American Mineralogist, Volume 64, pages 376–382, 1979

The crystal structure of köttigite

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Abstract

Köttigite, $(Zn_{2.44}Co_{0.42}Ni_{0.14})(AsO_4)_2 \cdot 8H_2O$, from the type locality (Schneeberg, East Germany) crystallizes in space group $C2/m$ with a = 10.241(3), b = 13.405(3), c = 4.757(2)A, β = 105.21(2)°, and Z = 2. Isotypy with vivianite is confirmed: the hydrogen atoms have been located and the crystal structure refined using 812 Zr-filtered Mo$K\alpha$ data to an R value of 0.054 (R_w = 0.057). The transition metals are randomly distributed over insular single and double (edge-sharing) octahedral groups of O atoms and H_2O molecules connected by AsO_4 tetrahedra to form complex slabs parallel to (010). These sheets are held together by hydrogen bonding alone, thereby accounting for the perfect {010} cleavage of the mineral. Shortening of the shared edge relative to the unshared edges within the octahedral dimer (0.139A) is well within the rather wide range of values observed in other Zn compounds containing shared octahedral edges.

Introduction

The mineral köttigite, ideally $Zn_3(AsO_4)_2 \cdot 8H_2O$, has long been recognized as a member of the vivianite group of minerals with the general formula $M_3(TO_4)_2 \cdot 8H_2O$. The monoclinic members of this family include the phosphates vivianite (M = Fe), bobierrite (Mg), and barićite (Mg,Fe), and the arsenates köttigite, parasymplesite (Fe), hoernesite (Mg), annabergite (Ni), and erythrite (Co). In addition, both vivianite and parasymplesite have been observed in a closely-related triclinic modification as the minerals metavivianite and symplesite (Ritz *et al.*, 1974).

The topology of the monoclinic structure type was shown by Mori and Ito (1950)[2] to consist of octahedral edge-sharing dimers, $M_2O_6(H_2O)_4$, and insular octahedra, $MO_2(H_2O)_4$, linked by TO_4 tetrahedra into complex sheets parallel to (010). However, the atomic coordinates were not refined, and the details of this interesting structure remain in doubt. The structure of the triclinic dimorph is still unknown.

The structural analysis of köttigite was initiated as part of a continuing study of Zn stereochemistry and, in particular, of the characteristics of Zn octahedron shared-edge shortening. Material from the type locality in Schneeberg, East Germany, was kindly made available for study by B. D. Sturman of the Royal Ontario Museum (ROM specimen number M15537).

Experimental

The crystal selected for data collection was a pale red transparent platelet displaying well-developed {010} faces, and having the dimensions 0.098 × 0.093 × 0.037 mm. Detailed morphological, optical, chemical and X-ray data for the material have been reported by Sturman (1976); the chemical composition determined in that study has been included in the abstract. The crystal was oriented with the c^* axis slightly displaced from the ϕ axis of a Picker FACS 1 four-circle diffractometer. Unit-cell parameters were refined by least-squares methods to give the best fit between calculated and observed angles 2θ, χ, and ϕ, measured at 25±2°C with Mo$K\alpha_1$ radiation (λ = 0.70926A), for 30 automatically centered reflections in the range 2θ = 30–45°. The resultant cell dimensions a = 10.241(3)[3], b = 13.405(3), c = 4.757(2)A, β = 105.21(2)° [unit-cell volume = 630.2(2)A^3] agree well with values reported by Sturman (1976).

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[2] Note that monoclinic $Fe_3(AsO_4)_2 \cdot 8H_2O$ is (incorrectly) referred to as symplesite rather than parasymplesite by Mori and Ito (1950).

[3] E.s.d.'s, given in parentheses, refer to the last decimal place.

0003–004X/79/0304–0376$02.00

Table 2. Fractional atomic coordinates and temperature factor coefficients for köttigite

Atom	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn(1)	0.0	0.0	0.0	18(2)	14(1)	102(8)	0	-2(3)	0
Zn(2)	0.0	0.38521(9)	0.0	21(1)	13(1)	115(6)	0	5(2)	0
As	0.31541(9)	0.0	0.3744(2)	11(1)	11(1)	67(5)	0	-3(1)	0
O(1)	0.1498(6)	0.0	0.3754(14)	15(6)	21(4)	24(26)	0	-1(10)	0
O(2)	0.4049(7)	0.0	0.7226(16)	32(7)	13(4)	102(32)	0	-2(12)	0
O(3)	0.3432(5)	0.1066(4)	0.2135(12)	25(4)	11(3)	133(21)	2(3)	10(7)	5(6)
O(4)	0.0975(5)	0.1144(4)	0.8081(12)	23(4)	22(3)	146(23)	0(3)	11(8)	-2(7)
O(5)	0.4000(6)	0.2262(5)	0.7179(13)	42(5)	22(3)	145(26)	3(4)	6(10)	7(8)
H(41)	0.384(10)	0.425(8)	0.364(22)	2.1(19)					
H(43)	0.340	0.371	0.119	4.0					
H(53)	0.121(10)	0.305(8)	0.436(24)	1.7(20)					
H(54)	0.044(8)	0.236(6)	0.289(19)	0.3(15)					

* *Thermal parameters* × 10^4 *for* Zn, As *and* O. *Parenthesized figures here and in all subsequent tables represent the e.s.d. in terms of the least significant figure to the left. The* H *atoms are identified by two digits indicating the donor and acceptor* O *atoms respectively.*

X-ray intensity data for the structure analysis were collected at 25°C using Zr-filtered Mo$K\alpha$ radiation ($\lambda = 0.71069$A) and a 2θ scan rate of 1° per minute. Backgrounds were determined from 10-second stationary counts at both ends of each dispersion-corrected (Alexander and Smith, 1964) scan range (minimum width = 3.0° in 2θ). All reflections consistent with a C-face-centered lattice were collected to a maximum 2θ value of 60°, using three reflections to monitor instrument and crystal stability at frequent intervals: these showed no significant change. The resultant 4045 reflections were corrected for background, Lorentz, polarization and absorption effects using a μ value of 107.7 cm^{-1} (the transmission factors ranged from 0.402 to 0.680). Multiply-measured and symmetry-equivalent reflections (consistent with point group $2/m$) were averaged (using weights based on counting statistics) to yield a set of 962 unique structure factors, each with a standard deviation estimated from the equation $\sigma = [\sigma_I^2 + (0.02I)^2]^{0.5}/2I^{0.5}$, where I is the corrected raw intensity and σ_I is derived from counting and averaging statistics. Of these data only those 812 observations with $I > 2\sigma_I$ were included in the subsequent least-squares refinement.

Location of the hydrogen atoms and refinement

Refinement of the heavy-atom positions and isotropic temperature factors was initiated in space group $C2/m$, using the atomic coordinates determined for parasymplesite by Mori and Ito (1950). Although significant amounts of Co and Ni substitute for Zn in type köttigite from Schneeberg (Sturman, 1976), the rather small differences in X-ray scattering abilities of the three atoms were ignored in the initial refinements and octahedral sites were assigned to Zn alone. Least-squares minimization of the function $\Sigma w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors, and $w = 1/\sigma^2$, resulted in convergence at a conventional R value of 0.069. At this point it was observed that the isotropic temperature factors of the isolated and dimeric octahedral atoms were 0.98(4) and 1.05(3) respectively, indicating that there may be little if any difference in the chemistry of the two sites. Refinement with anisotropic temperature factors[4], incorporating the symmetry restrictions of Levy (1956), further reduced R to 0.059. The site multiplicities of the octahedral atoms were then released ($R = 0.057$) in a crude attempt to account for the presence of Co and Ni. The resultant occupancies of 0.951(9) and 0.947(8) are consistent with the observed chemistry and, furthermore, suggest again that the three transition metals are distributed randomly over the octahedral sites. The inclusion of an isotropic extinction parameter as defined by Coppens and Hamilton (1970) produced a value statistically identical to zero, and the parameter was therefore removed from further consideration.

A Fourier difference synthesis utilizing only those data with $\sin\theta/\lambda < 0.4$A^{-1} was computed, and peaks ranging from 0.45 to 0.62eA^{-3} were found for the four hydrogen atoms in the asymmetric unit. There were also a small number of other peaks with maximum density 1.06eA^{-3} (less than 10 percent of the magnitude of an O atom peak), but these were all located well within the coordination spheres of Zn and As and were interpreted as regions of charge

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[4] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table 3. Magnitudes and orientations of the principal axes of thermal ellipsoids in köttigite

Atom	Axis	R.m.s. displacement (A)	Angle in degrees to +*a*	+*b*	+*c*
Zn(1)	1	0.085(4)	44(5)	90	61(5)
	2	0.111(4)	90	180	90
	3	0.119(5)	46(5)	90	151(5)
Zn(2)	1	0.098(3)	39(6)	90	67(6)
	2	0.109(3)	90	180	90
	3	0.118(4)	51(6)	90	157(6)
As	1	0.067(3)	44(4)	90	62(4)
	2	0.098(3)	134(4)	90	28(4)
	3	0.100(3)	90	0	90
O(1)	1	0.049(26)	81(23)	90	24(23)
	2	0.091(19)	171(23)	90	66(23)
	3	0.139(13)	90	0	90
O(2)	1	0.098(15)	69(15)	90	36(15)
	2	0.108(16)	90	180	90
	3	0.140(16)	21(15)	90	126(15)
O(3)	1	0.095(12)	106(26)	25(24)	104(18)
	2	0.112(10)	148(36)	113(27)	98(38)
	3	0.124(12)	63(36)	100(24)	164(23)
O(4)	1	0.106(10)	20(22)	91(13)	85(22)
	2	0.127(12)	70(22)	99(31)	170(30)
	3	0.142(10)	87(17)	9(32)	99(31)
O(5)	1	0.116(11)	108(13)	68(16)	139(15)
	2	0.145(11)	85(52)	155(28)	115(31)
	3	0.154(12)	19(19)	78(50)	120(28)
H(41)		0.16(16)			
H(43)		0.23			
H(53)		0.15(16)			
H(54)		0.06(14)			

deformation due to chemical bonding. The H atom positional and isotropic thermal parameters were then included in the refinement, using all 812 reflections, but the proton associated with the smallest of the four residual electron density peaks began to wander away from its donor O atom. This H atom was therefore reassigned its original coordinates and was held fixed for the remainder of the calculations. The refinement then proceeded smoothly to convergence (parameter shifts in the final cycle were less than one-tenth of the corresponding e.s.d.). The final values of R and R_w[5] were 0.054 and 0.057 respectively (0.066 and 0.058 for the entire data set of 962 structure factors). Values for F_o and F_c (×10) are listed in Table 1[6]. Atomic coordinates and thermal parameters along with their standard deviations estimated from the inverted full matrix are given in Table 2. The r.m.s. components of thermal displacement, and thermal ellipsoid orientations, appear in Table 3.

Scattering factors for Zn, As, and O (neutral atoms) were obtained from *International Tables for X-ray Crystallography* (1974) and were corrected for both real and imaginary anomalous dispersion components. For H, the spherical scattering factor suggested by Stewart *et al.* (1965) was used. Programs utilized for solution, refinement, and geometry calculations were local modifications of DATALIB, DATASORT, FOURIER, ORXFLS3, ORFFE3 and ORTEP2[7].

Discussion of the structure

Köttigite crystallizes with the topology displayed in Figure 1 and the bonding dimensions summarized in Table 4. The results confirm the proposed isostructural relationship between köttigite and the members of the vivianite group of minerals. Indeed, the atomic coordinates of the nonhydrogen atoms in Table 2 are in very close agreement with those determined for parasymplesite by Mori and Ito (1950) using trial and error methods: mean values of Δx, Δy, and Δz for the two structures are only 0.08, 0.08, and 0.13A respectively, reflecting the closely similar radii of Zn^{2+} and high-spin Fe^{2+} (Shannon, 1976).

In summary, the structure consists of insular single and double (edge-sharing) octahedral groups of O atoms and H_2O molecules around Zn (plus minor Co and Ni), connected by isolated AsO_4 tetrahedra to form complex sheets, with mirror symmetry, parallel to (010). Each sheet is corrugated parallel to the *c* axis, with the ridges (formed by the double octahedra) neatly fitting into the troughs (formed by the single octahedra) in the neighboring sheets. The sheets are held together by hydrogen bonding between adjacent single and double octahedra.

The transition metals are randomly distributed over both octahedral sites. Zn(1) is coordinated by four H_2O molecules and two *trans* O atoms from the AsO_4 units. Zn(2) is surrounded by two H_2O molecules in *cis* configuration, two O atoms from AsO_4 groups, and two O atoms from a mirror-equivalent octahedron on the opposite side of the sheet. Bond length and angle variations within and between the octahedra are relatively small (Table 4), with mean lengths close to the value 2.10A expected for Zn^{2+} (and high-spin Co^{2+}) in octahedral coordination (Shannon, 1976). However, as usually observed when an edge (or face) is shared between coordination polyhedra, the length of the shared edge, O(2) ···O(2), and the angle it subtends at the central cation, Zn(2), are both significantly smaller than any

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[5] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$

[6] To obtain a copy of Table 1, order Document AM-78-088 from the Mineralogical Society of America, Business Office, 1909 K St., NW, Washington, DC 20006. Please remit $1.00 in advance for a copy of the microfiche.

[7] All programs are included in the *World List of Crystallographic Computer Programs* (3rd ed. and supplements).

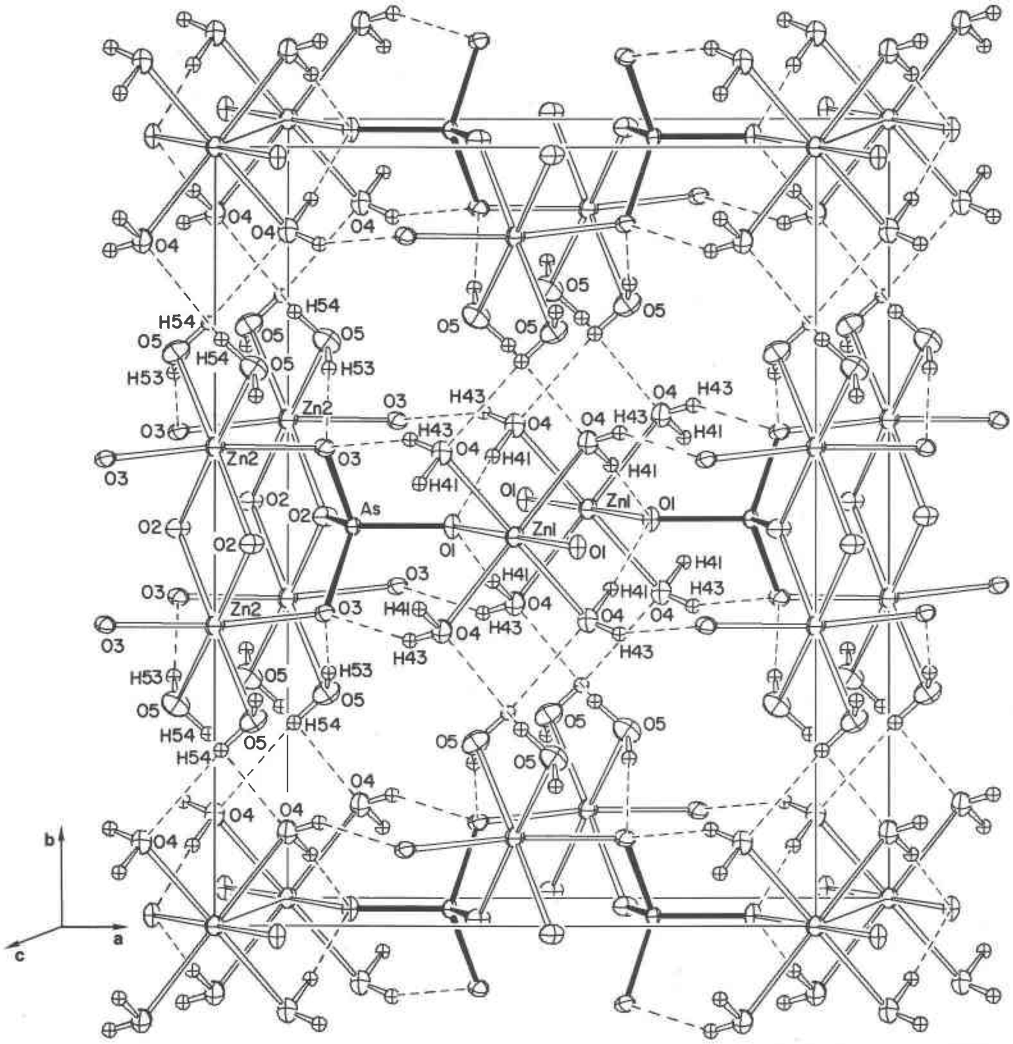

Fig. 1. Unit-cell diagram of the köttigite crystal structure. Thermal ellipsoids for all atoms (*B* for hydrogen set = 0.5A^2) represent 50 percent probability surfaces. The arsenate groups have been indicated by filled bonds, while the hydrogen bonds are shown as dashed lines.

of the other edges or valence angles within the polyhedron. Distortions of this kind are generally discussed in terms of the competition between cation–cation and anion–anion interactions along and across the shared polyhedral elements (Pauling, 1960; Baur, 1972a).

For an ideal shared edge model in which the Zn and O_{br} atoms are coplanar, all Zn–O_{br} bond lengths are equal, and the vectors $O_{br}\cdots O_{br}$ and $Zn\cdots Zn$ are perpendicular bisectors of each other, the relationship between shared edge length and cation–cation distance is given by

$$d(O_{br}\cdots O_{br}) = 2[d(Zn\text{–}O_{br})^2 - \{d(Zn\cdots Zn)/2\}^2]^{0.5}$$

In Figure 2(a) this relationship has been plotted for a total of 17 shared edges observed in 11 compounds containing octahedrally-coordinated Zn atoms. As found in a similar analysis of Al octahedra by Burnham (1963), almost all of the data points lie between lines defining the variation of $O_{br}\cdots O_{br}$ and $Zn\cdots Zn$ distance in ideal edge-sharing octahedra having the extremes of observed Zn–O bond lengths. In Figure 2(b) the relatively small variation in Zn–O_{br} distances has been removed from consideration by replotting the same data with the bridging bonds normalized to a mean length of 2.11A. For all but one shared edge (with an e.s.d. of ≃0.1A: Iitaka *et al.*, 1962) the figure clearly demonstrates an inverse relationship between the two parameters which is consistent with the other assumptions inherent in the ideal

Table 4. Interatomic distances (A) and angles (deg.) in köttigite*

AsO_4 tetrahedron:	
As-O(2)	1.669(7)
O(3) ×2	1.680(5)
O(1)	1.697(7)
average =	1.682(5)
O(2)···O(3) ×2	2.739(8)
O(1)	2.700(9)
O(3)···O(3)^{i}	2.857(10)
O(1) ×2	2.712(8)
average =	2.743(7)
∠O(2)-As-O(3) ×2	109.7(2)
O(1)	106.6(4)
O(3)-As-O(3)^{i}	116.5(4)
O(1) ×2	106.9(2)
average =	109.4(2)

$Zn(1)O_2(H_2O)_4$ octahedron:	
Zn-O(1) ×2	2.026(6)
O(4)^{ii} ×4	2.159(6)
average =	2.115(5)
O(1)···O(4)^{ii} ×4	3.027(8)
O(4)^{iii} ×4	2.893(7)
O(4)^{ii}···O(4)^{iv} ×2	3.084(10)
O(4)^{v} ×2	3.068(11)
average =	2.999(7)
∠O(1)-Zn-O(4)^{ii} ×4	92.6(2)
O(4)^{iii} ×4	87.4(2)
O(4)^{ii}-Zn-O(4)^{iv} ×2	90.5(3)
O(4)^{v} ×2	89.5(3)
average =	90.0

$Zn(2)O_4(H_2O)_2$ octahedron:	
Zn-O(5)^{vi} ×2	2.088(6)
O(2)^{vi} ×2	2.094(4)
O(3)^{vii} ×2	2.117(6)
average =	2.100(5)
O(5)^{vi}···O(5)^{viii}	2.918(11)
O(2)^{vi} ×2	3.032(7)
O(3)^{vii} ×2	3.031(9)
O(3)^{viii} ×2	3.024(8)
O(2)^{ix}···O(2)^{vi}	2.840(13)
O(3)^{vii} ×2	2.895(8)
O(3)^{viii} ×2	2.944(9)
average =	2.968(7)
∠O(5)^{vi}-Zn-O(5)^{viii}	88.7(3)
O(2)^{vi} ×2	93.0(2)
O(3)^{vii} ×2	92.3(2)
O(3)^{viii} ×2	92.0(2)
O(2)^{ix}-Zn-O(2)^{vi}	85.4(3)
O(3)^{vii} ×2	86.9(3)
O(3)^{viii} ×2	88.7(3)
average =	90.0(2)

Anions:	
∠As-O(1)-Zn(1)	121.6(4)
As-O(2)-Zn(2)^{vi} ×2	132.0(2)
Zn(2)^{x}-O(2)-Zn(2)^{vi}	94.6(3)
As-O(3)-Zn(2)^{vii}	120.2(3)

Water molecules:

O_d	H	O_a	O_d-H	H···O_a	O_d···O_a	∠O_d-H···O_a	∠Zn-O_d-H	H···H	∠H-O_d-H
O(4)	-H(41)···	O(1)	1.03(11)	1.70(11)	2.731(8)	174(9)	100(6)	1.34	102
	-H(43)···	O(3)	0.67	2.14	2.741(6)	151	118		
O(5)	-H(53)···	O(3)	0.82(11)	2.00(11)	2.817(8)	173(10)	100(7)	1.30(13)	109(10)
	-H(54)···	O(4)	0.78(9)	2.15(8)	2.896(8)	162(9)	104(6)		

* *Symmetry transformations for atoms outside the asymmetric unit:*

i. x, -y, z
ii. x, y, z-1
iii. -x, -y, 1-z
iv. x, -y, z-1
v. -x, y, 1-z
vi. 1/2-x, 1/2-y, 1-z
vii. 1/2-x, 1/2-y, -z
viii. x-1/2, 1/2-y, z
ix. x-1/2, 1/2+y, z-1
x. 1/2+x, y-1/2, 1+z

shared-edge model. However, the wide range of cation–cation and anion–anion distances suggests that, as for the Al octahedra, the detailed geometry is extremely flexible and subject to the influence of structural features external to the shared edge itself.

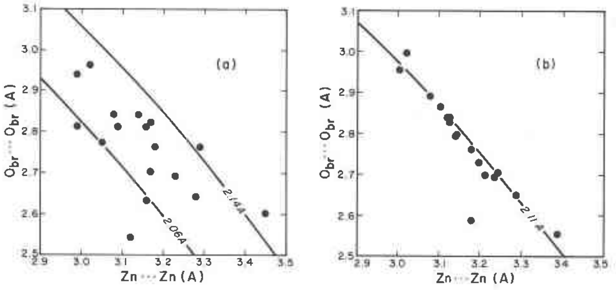

Fig. 2. Relationship between shared-edge length $O_{br}\cdots O_{br}$, and Zn···Zn distance for the 17 octahedron shared edges in köttigite (present study), adamite (Hill, 1976), tsumcorite (Tillmanns and Gebert, 1973), legrandite (McLean *et al.*, 1971), hydrozincite (Ghose, 1964), $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (Stählin and Oswald, 1970), $Zn_5(OH)_8Cl_2 \cdot 1H_2O$ (Allmann, 1968), $Zn(OH)_2 \cdot ZnSO_4$ (Iitaka *et al.*, 1962), $ZnSeO_3 \cdot 2H_2O$ (Gladkova and Kondrashev, 1964), $ZnSe_2O_5$ (Meunier and Bertaud, 1974), and β-$Zn_2P_2O_7$ (Calvo, 1965): (a) observed interatomic distances, (b) distances normalized in accordance with a mean bond length of 2.11A. Curved lines represent the variation of the two parameters for the ideal shared edge model and Zn–O distances as indicated.

For example, while the mean bond length for a very similar Zn octahedral dimer in $ZnSeO_3 \cdot 2H_2O$ (Gladkova and Kondrashev, 1964) is only 0.013A larger than in köttigite, the $O_{br}\cdots O_{br}$ and Zn···Zn separations are 0.15A shorter and 0.15A longer respectively. Indeed, the range of Zn···Zn distances across the 17 shared octahedral edges in Figure 2 (2.99 to 3.45A) is as wide as the corresponding range of cation separations (3.02 to 3.58A) observed between 42 *corner*-sharing ZnO_4 tetrahedra (Hill, in preparation), although the mean separation is, as expected, 0.17A larger in the latter case. While the number and nature of the other cations bonded to the bridging O atoms are undoubtedly of importance in determining the geometry of the shared edge, recent CNDO/2 molecular orbital calculations on clusters of edge-sharing Al octahedra have shown that the minimum energy configuration is also a sensitive function of the number and arrangement of the shared edges (Peterson *et al.*, 1978). Since the number of shared edges per octahedron for the structures used in Figure 2 varies from 1 to 4 it is not surprising that a wide range of $O_{br}\cdots O_{br}$ and Zn···Zn distances is observed.

In Table 5 the shared-edge distortions for the octahedral dimer in köttigite are compared in detail with the ranges of values, and their means, found for

Table 5. Distortion of shared edge length $O_{br}\cdots O_{br}$, $Zn\cdots Zn$ distance, mean bridge bond length $Zn–O_{br}$, and mean valence angle $O_{br}ZnO_{br}$ resulting from the sharing of edges in ZnO_6 octahedral clusters

		$\Delta(O_{br}\cdot\cdot O_{br})$*	$\Delta(Zn\cdot\cdot Zn)$#	$\Delta(Zn–O_{br})$*	$\Delta(O_{br}ZnO_{br})$#
köttigite		-0.139 A	+0.107 A	-0.007 A	-4.6°
other†	mean	-0.30	+0.17	-0.07	-8.0
	max.	-0.52	+0.45	-0.21	-16.2
	min.	-0.09	-0.02	+0.07	-0.2

* *Distortion relative to corresponding parameters involving non-bridging anions.*

\# *Distortion relative to the value expected for regular octahedra.*

† *Data from the ten compounds (excluding köttigite) in Figure 2.*

the other compounds in Figure 2. The data indicate that although the distortions in köttigite are somewhat smaller than average, they are well within the ranges of observed values. The shared edges are, on average, 7.5 percent shorter, and the $Zn\cdots Zn$ separations 5.6 percent longer, than the corresponding distances in regular octahedra with the same mean bond length. These distortions may be compared with values of 5.5 and 4.9 percent respectively for the 14 Al octahedron edges considered by Burnham (1963). The consistently larger distortions found for the $O_{br}\cdots O_{br}$ distances relative to $Zn\cdots Zn$ are in agreement with the ideal shared-edge model, as is the fact (first suggested by Pauling, 1960) that the shared-edge distortions (for both the Zn and Al polyhedra) generally take place with little or no change in the relative lengths of the bonds to the bridging O atoms (Table 5). As expected, the valence angles subtended at the Zn atoms by the shared edges show a wide range of values, but the mean distortion (−8°) is close to the corresponding average value (−7°) observed for the Al octahedra studied by Burnham.

Bond lengths within the AsO_4 group are all close to the mean value of 1.682A (Table 4), but the O–As–O valence angles display a large variation. The widest angle (116.5°) is associated with the tetrahedron edge connecting the O(3) vertices of the Zn(2) octahedron (Fig. 1), and is therefore related to the Zn–O(2) bond length and $Zn\cdots Zn$ distance across the shared edge in the octahedral dimer. The narrowest angle (106.6°), on the other hand, is associated with the tetrahedron edge $O(1)\cdots O(2)$, the length of which is controlled by the length of the shared edge in the dimer and the Zn(1)–O(1) bond length in the isolated octahedron (Fig. 1). These angular distortions are therefore an expression of a compromise between the tendency for the AsO_4 group to assume regular tetrahedral geometry, and the tendency for the dimer to distort to accommodate the shared edge. The shorter bond from Zn(1) to O(1), relative to other bonds within the polyhedron, is also consistent with this proposal.

Hydrogen bonding

The distance and angle parameters describing the two water molecules are given in Table 4. Although the two O–H bonds in the O(4) water molecule show a wide variation in length, the average value for all four bonds (0.82A) is, as expected, about 0.14A shorter than the mean value measured in other crystalline hydrates by neutron diffraction (Baur, 1972b; Ferraris and Franchini-Angela, 1972). Similar shifts of the apparent hydrogen atom position toward the atom to which it is bonded have been documented in a large number of structures and are generally ascribed to the relatively large distortion of electron density which takes place during formation of the O–H bond (Coppens, 1974). Both water molecules display $H–O_d–H$ bond angles (where O_d represents the donor O atom) close to the mean values of 108 and 109° observed in other hydrates by Ferraris and Franchini-Angela (1972) and Baur (1972b), respectively.

In contrast to the hydrogen bonding schemes proposed for the vivianite structure type by Mori and Ito (1950) and Moore (1971), only one of the four hydrogen bonds in köttigite is directed between water molecules (Table 4, Fig. 1). Moreover, in spite of the fact that the $Zn–O_d–H$ angles are relatively small (100–118°), none of the hydrogen bond acceptors, O_a, are anions in the same coordination polyhedron as O_d. In each case the two O_a atoms are not only the anions closest to O_d, but they would be slightly underbonded were it not for the additional electrostatic bond strength (Brown and Wu, 1976) provided by the hydrogen bonds. In this regard it should be noted that, although not obvious from Table 4, the O(1) atom is the receptor of two symmetry equivalent hydrogen bonds from H(41). For all bonds the distances $H\cdots O_a$ and angles $O_d–H\cdots O_a$ are within the ranges of values expected (Baur, 1972b). From the classification scheme of Ferraris and Franchini-Angela (1972), the O(4) water molecule may be assigned to Class 2, Type *H*, with one lone pair directed toward a divalent cation and the other toward a proton. The O(5) molecule, on the other hand, has a single (divalent) cation directed toward one of its lone pairs and is therefore of Class 1′, Type *J*.

As discussed above, cohesion between the sheets of octahedra and tetrahedra parallel to (010) is provided solely by hydrogen bonds, thereby accounting for the perfect {010} cleavage exhibited by the mineral. In fact, only one of the four bonds, O(5)–H(54)· · ·O(4), serves to connect the sheets together. The remaining three hydrogen bonds are directed toward O(1) and O(3) atoms in the same sheet, and provide additional stability to the orientation of the *trans*-connected Zn(1) octahedron.

Acknowledgments

This study was supported by grant DMR75-03879 from the Materials Research Division of the National Science Foundation. I am grateful to the Research Division at VPI and SU for defraying the computer costs, and to Mrs. Ramonda Haycocks for typing the manuscript.

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Manuscript received, March 6, 1978;
accepted for publication, June 21, 1978.