Goodness-of-fit:	1.079	

EXPERIMENTAL

A sample of hummerite from the type locality, the Hummer mine, Paradox Valley, Montrose County, Colorado, was obtained for structure analysis. The chemical content of hummerite was confirmed by qualitative energy-dispersion analysis, which showed that of elements with Z ≥ 8, only K, Mg, V, and O were detectable.

A crystal was mounted on a Bruker Apex CCD diffractometer equipped with MoK α radiation. Refined unit-cell parameters and other crystal data are listed in Table 1. Redundant data were collected for an approximate sphere of reciprocal space, and were integrated and corrected for Lorentz and polarization factors using the Bruker program SAINTPLUS (Bruker AXS Inc., 2001).

The structure was solved by direct methods and difference-Fourier synthesis; the solution and subsequent least-squares refinement utilized programs in the Bruker SHELXTL, version 6.10 package of programs, with neutral-atom scattering factors and terms for anomalous dispersion. The refinement was done with anisotropic thermal parameters for all non-hydrogen atoms. In Table 2, we list the atom parameters, and in Table 3, we present selected interatomic distances. In Table 4, we report the bond-valence sums of all atoms in hummerite and illustrate the extensive hydrogen-bond network in the phase.

A note on the site nomenclature is in order. In designating the oxygen atoms, we separate those that coordinate vanadium in the structural unit and those that form (H₂O) groups in the interstitial complex. In addition to the V atoms in the structural unit, the O atoms are designated as OV#. In the interstitial complex, in addition to K and Mg, O atoms are designated as OI#, and associated hydrogen atoms of the (H₂O) groups are labeled as HI#a and HI#b.

THE ARRANGEMENT OF ATOMS

Hawthorne (1983) recognized two distinct parts of complex mineral structures: (a) the structural unit, a usually anionic portion of the structure that contains bonds of higher bond-valence, and (b) the interstitial complex, a usually cationic part of the structure, with bonds of lower bond-valence between alkaline and earth-alkaline cations and (H₂O), (OH) and Cl groups. Schindler *et al.* (2000a) applied that concept to vanadium minerals, and elucidated the nature of the bonding between the two distinct parts of the structure. In our description of the atom arrangement in hummerite, we describe the two parts sequentially, and subsequently analyze the bonding between these components of the structure. We note that our structure solution revealed an arrangement of atoms identical to that described by Griffen (1990). Griffen described the arrangement in a non-conventional, mixed obtuse-acute unit-cell and did not locate H atoms, but the location of his non-H atoms

TABLE 2. ATOM PARAMETERS IN HUMMERITE

Atom	x	y	z	U_{eq}
<i>The $(V_{10}O_{28})^{6-}$ structural unit</i>				
V1	0.67554(2)	0.50637(2)	0.51942(2)	0.01666(4)
V2	0.38822(2)	0.77792(2)	0.45258(2)	0.01881(4)
V3	0.35314(2)	0.54862(2)	0.73003(2)	0.01796(4)
V4	0.69385(3)	0.73938(2)	0.24167(2)	0.02152(5)
V5	0.63029(3)	0.27648(2)	0.79897(2)	0.02128(5)
OV1	0.2994(1)	0.89304(9)	0.52256(9)	0.0265(2)
OV2	0.2848(1)	0.83219(9)	0.31048(9)	0.0222(2)
OV3	0.5243(1)	0.64321(8)	0.59189(8)	0.0173(1)
OV4	0.7659(1)	0.40873(9)	0.65734(9)	0.0212(2)
OV5	0.7965(1)	0.61357(9)	0.41051(9)	0.0215(2)
OV6	0.51599(9)	0.59950(8)	0.37888(8)	0.0174(2)
OV7	0.2619(1)	0.66643(9)	0.79624(9)	0.0262(2)
OV8	0.2222(1)	0.42672(9)	0.80217(8)	0.0217(2)
OV9	0.5080(1)	0.43901(8)	0.83715(8)	0.0207(2)
OV10	0.5677(1)	0.84241(8)	0.34664(9)	0.0215(2)
OV11	0.4542(1)	0.19578(9)	0.87099(8)	0.0235(2)
OV12	0.8291(1)	0.8273(1)	0.1546(1)	0.03200(2)
OV13	0.7389(1)	0.36696(8)	0.43906(8)	0.0182(2)
OV14	0.7376(1)	0.1985(1)	0.9158(1)	0.0328(2)
<i>The $\{K_2Mg_2(H_2O)_{16}\}^{6+}$ interstitial complex</i>				
K	0.32958(4)	0.90849(3)	0.78152(4)	0.03728(8)
Mg	0.78293(5)	0.73370(4)	0.78507(4)	0.02159(8)
O11	0.9105(2)	0.5704(2)	0.7195(2)	0.0478(3)
H11A	0.878(2)	0.526(2)	0.698(2)	0.039(5)
H11B	0.992(3)	0.550(3)	0.731(2)	0.061(7)
O12	0.6407(1)	0.8942(1)	0.8556(1)	0.0286(2)
H12A	0.646(3)	0.963(2)	0.820(2)	0.050(6)
H12B	0.623(2)	0.874(2)	0.932(2)	0.034(5)
O13	0.0601(2)	1.1546(2)	0.5971(2)	0.0529(4)
H13A	-0.016(5)	1.148(4)	0.622(4)	0.12(1)
H13B	0.087(4)	1.225(3)	0.583(3)	0.09(1)
O14	0.0027(2)	0.9361(2)	0.8764(4)	0.0489(3)
H14A	-0.020(5)	0.893(5)	0.945(5)	0.16(2)
H14B	0.001(7)	1.004(7)	0.856(6)	0.23(3)
O15	0.9203(1)	0.6579(1)	0.9340(1)	0.0326(2)
H15A	0.896(3)	0.628(3)	1.003(2)	0.057(7)
H15B	1.012(4)	0.652(3)	0.934(3)	0.087(9)
O16	0.6492(1)	0.8212(1)	0.6308(1)	0.0306(2)
H16A	0.622(2)	0.773(2)	0.608(2)	0.032(5)
H16B	0.673(3)	0.866(3)	0.571(3)	0.074(9)
O17	0.6060(1)	0.6259(1)	0.8963(1)	0.0333(2)
H17A	0.592(2)	0.567(2)	0.874(2)	0.032(5)
H17B	0.583(2)	0.606(2)	0.973(2)	0.040(5)
O18	0.9457(2)	0.8538(2)	0.6639(2)	0.0422(3)
H18A	1.009(4)	0.857(3)	0.686(3)	0.10(1)
H18B	0.954(6)	0.868(5)	0.599(5)	0.17(2)

cast into our all-acute cell yields the atom arrangement found in this study.

The structural unit

The $[V_{10}O_{28}]^{6-}$ decavanadate structural unit is the fundamental building block of the hummerite atomic arrangement. Figure 1 shows the structural unit, and Figure 2 illustrates the linkage of adjacent structural units by the interstitial contents. The structural unit is centrosymmetric, and formed of ten edge-sharing octahedra; there is a similar fundamental building block in pascoite, $Ca_3V_{10}O_{28} \cdot (H_2O)_{17}$ (Swallow *et al.* 1966). Numerous synthetic compounds also contain this structural unit, as discussed by Griffen (1990).

In the structural unit, each of the octahedra contains a single vanadyl bond (defined by Schindler *et al.* 2000b as being less than 1.74 Å), save for V1, which contains two vanadyl bonds. In V2–V5, the vanadyl bond is *trans* to a long V–O bond, with four equatorial bonds of intermediate length approximately perpendicular to this O–V–O direction. In addition to bonding to the vanadium atoms of the structural unit, the oxygen atoms of the structural unit bond to the potassium atom of the interstitial complex and to the hydrogen atoms of the (H_2O) groups of the interstitial complex.

Oxygen OV6 of the structural unit is of particular interest in the structural unit. As depicted in Figure 1, OV6 bonds to six vanadium atoms, an unusual coordination for oxygen, particularly when bonded to such a highly charged cation as pentavalent vanadium. The vanadium–oxygen bonds to OV6 are the longest in each vanadium polyhedron, and thus the bond-valence is the lowest among the bonds. The bond-valence sum of 1.98 valence units, νu , for OV6 demonstrates that despite the unusually large coordination number for oxygen, the atom arrangement maintains the valence-matching principle.

The interstitial complex

The symmetry-equivalent structural units in hummerite are connected by the interstitial complex (Schindler *et al.* 2000a). The interstitial complex in hummerite is $\{K_2Mg_2(H_2O)_{16}\}^{6+}$. All oxygen atoms in the interstitial complex occur as (H_2O) groups, in contrast to the structural unit, which is devoid of hydrogen atoms. The Mg atom bonds to six (H_2O) groups in a

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN HUMMERITE

K –	O14	2.750(2)	Mg –	O17	2.046(1)					
	OV10	2.7683(9)		O18	2.048(1)					
	OV7	2.7721(9)		O11	2.055(1)					
	O16	2.9420(1)		O15	2.057(1)					
	OV14	3.013(1)		O16	2.071(1)					
	O12	3.016(1)		O12	2.089(1)					
	OV12	3.019(1)		Mean	2.061					
	OV1	3.026(1)								
	O17	3.268(1)								
	O13	3.335(2)								
	Mean	2.991								
	V1 –	OV5		1.6832(9)	V2 –	OV1	1.6082(9)	V3 –	OV7	1.6071(9)
		OV4		1.7030(9)		OV2	1.8307(9)		OV8	1.8051(8)
		OV13		1.9068(8)		OV10	1.8316(9)		OV9	1.8437(9)
OV3		1.9322(8)	OV13	1.9815(8)		OV13	1.9923(8)			
OV6		2.1097(8)	OV3	2.0040(8)		OV3	2.0149(8)			
OV6		2.1238(8)	OV6	2.2423(8)		OV6	2.2299(8)			
Mean		1.9098	Mean	1.9164		Mean	1.9155			
V4 –	OV12	1.6012(9)	V5 –	OV14	1.600(1)					
	OV11	1.8336(9)		OV11	1.8401(9)					
	OV10	1.8400(9)		OV2	1.8715(9)					
	OV8	1.9095(9)		OV9	1.8874(9)					
	OV5	2.0576(9)		OV4	2.0254(9)					
	OV6	2.3034(8)		OV6	2.3428(8)					
	Mean	1.9242		Mean	1.9279					

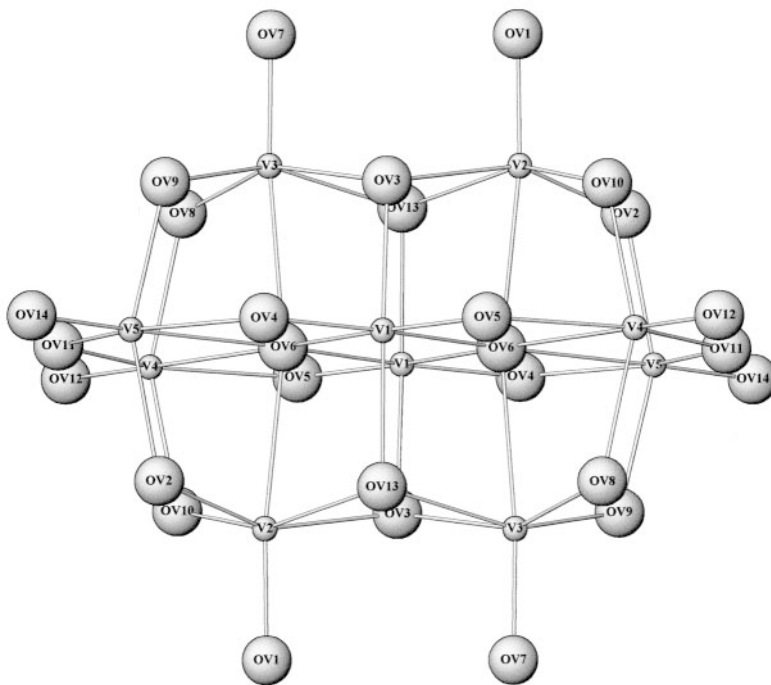


FIG. 1. $[\text{V}_{10}\text{O}_{28}]^{6-}$ structural units in hummerite.

regular octahedral arrangement (Table 3) and does not bond directly to the structural unit. Potassium bonds to ten atoms of oxygen, five of which belong to the decavanadate structural unit and five of which are (H_2O) groups of the interstitial complex.

In addition to the bonding between five oxygen atoms of the structural unit and the interstitial potassium, there is an extensive network of hydrogen bonds linking the two structural components. Table 4 lists the hydrogen bonds in hummerite, and Figure 2 depicts all hydrogen bonds with distance ≤ 2.5 Å. Schindler *et al.* (2000a) used the valence-matching principle to analyze the role and types of hydrogen bonds in vanadium minerals, and here we apply their method to the interaction between the structural unit and the interstitial complex in hummerite.

INTERSTITIAL BONDING

The interaction between the structural unit and interstitial complex can be understood by the affinity of each component to accept or to donate electrons, *i.e.*, by their Lewis basicity and Lewis acidity (Brown 1981). Schindler *et al.* (2000a) introduced a characteristic range in Lewis basicity of the structural unit, which is defined as the effective charge of that unit divided by the maxi-

mum and minimum number of accepted bonds. In the same way, they defined the Lewis acidity of an interstitial complex as its effective charge divided by the number of bonds emanating from the interstitial complex.

In order to calculate the characteristic range in Lewis basicity of a structural unit, one requires the variation in the coordination number of oxygen in the structural unit. Schindler *et al.* (2000a) found that those average coordination numbers of oxygen vary within a characteristic range. For example, ranges in average coordination number of oxygen for $[\text{VO}_3]^-$ and $[\text{V}_{10}\text{O}_{28}]^{6-}$ are [3.2]–[4.0] and [3.4]–[3.6], respectively. The corresponding ranges in Lewis basicity are 0.14–0.22 and 0.15–0.17 *vu*, respectively. The valence-matching principle requires that the Lewis acidity of the interstitial complex must closely match the range in Lewis basicity of the structural unit. On the basis of this principle, Schindler *et al.* (2000a) used the observed ranges in Lewis basicity for different vanadate structural units to predict possible interstitial complexes in minerals.

The structure refinement of dickthomssenite, $\{\text{Mg}_2(\text{H}_2\text{O})_{10}\}[\text{VO}_3]_2(\text{H}_2\text{O})_4$, is in accord with the predicted range in Lewis basicity for the $[\text{VO}_3]^-$ structural unit (Hughes *et al.* 2001). In dickthomssenite, the Lewis acidity of the interstitial complex, 0.18 *vu*, matches the corresponding range in Lewis basicity: 0.14–0.22 *vu*.

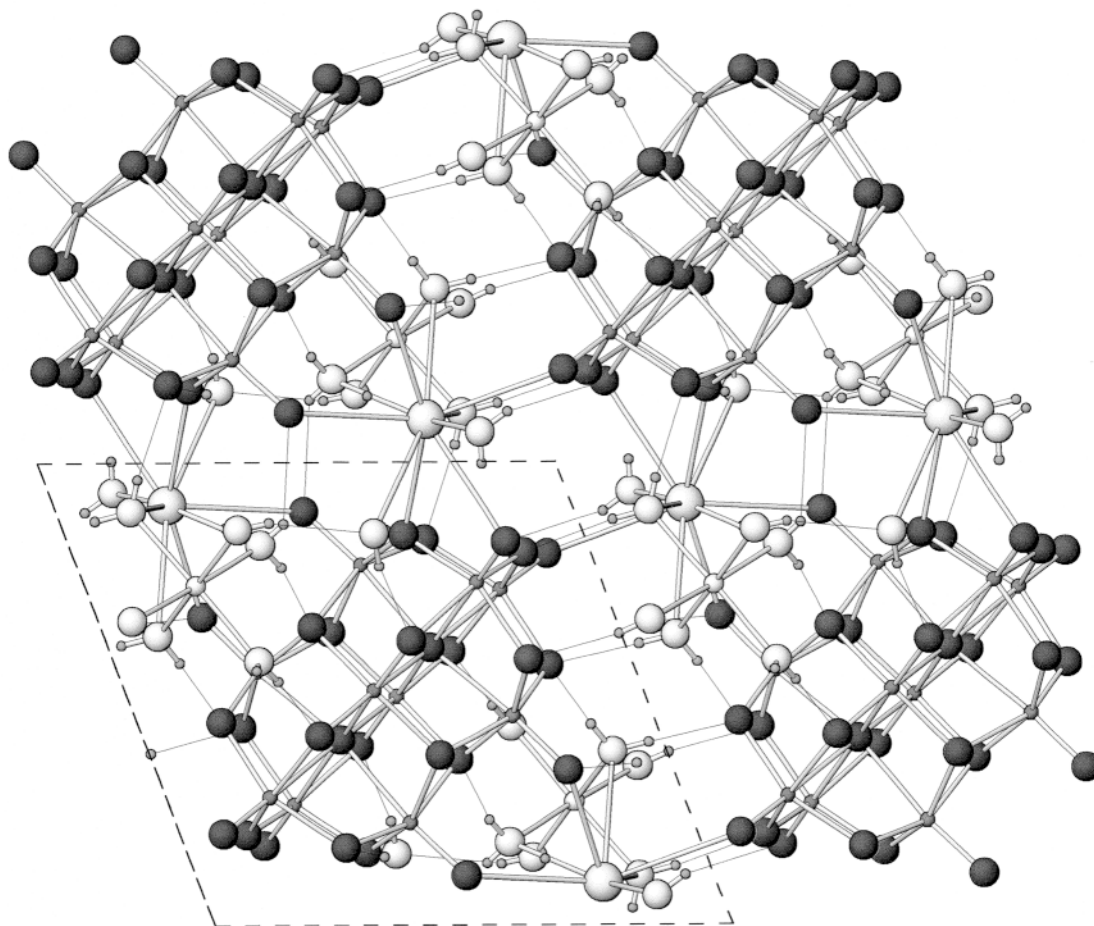


Fig. 2. Atomic arrangement of hummerite. $[V_{10}O_{28}]^{6-}$ Structural units in darker atoms, as in Figure 1. Interstitial $Mg(OH)_2$ and $K[O_5(OH)_2]_5$ atoms are depicted. Hydrogen bonds ($\leq 2.5 \text{ \AA}$) are shown with thin bonds.

Application to hummerite

Hummerite contains the interstitial complex $\{K_2Mg_2(H_2O)_{16}\}^{6+}$ and the structural unit $[V_{10}O_{28}]^{6-}$. In order to test whether the Lewis acidity of the interstitial complex matches the range in Lewis basicity of the structural unit, we must calculate the number of bonds emanating from the complex. This step requires detailed information of the types of (H_2O) groups in the interstitial complex, including: (a) transformer (H_2O) groups, which accept one bond (Fig. 3a), (b) non-transformer (H_2O) groups (Fig. 3b), and (c) reverse transformer (H_2O) groups, which accept three bonds (Fig. 3c). Inspection of the bond-valence table for hummerite shows that OI1, OI5 and OI8 are transformer (H_2O) groups (Table 4).

The (H_2O) group OI1 accepts one bond from Mg with two emanated hydrogen bonds to OV4 and OV8 (Fig. 3a). Non-transformer (H_2O) groups occur at OI2, OI4, OI6 and OI7; for example, OI2 accepts bonds from Mg and K, with hydrogen bonds to OV2 and OV11 (Fig. 3b). OI3 is the only reverse transformer (H_2O) group; it accepts two hydrogen bonds from H4B and H8B and one weak bond from K, with two hydrogen bonds accepted by OV2 and OV5 (Fig. 3c).

This detailed information of the interstitial complex in hummerite can be given by the general formula: $\{^{10}K_2^{16}Mg_2(H_2O)_6(H_2O)_8(H_2O)_2\}^{6+}$. Here, the different H_2O groups are listed in the sequence *transformer*, *non-transformer* and *reverse-transformer* (H_2O) groups. The number of bonds from this complex can be calculated: 2×10 (K) + 2×6 (Mg) + 6 [transformer (H_2O)

TABLE 4. BOND VALENCES (*vu*) FOR ATOMS IN HUMMERITE

	K	Mg	V1	V2	V3	V4	V5	HI 1A	HI 1B	HI 2A	HI 2B	HI 3A	HI 3B	HI 4A	HI 4B	HI 5A	HI 5B	HI 6A	HI 6B	HI 7A	HI 7B	HI 8A	HI 8B	SUM
OV1	0.09			1.69															0.25					2.03
OV2				0.93			0.83			0.20	0.20													2.16
OV3			0.71	0.58	0.56													0.25						2.10
OV4			1.31				0.55	0.20																2.06
OV5			1.38			0.50					0.20													2.08
OV6			0.42	0.31	0.32	0.26	0.23																	1.98
			0.44																					
OV7	0.18				1.70												0.20							2.08
OV8					0.99	0.75			0.20							0.20								2.14
OV9					0.90		0.80														0.20	0.20		2.10
OV10	0.18			0.93			0.90																	2.01
OV11							0.92	0.90			0.20													2.02
OV12	0.09						1.73								0.20									2.02
OV13			0.76	0.62	0.60																			1.98
OV14	0.09						1.73																	1.82
OI1		0.38						0.80	0.80															1.98
OI2	0.09	0.34								0.80	0.80													2.03
OI3	0.04											0.80	0.80		0.20								0.20	2.04
OI4	0.19													0.80	0.80							0.20		1.99
OI5		0.38														0.80	0.80							1.98
OI6	0.11	0.36																0.75	0.75					1.97
OI7	0.05	0.38																		0.80	0.80			2.03
OI8		0.38																				0.80	0.80	1.98
SUM	1.11	2.22	5.02	5.06	5.07	5.06	5.04	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	44.58

groups] - 2 [reverse transformer (H₂O) groups] = 36 bonds (Schindler & Hawthorne 2001). This number of bonds results in a Lewis acidity of $6 / 36 = 0.167$ *vu*, which matches the range in Lewis basicity of the structural unit [V₁₀O₂₈]⁶⁻ (0.15–0.17 *vu*), thus satisfying the valence-matching principle and explaining the stability of the arrangement of atoms in hummerite.

SUMMARY

The atom arrangement in hummerite can be divided into two components, the {K₂Mg₂(H₂O)₁₆}⁶⁺ interstitial complex and the [V₁₀O₂₈]⁶⁻ structural unit. Analysis of the hydrogen bonding in hummerite demonstrates the efficacy of the valence-matching principle in the

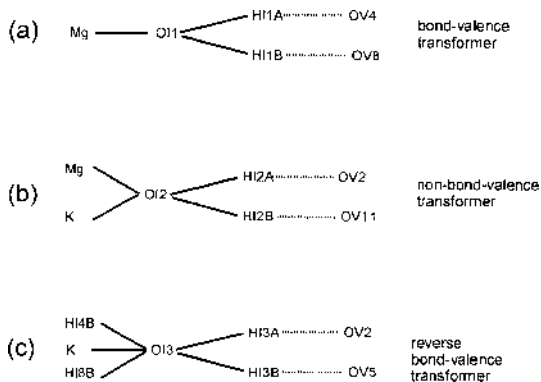


FIG. 3. Types of H₂O groups in the interstitial complex of hummerite.

analysis of bonding between the structural unit and interstitial complex in complex minerals. Vanadium minerals are particularly amenable to such an analysis, and application of the valence-matching principle to the bonding between the structural unit and interstitial complex has led to increased understanding of the stability of these minerals.

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