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The Crystal Structure of Hummerite, with Comments on the Crystallochemical Stability of the Decavanadate Isopolyanion

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ABSTRACT

The crystal structure of a natural hummerite, $K_2Mg_2V_{10}O_{28}\cdot 16H_2O$, was refined in space group $P\bar{1}$ by least-squares techniques, using 4565 unique, observed [$I > 3\sigma(I)$] reflections collected with an automated four-circle X-ray diffractometer. Unit-cell parameters are $a = 10.735(2)$Å, $b = 11.085(2)$Å, $c = 8.831(1)$Å, $\alpha = 106.01°(1)$, $\beta = 108.04(1)°$, $\gamma = 65.81°(1)$, $V = 897.9(2)$Å^3. The final conventional residuals were $R = 0.033$ and $R_w = 0.029$. Positions of the hydrogen atoms were not determined. The unit cell contains three types of structural entities: (1) the centrosymmetric $[V_{10}O_{28}]^{6-}$ isopolyvanadate anion, a highly condensed complex consisting of ten edge-sharing and severely distorted octahedra; (2) a nearly ideal octahedron of water molecules surrounding the Mg atom; and (3) a K atom in irregular 10-coordination by 5 oxygens of the decavanadate complex, 3 water molecules of the $Mg(OH_2)_6$ octahedron, and two other water molecules not bonded directly to anything else except by hydrogen bonds. The hydrogen-bonding network is extensive and involves the entire range from strong interactions represented by O···O distances as short as 2.7Å to weak ones represented by O···O distances as long as 3.3Å.

The geometrical features of the distorted vanadate octahedra are not entirely consistent with the predictions of Pauling's rules, but tend toward geometries known in many other vanadate structures and are explicable only as preferences due to partial covalency of the V^{5+}—O bond. The two central oxygens of the isopolyvanadate complex are 6-coordinated, and consequently form relatively weak, long bonds to the surrounding vanadium atoms. This shortens the V-O bonds *trans* to the long ones, and allows the four *cis* bonds to bend toward the long ones, simulating the square pyramidal coordination preferred by V^{5+}. Considered in an ionic sense, the decavanadate complex should, by Pauling's third rule (i.e., destabilization due to shared edges), be less stable than alternative configurations. In fact, it turns out to be quite stable owing to this approximation to favorable covalent geometry. A strong, negative linear correlation between the mean of two adjacent V-O distances and the O-V-O angle they form suggests that repulsion between concentrations of electrons in bonding orbitals significantly influences the distorted geometry.

INTRODUCTION

Hummerite, a potassium magnesium decavanadate hydrate ($K_2Mg_2V_{10}O_{28}\cdot 16H_2O$) first recognized in samples collected in 1949 from the Hummer Mine, Paradox Valley, Montrose County, Colorado, was initially described by Weeks and others (1951). They correctly determined the crystal system and class, along with some other rather approximate mineralogical data, from artificially recrystallized material. Like several other vanadates from the same region, this mineral occurs as small drusy crystals in veins, and as efflorescences in sandstones, but not as large crystals. Nevertheless, hummerite is easily dissolved in water, and larger crystals can be precipitated from solution.

In an investigation of compounds containing the decavanadate complex, Evans (1966) reported the crystal structure of synthetic $K_2Zn_2V_{10}O_{28}\cdot 16H_2O$, determined by X-ray diffraction methods. This compound is triclinic, $P\bar{1}$, with lattice parameters $a = 10.778$, $b = 11.146$, $c = 8.774$Å, $\alpha = 105.0$, $\beta = 109.5$, $\gamma = 65.0°$; Evans assumed that it was isostructural with hummerite and other triclinic double salts with analogous formulas. He found that the decavanadate complex is a highly condensed polyanion consisting of six edge-sharing VO_6 octahedra disposed in a block two octahedra by three octahedra, with four other octahedra, two above and two below this block, sharing edges with it. (See his figure 3 or figure 3 of this work.) The Zn atom is octahedrally coordinated by H_2O molecules, which are absent from the decavanadate complex. K has an irregular coordination sphere of nine oxygens and water molecules, and hydrogen bonding plays a major role in the structure.

The discovery of a small amount of bright orange hummerite in association with drusy orange pascoite in a specimen collected from the Corvusite Mine, Beaver Mesa, La Sal Mountains, Utah, by Dr. Bart J. Kowallis has made it possible to determine the crystal structure of this mineral from a natural (that is, nonrecrystallized) specimen. This study was undertaken in order to compare the structure with that of synthetic $K_2Zn_2V_{10}O_{28}\cdot 16H_2O$, to investigate the distortions in the isopolyvanadate anion $[V_{10}O_{28}]^{6-}$, and to elucidate further the hydrogen bonding with the aid of bond-length–bond-valence calculations.

STRUCTURE REFINEMENT

The crystal selected was a clear orange fragment 0.17 × 0.20 × 0.25 mm in size and crudely prismatic in shape. A Nicolet R3 four-circle single-crystal diffractometer with graphite monochromatized Mo$K\alpha$ radiation was used for data collection, and unit cell parameters (a = 10.735(2), b = 11.085(2), c = 8.831(1)Å, α = 106.01(1), β = 108.04(1), γ = 65.81(1)°, V = 897.9(2)Å^3) were obtained by least-squares refinement of 25 automatically centered reflections, 4°<2<31°. A fragment from the same crystal was examined by scanning electron microscopy using energy dispersive X-ray analysis; only Mg, K, and V were detected. Based on this result, ideal chemistry was postulated for purposes of the structure refinement (and effectively confirmed by the success of the model). A total of 6394 intensities (a unique hemisphere to $\sin\theta/\lambda$ = 0.76) were measured in the θ–2θ mode with the scan rate automatically varied from 2.9 to 29.3° min^{-1}, depending on reflection intensity. Of these, 6188 reflections were unique, and 4565 were considered observed [$I>3\sigma(I)$]. Three standards were collected once every 100 reflections. Background and Lorentz-polarization corrections were applied.

Space group $P\bar{1}$ was assumed by analogy with the potassium zinc decavanadate hydrate of Evans (1966), and was confirmed by the refinement. The program package SHELX–76 (Sheldrick 1976) was used for all data processing except for the absorption correction (see below). Atomic scattering factors were taken from Cromer and Mann (1968), and anomalous-dispersion factors from Cromer and Liberman (1970). During the first three cycles of the refinement, oxygen atoms were excluded from the model, starting positional parameters for the metal atoms were obtained from Evans (1966), and isotropic temperature-factor coefficients were used; this resulted in convergence to R = 0.35, suggesting that hummerite was indeed isostructural with $K_2Zn_2V_{10}O_{28}\cdot 16H_2O$. At this stage all 22 oxygen atoms were resolved unambiguously on a difference-Fourier map as peaks ranging in height from 1.2 to 1.7e/Å^3, and they were subsequently included in the model. Further refinement with isotropic temperature factors reduced the residual to 0.093, and the introduction of anisotropic temperature factors for the metal atoms lowered it to 0.060.

The mass absorption coefficient of hummerite is 27.4 cm^{-1}, large enough to warrant an absorption correction. The method of Walker and Stuart (1983) was used, and thereafter anisotropic temperature factors were applied to all atoms. During the final cycles of refinement, reflections were weighted proportional to $1/\sigma^2(F_o)$. Examination of the observed and calculated structure factors showed that three intense reflections appeared to suffer substantially from extinction, so they were removed from the data set; an isotropic extinction correction was applied to the rest of the data. The final residuals were R = 0.033 and R_w = 0.029. A final difference-Fourier was essentially flat and failed to show the locations of the hydrogens—not an unexpected result considering the number of heavy atoms in the structure.

Table 1 lists the final refined fractional coordinates, and selected interatomic distances and angles are given in table 2. A listing of observed and calculated structure amplitudes is available from the author upon request.

DISCUSSION

CRYSTAL STRUCTURE

Three types of structural units make up the atomic arrangement of hummerite: a centrosymmetric $[V_{10}O_{28}]^{6-}$ complex; an $Mg(OH_2)_6$ octahedron; and an irregular $KO_5(OH_2)_5$ polyhedron that shares its five oxygens with decavanadate groups, three of its water molecules with the Mg atom, and is also bonded to two water molecules that are not attached to anything else. Bond-valence calculations (Brown 1981) are reported in table 3 and clearly show that O(15) through O(22) are H_2O molecules. Hummerite is, indeed, identical in its bond topology to $K_2Zn_2V_{10}O_{28}\cdot 16H_2O$ as determined by Evans (1966), and his figure 1 shows the arrangement of these structural entities in the unit cell. For each of the metal atoms, the sum of bond valences is very close to the nominal oxidation number, except for Mg; a comment on this discrepancy is made below under the discussion of the $Mg(OH_2)_6$ octahedron.

The Potassium Site

The K atom in hummerite is 8- to 10-coordinated, depending on the maximum K-O distance that one wishes to call a bond. The nearest eight oxygens, three of which belong to water molecules, range from 2.76 to 3.03Å from the cation, and are clearly bonded to it. The other two, O(15) and O(21), are 3.28 and 3.37Å from the potassium, and if one of them is considered bonded, there is no obvious reason why the other should not be. The mean

Table 1. Fractional coordinates and anisotropic temperature-factor coefficients ($\times 10^4$) for hummerite.

Atom	*x*	*y*	*z*	U_{11}*	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V(1)	0.22224(5)**	0.54719(5)	0.38861(6)	141(2)	158(2)	184(2)	33(2)	14(2)	−57(2)
V(2)	0.45160(5)	0.26976(5)	0.35320(6)	166(2)	147(2)	154(2)	11(2)	34(2)	−69(2)
V(3)	0.27665(5)	0.79892(5)	0.37021(6)	183(2)	164(2)	211(3)	68(2)	17(2)	−51(2)
V(4)	0.50654(5)	0.51939(5)	0.32462(5)	166(2)	155(2)	118(2)	30(2)	33(2)	−62(2)
V(5)	0.73954(5)	0.24157(5)	0.30593(6)	187(2)	179(2)	203(3)	1(2)	78(2)	−52(2)
K	0.0923(1)	0.2177(1)	0.3306(1)	326(4)	441(4)	346(4)	−6(3)	155(3)	−177(3)
Mg	0.7338(1)	0.7848(1)	0.2165(1)	222(5)	188(5)	167(5)	28(4)	49(4)	−75(4)
O(1)	0.6434(2)	0.5915(2)	0.4759(2)	177(9)	161(9)	144(9)	44(7)	41(7)	−60(7)
O(2)	0.4391(2)	0.8373(2)	0.4927(2)	202(10)	146(9)	220(10)	48(7)	45(8)	−65(8)
O(3)	0.5993(2)	0.3789(2)	0.4837(2)	161(9)	149(9)	153(9)	28(7)	30(7)	−55(7)
O(4)	0.8042(2)	0.1292(2)	0.4538(3)	198(10)	174(10)	253(11)	35(8)	63(8)	−50(8)
O(5)	0.8424(2)	0.3470(2)	0.4321(2)	170(9)	201(10)	227(11)	34(8)	58(8)	−57(8)
O(6)	0.1070(2)	0.4769(2)	0.3000(3)	199(10)	244(11)	301(12)	59(9)	14(9)	−104(9)
O(7)	0.3341(2)	0.2030(2)	0.2624(3)	248(11)	250(11)	232(11)	9(9)	32(9)	−147(9)
O(8)	0.1679(2)	0.6893(2)	0.2856(2)	184(9)	197(10)	204(10)	61(8)	11(8)	−70(8)
O(9)	0.3674(2)	0.4385(2)	0.2616(2)	167(9)	163(9)	133(9)	25(7)	18(7)	−73(7)
O(10)	0.5737(2)	0.1971(2)	0.2222(2)	200(10)	190(10)	190(10)	−7(8)	64(8)	−75(8)
O(11)	0.1993(2)	0.9155(2)	0.2637(3)	303(12)	263(12)	336(13)	148(10)	10(10)	−74(9)
O(12)	0.4091(2)	0.6569(2)	0.2348(2)	209(10)	211(10)	184(10)	70(8)	31(8)	−81(8)
O(13)	0.6137(2)	0.4104(2)	0.2040(2)	220(10)	230(10)	147(10)	25(8)	62(8)	−83(8)
O(14)	0.8274(2)	0.1545(2)	0.1714(3)	326(13)	288(12)	298(13)	−38(10)	169(10)	−108(10)
O(15)	0.6243(2)	0.8966(2)	0.3935(3)	365(13)	240(11)	388(14)	−24(10)	238(11)	−108(10)
O(16)	0.8209(2)	0.6296(2)	0.3497(3)	307(12)	237(11)	337(13)	104(9)	117(10)	−64(9)
O(17)	0.8944(2)	0.8556(2)	0.3580(3)	230(11)	223(11)	323(13)	53(9)	37(9)	−85(9)
O(18)	0.5692(3)	0.7191(3)	0.0883(3)	512(16)	710(20)	237(13)	130(12)	−42(11)	−463(15)
O(19)	0.6578(2)	0.9340(2)	0.0784(2)	392(13)	235(11)	256(12)	74(9)	63(10)	−84(10)
O(20)	0.8535(3)	0.6634(3)	0.0527(3)	453(15)	405(15)	302(14)	−6(11)	208(12)	−39(12)
O(21)	0.8435(3)	0.4027(3)	0.0584(3)	648(21)	466(18)	434(17)	−54(13)	126(15)	−286(16)
O(22)	0.9370(3)	0.8763(3)	−0.0023(3)	577(19)	538(18)	406(16)	30(13)	183(14)	−238(16)

*Numbers in parentheses are e.s.d.'s, and refer to last digit cited.
**U_{ij} are coefficients in the expression $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}\ell^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}h\ell + 2b^*c^*U_{23}k\ell)]$.

bond lengths predicted from ionic radii (Shannon 1976) do not distinguish between these two possibilities. For KO_8 and KO_{10} groups, respectively, they are expected to be about 2.9 and 3.0Å, and the mean bond lengths observed in this structure are 2.92 (8-coordination) and 3.00Å (10-coordination).

Table 3 shows that the sum of bond strengths reaching K is 0.97 v.u. (valence units). The contributions from O(15) and O(21) are 0.04 and 0.03 v.u., respectively, and elimination of these would result in a bond-strength sum of 0.90 v.u. for K. This is a greater deficiency than would be expected, and suggests that both O(15) and O(21) should be considered bonded to potassium. An additional observation bearing on the question is that the metal atoms taken together are close to charge-balanced, on average, if the sum for K is 0.97 v.u., but not if it is 0.90 v.u. The potassium coordination is shown in figure 1.

Of interest are the differences between the K site in hummerite and that in $K_2Zn_2V_{10}O_{28}\cdot 16H_2O$. Whereas all but one of the corresponding K-O bond lengths in the two structures are essentially identical, the K-O(21) bond lengths differ by nearly 0.3Å: 3.372Å in hummerite and 3.080Å in the Zn compound. In the latter, O(21) is unambiguously within the coordination sphere of potassium, and Evans omits the much further O(15) to give a KO_9 polyhedron. The reason for the difference in positions of this H_2O molecule is not clear, but because it is not a part of any other coordination polyhedron, its position is restricted only by its interaction with the K atom and some weak hydrogen bonds in which it is involved (see below).

*Table 2. Interatomic distances (Å) and bond angles (°) in hummerite.**

V(1) −O(6)	1.613	O(6) −O(5)	2.689	102.4	σ^2oct=118.7°²**
−O(5)	1.831	−O(8)	2.732	104.7	
−O(8)	1.832	−O(9)	2.765	99.9	
−O(9)	1.984	−O(1)	2.748	98.4	
−O(1)	2.001	O(5) −O(8)	2.674	93.8	
−O(3)	2.248	−O(1)	2.692	89.1	
Mean	1.918	−O(3)	2.652†	80.4	
		O(8) −O(9)	2.727	91.1	
		−O(3)	2.668†	81.0	
		O(9) −O(1)	2.474†	76.7	
		−O(3)	2.621†	76.2	
		O(1) −O(3)	2.609†	75.5	
		Means	2.671	89.1	
V(2) −O(7)	1.611	O(7) −O(10)	2.676	102.9	σ^2oct=116.7°²
−O(10)	1.807	−O(2)	2.681	101.6	
−O(2)	1.843	−O(9)	2.778	100.4	
−O(9)	1.991	−O(1)	2.791	100.0	
−O(1)	2.017	O(10)−O(2)	2.700	95.4	
−O(3)	2.231	−O(9)	2.701	90.5	
Mean	1.917	−O(3)	2.639†	80.9	
		O(2) −O(1)	2.709	89.0	
		−O(3)	2.664†	81.1	
		O(9) −O(1)	2.474†	76.2	
		−O(3)	2.612†	76.2	
		O(1) −O(3)	2.614†	75.8	
		Means	2.670	89.2	
V(3) −O(11)	1.598	O(11)−O(4)	2.688	102.6	σ^2oct=122.1°²
−O(4)	1.841	−O(8)	2.727	103.2	
−O(8)	1.875	−O(2)	2.717	101.9	
−O(2)	1.892	−O(12)	2.831	102.1	
−O(12)	2.028	O(4) −O(8)	2.636	90.3	
−O(3)	2.347	−O(2)	2.656	90.7	
Mean	1.930	−O(3)	2.745†	80.9	
		O(8) −O(12)	2.627	84.5	
		−O(3)	2.668†	77.5	
		O(2) −O(12)	2.617	83.7	
		−O(3)	2.664†	77.0	
		O(12)−O(3)	2.657†	74.4	
		Means	2.686	89.1	
V(4) −O(13)	1.682	O(13)−O(12)	2.721	107.1	σ^2oct=93.9°²
−O(12)	1.701	−O(9)	2.724	98.4	
−O(9)	1.911	−O(1)	2.700	96.4	
−O(1)	1.934	−O(3)	2.646†	87.7	
−O(3)	2.112	O(12)−O(9)	2.718	97.5	
−O(3)	2.125	−O(1)	2.725	96.9	
Mean	1.911	−O(3)	2.657†	87.2	

Table 2. Continued

		O(9) −O(3)	2.612†	80.8	
		−O(3)	2.621†	80.8	
		O(1) −O(3)	2.609†	80.2	
		−O(3)	2.614†	80.0	
		O(3) −O(3)	2.664†	77.9	
		Means	2.668	89.2	
V(5) −O(14)	1.596	O(14)−O(4)	2.681	102.5	σ^2oct=115.0°^{2}
−O(4)	1.835	−O(5)	2.687	102.4	
−O(5)	1.845	−O(10)	2.725	101.5	
−O(10)	1.913	−O(13)	2.832	100.8	
−O(13)	2.059	O(4) −O(5)	2.674	93.2	
−O(3)	2.306	−O(10)	2.657	90.3	
Mean	1.926	−O(3)	2.745†	82.2	
		O(5) −O(13)	2.624	84.3	
		−O(3)	2.652†	78.6	
		O(10)−O(13)	2.624	82.6	
		−O(3)	2.639†	76.8	
		O(13)−O(3)	2.646†	74.4	
		Means	2.682	89.2	
Mg −O(20)	2.053	O(20)−O(19)	2.867	88.1	σ^2oct=6.8°^{2}
−O(15)	2.058	−O(18)	2.956	91.5	
−O(19)	2.069	−O(16)	2.891	88.7	
−O(18)	2.073	−O(17)	2.978	91.8	
−O(16)	2.082	O(15)−O(19)	3.070	96.1	
−O(17)	2.094	−O(18)	2.920	90.0	
Mean	2.072	−O(16)	2.849	87.0	
		−O(17)	2.849	86.7	
		O(19)−O(18)	2.934	90.2	
		−O(17)	2.965	90.9	
		O(18)−O(16)	2.969	91.3	
		O(16)−O(17)	2.896	87.8	
		Means	2.929	90.0	
K −O(22)	2.762				
−O(5)	2.772				
−O(7)	2.774				
−O(16)	2.955				
−O(11)	3.011				
−O(17)	3.023				
−O(14)	3.028				
−O(6)	3.030				
−O(15)	3.279				
−O(21)	3.372				
Mean	3.001				

*e.s.d.'s as follows: V-O, Mg-O, and K-O distances, 0.002Å; O···O distances, 0.003Å; all angles, 0.1°.
**Octahedral angle variances (Robinson and others 1971).
† These edges are shared between adjacent VO_6 octahedra in the decavanadate isopolyanion.

Table 3. Bond strength sums for hummerite (excluding hydrogen bonds).

	V(1)	V(2)	V(3)	V(4)	V(5)	K	Mg	Σ
O(1)	0.57	0.55		0.68				1.80
O(2)		0.86	0.76					1.62
O(3)	0.32	0.33	0.25	0.42, 0.43	0.28			2.03
O(4)			0.87		0.88			1.75
O(5)	0.89				0.86	0.17		1.92
O(6)	1.71					0.07		1.78
O(7)		1.72				0.17		1.89
O(8)	0.89		0.79					1.68
O(9)	0.59	0.58		0.72				1.89
O(10)	0.96				0.71			1.67
O(11)			1.76			0.08		1.84
O(12)			0.53	1.30				1.83
O(13)				1.38	0.49			1.87
O(14)					1.80	0.07		1.87
O(15)						0.04	0.37	0.41
O(16)						0.09	0.35	0.44
O(17)						0.08	0.34	0.42
O(18)							0.35	0.35
O(19)							0.36	0.36
O(20)							0.37	0.37
O(21)						0.03		0.03
O(22)						0.17		0.17
	4.97	5.00	4.96	4.93	5.02	0.97	2.14	

It is likely that resolution of the hydrogen atoms is required to solve this problem.

The $Mg(OH_2)_6$ Octahedron

The H_2O molecules surrounding the Mg atom are disposed in a nearly regular octahedron, as shown in figure 2. The octahedral angle variance (Robinson and others 1971) is only 6.8°², the range in bond lengths is only 0.041Å, and the standard deviation of the population of six bond lengths is 0.014Å. The $Zn(OH_2)6$ octahedron of $K_2Zn_2V_{10}O_{28}\cdot 16H_2O$ (Evans 1966) is also fairly regular, but somewhat more distorted than its counterpart in hummerite; the octahedral angle variance, bond-length range, and corresponding standard deviation for it are 15.8°², 0.060Å, and 0.024Å, respectively. The mean Zn-OH_2 and Mg-OH_2 bond lengths are 2.099Å and 2.072Å, consistent with the ionic radii given in Shannon (1976) for the appropriate Zn, Mg, and O coordination numbers.

It is possible that the differences in distortions in the two octahedra are artifacts of inappropriate absorption or extinction corrections. In order to test this hypothesis, the bond lengths and angles were calculated for the positions determined in the final isotropic refinement preceding the application of these corrections. The results were similar to the final results for hummerite, yet still different, in the ways noted above, from those for $K_2Zn_2V_{10}O_{28}\cdot 16H_2O$. Moreover, the R-factor for hummerite at this stage was virtually identical to the final R-factor of Evans' refinement, which was also completed with isotropic temperature factors and no absorption or extinction corrections. The two data sets thus seem to be of comparable quality, and the differences in the $Mg(OH_2)_6$ and $Zn(OH_2)_6$ octahedra are taken to be real.

They are likely caused by differences in the strengths of hydrogen bonds involving O(15) through O(20). In particular, the differences in the positions of O(21) in the two structures results in a closer O(20)···O(21) approach for the $Zn(OH_2)_6$ octahedron, and thus a stronger hydrogen bond. This lengthens Zn-O(20) relative to Mg-O(20), which in turn drives adjustments in other Zn-O bond lengths in order to maintain an appropriate mean bond length. Such adjustments affect other hydrogen-bonded contacts, and consequently it is not surprising that the distortions in the two octahedra are slightly different.

The $Mg(OH_2)_6$ octahedron is more similar to $Mg(OH_2)_6$ octahedra in other structures than it is to the $Zn(OH_2)_6$ octahedron. Such octahedra occur in $MgSO_4\cdot 7H_2O$ (epsomite; Baur 1964) and $MgSO_4\cdot 6H_2O$ (Zalkin and others 1964). The octahedral angle variances for the three octa-

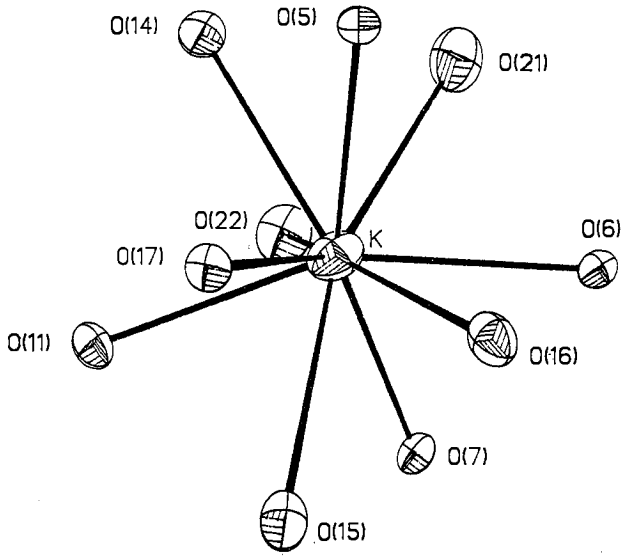

FIGURE 1.—*The irregular coordination sphere of potassium in hummerite. Thermal ellipsoids are drawn at 50% probability in this and subsequent figures.*

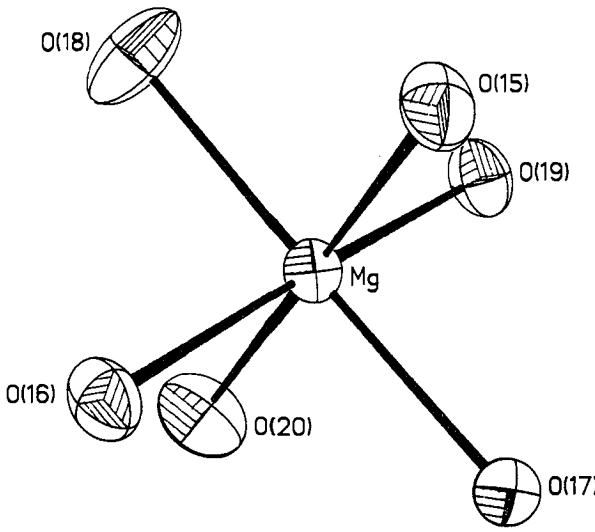

FIGURE 2.—*The $Mg(OH_2)_6$ octahedron in hummerite.*

hedra in those structures range from 3.5Å^2 to 4.4Å^2. Mean Mg-O bond lengths, 2.057Å to 2.065Å, are slightly smaller than in hummerite. It seems more than merely fortuitous that the sums of the bond valences to all three of these Mg atoms are in excess of 2.00 by about the same amount as in hummerite, and suggests some inadequacy in the bond-length–bond-valence relation for Mg given in Brown (1981). In fact, for a hypothetical MgO_6 octahedron in which all Mg-O distances are equal, this relation gives 2.00 only for bond lengths consistent with mean oxygen coordination numbers midway between 3 and 4; because all of the oxygens in the $Mg(OH_2)_6$ octahedron of each of these structures are 3-coordinated, the calculated excess bond strength is inevitable.

The $[V_{10}O_{28}]^{6-}$ Polyanion

The decavanadate polyanion is shown in figure 3. Perusal of both this figure and the stereo plot of figure 4 confirms that the octahedra are substantially distorted, but neither all equally nor in precisely the same ways. Each of the vanadium atoms is displaced from the center of its respective octahedron in a direction generally away from the center of the complex and also from all of its nearest-neighbor vanadium atoms. The octahedral angle variances (Robinson and others 1971) for the VO_6 octahedra are given in table 2, and it is clear that the octahedra on the top, bottom, and corners of the complex (that is, those that have one vertex not shared with any other octahedron, and have the smallest number of shared edges) are the most distorted, whereas the V(4) octahedron (which shares all of its oxygens with other vanadium atoms and has the largest number of shared edges) is the least distorted. Evans considered that the distortions in $K_2Zn_2V_{10}O_{28}\cdot 16H_2O$ were consistent with Pauling's rules, but also indicated that some of the O-V-O angles were reminiscent of those common to other vanadates, and implied that this might indicate some control by configurations of covalent bonding orbitals. Since Evans' work on $K_2Zn_2V_{10}O_{28}\cdot 16H_2O$, there have been several compounds, both inorganic (e.g., Durif and others 1980, Rivero and others 1984, Saf'yanov and others 1979, and Swallow and others 1966) and organic (e.g., Capparelli and others 1986, Debaerdemaeker and others 1982, Shao and others 1984, and Shao and others 1986), for which the structures have been determined. Following Evans' lead, most of these authors have ascribed the distortions in the decavanadate isopolyanion either to ionic repulsive forces between the vanadium cations or to the covalent bond-angle preferences of V^{5+}, or simply pointed out that the geometry is consistent with either interpretation.

Figure 4 and table 2 show that each of the VO_6 octahedra, except for the one involving V(4), has one short V-O bond, one long bond *trans* to the short one, and four *cis* bonds of intermediate length; this is obviously an approach to square pyramidal coordination, and is typical of octahedrally coordinated V^{5+} even when it is not part of an isopolyanion (see, for example, Bachman and others 1961, Calvo and Manolescu 1973, Gopal and Calvo 1974). V(4) has two relatively short bonds that form an angle at V

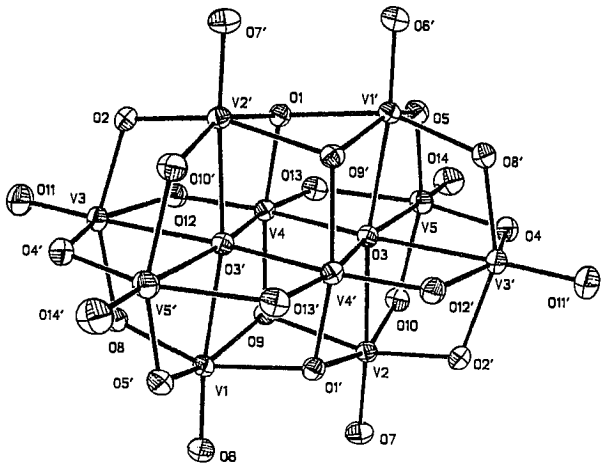

FIGURE 3.—*The $[V_{10}O_{28}]^{6-}$ isopolyvanadate anion in hummerite.*

of around 107°, two long ones *trans* to those, and two other bonds of intermediate length; this configuration is also known in other compounds (for example, Evans and Block 1966, Drew and others 1974, Scheidt and others 1971, Waltersson and others 1974). It was pointed out long ago (Hanic 1958) that the vanadium atom and its two nearest oxygens can be thought of as a VO_2^+ ion that coordinates from two to four other oxygens at greater distances, but the arrangement of atoms in compounds in which V^{5+} is surrounded by five oxygens with two short distances generally constitutes a trigonal bipyramid or very distorted square pyramid. It is clear from these and the many other examples that could be cited that V^{5+} prefers to be surrounded by five oxygens in approximate square pyramidal coordination, generally with one additional oxygen at considerable distance and *trans* to the shortest pyramidal bond. Moreover, this strongly directional preference must reflect the partial covalency of the $V^{5+}-O$ bond.

Evans' (1966) observation that the positions of the vanadium atoms within their respective octahedra of $K_2Zn_2V_{10}O_{28}\cdot 16H_2O$ are consistent with the electrostatic repulsions predicted by Pauling's rules is correct in a general way, but the detailed geometry of those octahedra is not entirely consonant with Pauling's rules either for the Zn compound or for hummerite. The V···V distances vary from 3.059 to 3.295Å; a plot of those distances versus the lengths of associated shared edges reveals a scatter of points with no discernible relationship, but the third shortest V···V separation (only 3.081Å) has the *longest* associated shared edge—a result inexplicable by Pauling's rules. Additionally, some of the unshared edges are shorter than some of the shared ones. Moreover, as shown in figures 5 through 7, trends in the geometrical relationships among O-V-O angles, the lengths of octahedral edges that subtend them, and the means of the two associated bond lengths are continuous from shared to unshared edges, indicating that the geometry of the decavanadate isopolyanion is not solely dictated by factors implicit in Pauling's rules.

The circled anomalies on figures 5, 6, and 7 represent the shortest shared edge (that between V(1) and V(2)) and the longest shared edge (that between V(3) and V(5)), and, while they fit reasonably well in figure 7, their positions are clearly independent of the trends in figures 5 and 6. The reason for the unusually short O(9)···O(1) edge is that

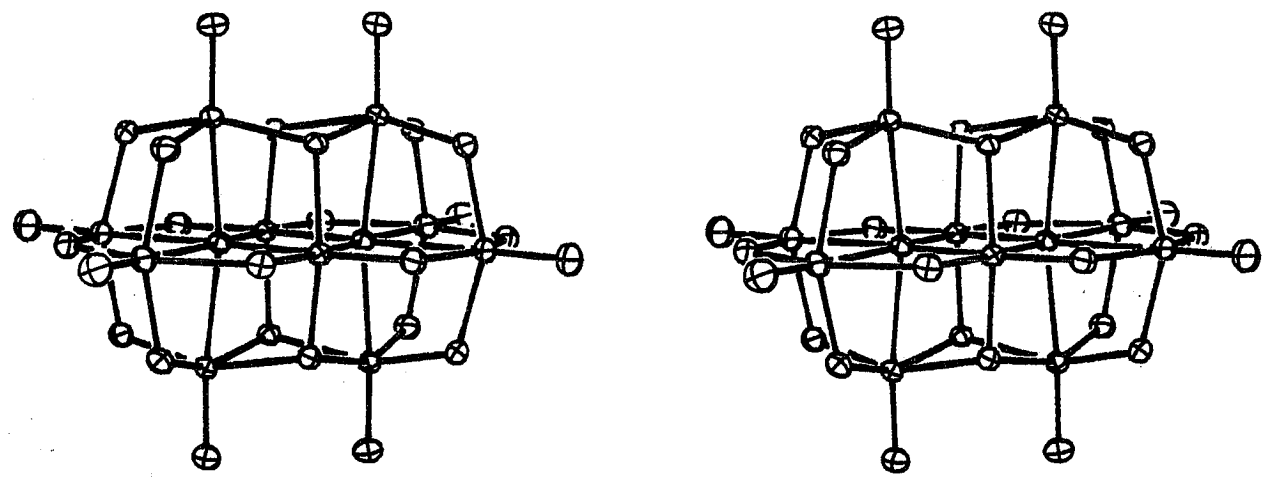

FIGURE 4.—*Stereo view of the decavanadate polyanion.*

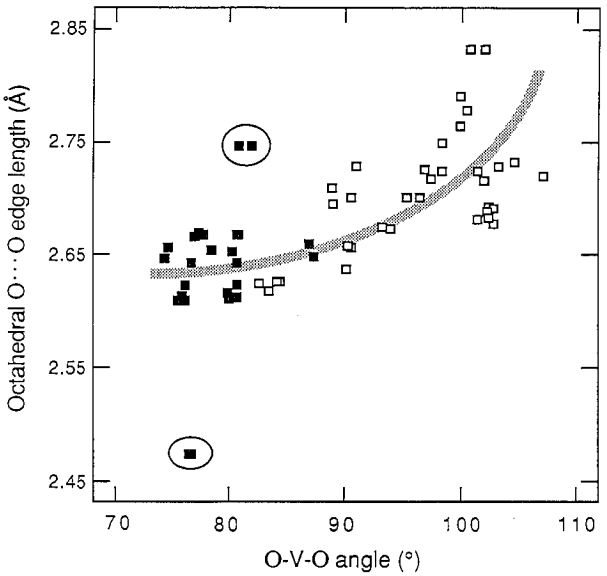

FIGURE 5.—*Octahedral angles versus octahedral edge lengths for the decavanadate polyanion in hummerite. Filled squares represent shared edges, empty squares unshared edges. The circled data points are for the shortest and longest of the shared edges, and are discussed in the text.*

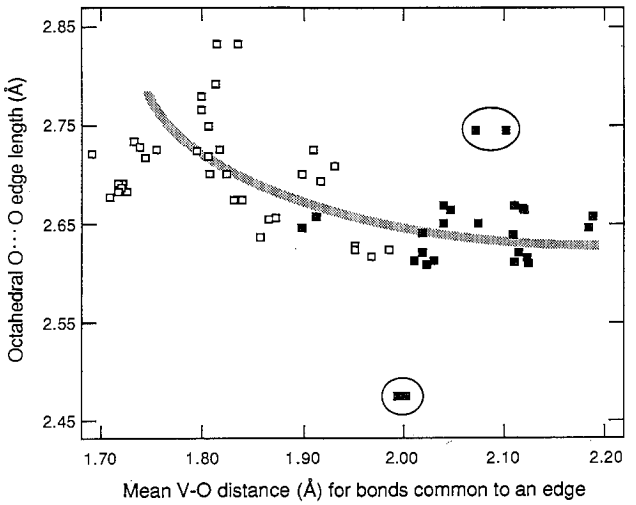

FIGURE 6.—*Mean of two adjacent V-O bond lengths versus the lengths of the octahedral edge subtending them in the $[V_{10}O_{28}]^{6-}$ isopolyanion of hummerite. Symbols and circled data have the same significance as in figure 5.*

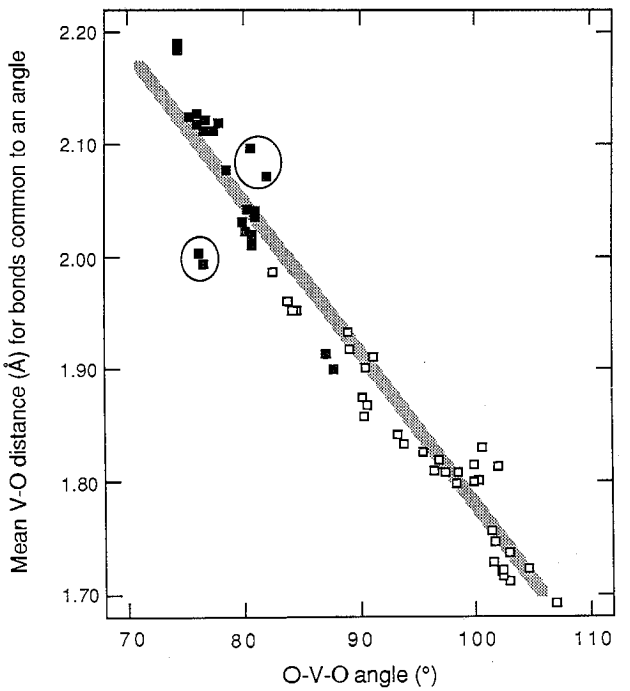

FIGURE 7.—*Mean of two adjacent V-O bond lengths versus the O-V-O angle formed by them. Symbols and circled data have the same significance as in figure 5.*

the positions of V(1) and V(2) are fixed, more or less, by the positions of the O(3) atoms below them to which they bond; these atoms constitute a short shared edge between two V(4) atoms, and so V(1) and V(2) are constrained to an unusually small interatomic separation. Because of this, O(1) and O(9) apparently move in to shield V(1) and V(2) from each other; this may be the single evident effect of repulsion between ions in the isopolyanion. The reason for the anomalously long shared edge is not apparent.

The most interesting of these three figures is figure 7, largely because the anomalies of the other figures fit quite well here, and because it is unexpectedly linear. Note that as the O-V-O angle closes, the associated average V-O distance increases. In the context of Pauling's rules, this would not only be unnecessary, but unexpected; V-O distances would be considered relatively constant, and the closing of the angle would serve only to increase the V···V separation. It is obvious that the closing of the O-V-O angle requires lengthening of the V-O bond for reasons other than increasing V···V separation, and that ionic repulsions between adjacent vanadium atoms is thus not an important factor in determining the geometry of the $[V_{10}O_{28}]^{6-}$ complex, with the possible exception of a V(1)-V(2) interaction mentioned above. Griffen (1987) analyzed distortions in tetrahedral oxyanions using *ab initio* molecular orbital calculations, and found that two factors predominated in limiting the O···O approach in highly distorted tetrahedra: (1) repulsions between electrons in *T*-O bonding orbitals (where *T* is the tetrahedrally coordinated atom), and (2) interactions between nonbonding orbitals of adjacent oxygen atoms. Coulombic repulsions between oxygen anions were not found to be significant.

While it is not obvious that those results can be generalized to the present case, which involves transition metals in octahedral coordination, the relation shown in figure 7 suggests that the same mechanisms may be important here. The O···O distances are probably too large for nonbonded interactions to affect the polyhedral geometry very much, but it appears that the V-O bonds must increase in length in order to achieve optimum separation of the bonding-electron concentrations when the O-V-O angle is narrow. (Based on figure 7 and assuming a fractional covalency of 0.5 for the V^{5+}-O bond, a very crude calculation suggests that this distance is in the neighborhood of 1.0Å.) That this has little to do with shared edges is shown by the fact that both shared and unshared edges fit the same line. The data shown in figure 8 represent 5- or 6-coordinated V^{5+} in four well-refined crystal structures (both inorganic and organic) in which the vanadate polyhedra are much less condensed than in $[V_{10}O_{28}]^{6-}$. The trend is approximately parallel to that in figure 7, but the correlation is not nearly as good. In fact, there is no reason to believe from figure 8 that the trends for shared and unshared edges are the same. A general tendency for bonds that are involved in narrow angles to be longer is certainly evident, but it appears that the strong and uniform correlation seen in figure 7 is a result of the highly condensed nature of the decavanadate complex with its geometrically interdependent octahedra.

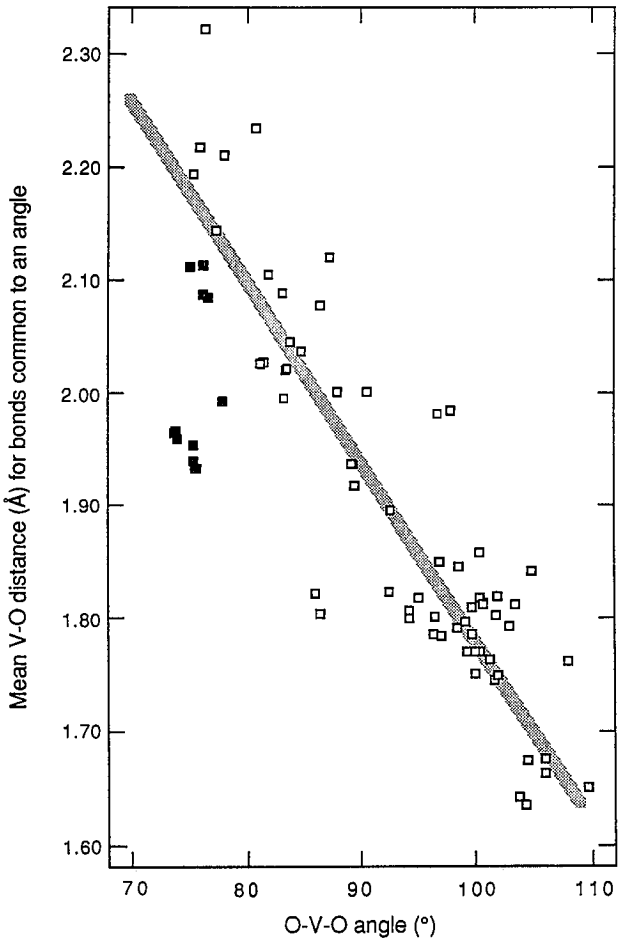

FIGURE 8.—*A plot similar to that of figure 7, but using data from vanadate structures that do not involve the* $[V_{10}O_{28}]^{6-}$ *isopolyanion. V is in 5- or 6-coordination, and polyhedra share corners, or one or two edges. Symbols have the same significance as in figure 5. Data are from Calvo and Manolescu (1973), Drew and others (1974), Scheidt and others (1971), and Waltersson and others (1974).*

HYDROGEN BONDING

The hydrogen positions were not explicitly located in this study, but hydrogen bonds can be inferred from O···O distances in which one of the oxygens belongs to a water molecule. Evans (1966) found the most significant hydrogen-bonded contacts—that is, those in which the O···O distances are less than 3.0Å—in $K_2Zn_2V_{10}O_{28}\cdot 16H_2O$ in this way, and they are not different in hummerite. In a study of hydrogen bonding in the calcium borosilicate howlite, in which the hydrogen positions were located by X-ray diffraction, Griffen (1988) found that long hydrogen-bonded contacts (perhaps even as large as 3.3Å) can be important in the overall charge balance in a structure. The hydrogen-bonding scheme proposed here for hummerite was based on two assumptions: First, it was assumed that no hydrogen bonding takes place between two oxygens that are both part of the $Mg(OH_2)_6$ octahedron (Donnay and Allmann 1970). Second, the outer limit for hydrogen bonding was assumed to correspond to an O···O separation of 3.3Å. Because the amount of bending, and thus the H···O distance, for any hydrogen bond was unknown, the H···O bond strength associated with a given O···O distance was estimated only crudely: 0.20 v.u. for distances in the range 2.70–2.79Å; 0.15 v.u. for 2.80–2.89Å; 0.10 v.u. for 2.90–2.99Å; and 0.05 v.u. for 3.00–3.30Å. Once the total sum of bond strengths due to H···O contacts was found in this way for a given hydrogen, it was subtracted from unity (assuming an ideal bond-strength sum of 1.00 for each hydrogen), and the result was assigned as the bond strength of the O-H bond for that hydrogen atom. The results are given in table 4, and the hydrogen-bonding network is shown in figure 9.

The surprising aspect about the hydrogen-bonding scheme proposed here is that it works so well, given the relatively crude assumptions above. The bond strengths for O-H bonds in the water molecules coordinating Mg all turned out to be in the expected range. Consistent with the requirements suggested by Baur (1972) for hydrogen bonding, all of the *M-D-A* angles for the proposed bonds turned out to be greater than 90°. (Here *M*, *D*, and *A* are

Table 4. Bond-strength sums including hydrogen bonds.

	Σ*						Σ**
O(1)	1.80	0.20-H(16)†					2.00
O(2)	1.62	0.20-H(15)	0.20-H(15)′				2.02
O(3)	2.03						2.03
O(4)	1.75	0.20-H(17)	0.05-H(17)′				2.00
O(5)	1.92	0.05-H(17)′					1.97
O(6)	1.78	0.10-H(16)′	0.05-H(20)	0.05-H(20)′	0.05-H(21)		2.03
O(7)	1.89	0.10-H(19)	0.05-H(20)′				2.04
O(8)	1.68	0.10-H(17)′	0.10-H(21)′				1.88
O(9)	1.89	0.05-H(18)					1.94
O(10)	1.67	0.15-H(18)′	0.20-H(19)′				2.02
O(11)	1.84	0.05-H(22)	0.05-H(22)′				1.94
O(12)	1.83	0.15-H(18)	0.05-H(21)′				2.03
O(13)	1.87	0.05-H(18)′	0.05-H(21)				1.97
O(14)	1.87	0.05-H(21)	0.10-H(22)	0.05-H(22)′			2.07
O(15)	0.41	0.80-H(15)	0.80-H(15)′				2.01
O(16)	0.44	0.80-H(16)	0.85-H(16)′				2.09
O(17)	0.42	0.80-H(17)	0.80-H(17)′				2.02
O(18)	0.35	0.80-H(18)	0.80-H(18)′				1.95
O(19)	0.36	0.90-H(19)	0.80-H(19)′				2.06
O(20)	0.37	0.85-H(20)	0.85-H(20)′				2.07
O(21)	0.03	0.05-H(16)′	0.10-H(20)	0.85-H(21)	0.85-H(21)′	0.05-H(22)′	1.93
O(22)	0.17	0.05-H(20)′	0.85-H(22)	0.85-H(22)′			1.92

†Primed and unprimed H atoms are bonded to oxygens with the same numerical designation to form the water molecules.
*Sums of bond strengths to oxygens, from table 3.
**Sums of bond strengths to oxygens, including proposed hydrogen bonds.

metal, donor, and acceptor atoms, respectively, and the assumption—which is most certainly incorrect—is that the bonds are linear. For bonds that are bent, the *M-D*-H angles may be greater still, which is even more favorable.) The only O···O distance meeting the criteria that was not taken to be a hydrogen bond was O(21)···O(16); the reason for this omission was that there were so many oxygens less than 3.30Å from O(21) that it was considered unlikely that the hydrogens could establish bonds with all of them, and O(16) was already charge balanced. Further characterization of the hydrogen-bonding network in hummerite requires neutron-diffraction experiments.

CONCLUSION

Pauling's third rule states that the sharing of polyhedral elements—specifically edges and faces—destabilizes a crystal structure; that is, given alternative possible arrangements of the same polyhedra, those with fewer shared edges and faces should be preferred. With as many shared edges as the decavanadate isopolyanion has (25 among 10 octahedra), it would be expected on this basis to be quite unstable relative to other configurations, but such is not the case. It has been shown to have the same structure in solution as in the crystalline state (O'Donnell and Pope 1976), and it is stable in solution in the pH range from 1 to ~6 (Pettersson and others 1983, Pettersson and others 1985). Moreover, it is also stable in the mono-, di-, and triprotonated species under these conditions, along with the VO_2^+ ion, and stability increases with increasing ionicity of the solvent. As the pH is raised, the highly condensed complexes are replaced by less condensed species containing vanadium in 4- or 5-coordination. The Discussion section of this paper provides a basis for considering the crystal-chemical reasons for the stability of $[V_{10}O_{28}]^{6-}$.

For all five symmetrically independent octahedra of the decavanadate isopolyanion, the longest V-O bonds are those to O(3). Figure 3 shows that O(3) is surrounded by six vanadium atoms—more than any other oxygen in the structure—and the idea that higher coordination numbers lead to greater "ionic" radii is familiar (Shannon

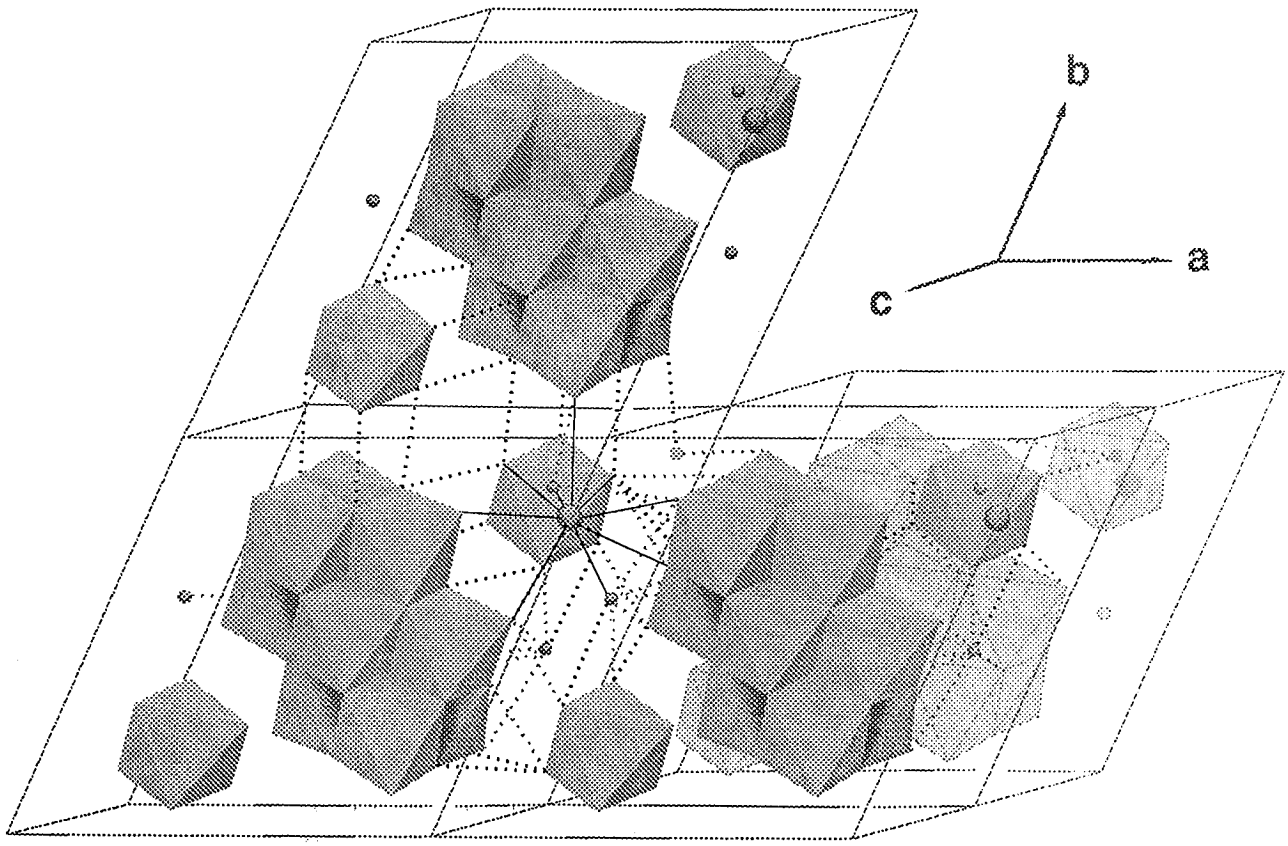

FIGURE 9.—*The hydrogen-bonding network in hummerite, shown by dotted lines. The coordination of the K atom is shown by solid lines (with one bond not visible in this projection).*

1976). Rationalization via the bond-length–bond-valence curves of Brown (1981) is straightforward—because O(3) must provide bonds to all six of the vanadium atoms surrounding it, it will contribute relatively little bond strength to each V, and each bond will therefore be relatively weak. Consequently, the bonds to O(3) are quite long, and all of the octahedra with only one such bond can geometrically simulate the preferred VO_5 square pyramidal configuration as follows: Lengthening of the "basal octahedral" bond (the one to O(3)) allows the apical V-O bond to shorten, which can be thought of either as a bond-strength–bond-length response or as a structural *trans* effect (e.g., Drew and others 1974). The shortening of the apical *trans* bond causes the four *cis* bonds to bend toward the long one, often rationalized by recourse to the "points-on-a-sphere" model of molecular geometry (Bartell and Plato 1973), completing the approach to a square pyramidal configuration. The final equilibrium bond lengths evidently reflect optimization of the mutual repulsion between electrons in V-O bonding orbitals (fig. 7), rather than ionic V-V or O-O repulsions. This explanation underscores the close correspondence between covalency and bond-strength shown by Brown and Shannon (1973). (Note that for explanatory purposes, the establishment of equilibrium geometry for the decavanadate polyanion has been treated as a dynamic process; in reality, the octahedra possess distorted configurations to begin with rather than developing them sequentially.

The V4) octahedron has two long bonds, both to O(3) atoms, and so the preceding paragraph may not strictly apply to it. As noted, the angle formed by the two shortest V(4)-O bonds is approximately the same as that found in the VO_2^+ ion, and this same angle occurs in a few other vanadates in which it separates the two shortest bonds of the polyhedron (Evans 1966). Evans suggests that this is an additional preferred configuration for V^{5+}; in light of this possibility, it may be more than merely coincidental that the VO_2^+ ion is stable in the same solutions as is the $[V_{10}O_{28}]^{6-}$ polyanion. On the other hand, the shortening of the V(4)-O(12) and V(4)-V(13) bonds may be a structural *trans* effect (e.g., Drew and others 1974) occurring in response to the lengthening of the V(4)-O(3) bonds for reasons related to bond strength. In either case, it ap-

pears that each octahedron of the decavanadate isopolyanion provides a geometrical environment favorable to the covalent-bonding preferences of V^{5+}, and that "ionic" factors are of only minor significance in establishing the stability of the complex.

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