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THE CRYSTAL STRUCTURE OF MOTTRAMITE, AND THE NATURE OF Cu ⇌ Zn SOLID SOLUTION IN THE MOTTRAMITE–DESCLOIZITE SERIES

MARK A. COOPER AND FRANK C. HAWTHORNE

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

ABSTRACT

The crystal structure of mottramite, $Pb(Cu_{0.81}Zn_{0.12})VO_4(OH)$, *a* 7.667(4), *b* 6.053(2), *c* 9.316(4) Å, *V* = 432.3(3) Å^3, *Pnma*, *Z* = 4, has been refined to an *R* index of 3.6% for 550 observed reflections measured with Mo*K*α X-radiation. Mottramite is isostructural with descloizite, $PbZn(VO_4)(OH)$. The Pb^{2+} cation is coordinated by seven anions between 2.45 and 2.80 Å, with a further two anions at 3.195 Å. The Cu^{2+} cation is coordinated by six anions in a [2 + 2 + 2]-distorted octahedral arrangement, with a <Cu–O> distance of 2.112 Å. The V^{5+} cation is coordinated by four anions in a distorted tetrahedral arrangement, with a <V–O> distance of 1.722 Å. The H atom was located; it forms a strong H-bond with the O(2) anion, H...O(2) being equal to 1.90 Å. There is complete solid-solution between mottramite and descloizite, despite the fact that Zn in descloizite has a [2 + 4]-distorted octahedral arrangement. The local coordination requirements of Cu^{2+} in mottramite are accommodated by cooperative bond-length relaxations throughout the structure that allow the formation of a [2 + 2 + 2]-distorted octahedral arrangement while maintaining satisfaction of local bond-valence requirements.

Keywords: mottramite, crystal-structure refinement, descloizite, Jahn–Teller effect.

SOMMAIRE

Nous avons affiné la structure cristalline de la mottramite, $Pb(Cu_{0.81}Zn_{0.12})VO_4(OH)$, *a* 7.667(4), *b* 6.053(2), *c* 9.316(4) Å, *V* = 432.3(3) Å^3, *Pnma*, *Z* = 4, jusqu'à un résidu *R* de 3.6% en utilisant 550 réflexions observées et mesurées avec rayonnement Mo*K*α. La mottramite possède le même motif structural que la descloizite, $PbZn(VO_4)(OH)$. Le cation Pb^{2+} est coordonné par sept anions situés à une distance entre 2.45 et 2.80 Å, et deux autres à 3.195 Å. Le cation Cu^{2+} est coordonné par six anions dans un agencement [2 + 2 + 2] octaédrique difforme, la distance moyenne <Cu–O> étant égale à 2.112 Å. Le cation V^{5+} est entouré de quatre anions dans un agencement tétraédrique difforme, la distance moyenne <V–O> étant égale à 1.722 Å. Nous avons localisé l'atome H atom; il forme une forte liaison H avec l'anion O(2), la distance H...O(2) étant égale à 1.90 Å. La solution solide est complète entre mottramite et descloizite, malgré le fait que le Zn dans la descloizite possède un agencement octaédrique [2 + 4] difforme. Les exigeances locales en coordinence du Cu^{2+} dans la mottramite seraient assurées par une décontraction coopérative dans la longueur des liaisons à travers la structure, pour permettre la formation d'un agencement octaédrique difforme de type [2 + 2 + 2] tout en satisfaisant les exigeances locales des valences de liaisons.

(Traduit par la Rédaction)

Keywords: mottramite, affinement de la structure cristalline, descloizite, effet de Jahn–Teller.

INTRODUCTION

Mottramite, ideally $PbCu(VO_4)OH$, is one of a large group of minerals of the general form $A_2(XO_4)Z$, where *A* represents large and intermediate-size divalent cations such as Ca and Pb, Cu and Zn, *X* represents P, As^{5+} and V^{5+}, and *Z* represents OH, F, Cl (Richmond 1940). It is isostructural with descloizite, $PbZn(VO_4)OH$, and several other minerals of the descloizite group, and has both chemical and structural affinities to the minerals of the conichalcite group, being the vanadate analogue of duftite, $PbCu(AsO_4)OH$. There is complete solid-solution along the mottramite – descloizite join (Van der Westhuizen *et al.* 1986) with no structural discontinuities. As part of our general work on the structures of Cu^{2+} oxysalt minerals (Eby & Hawthorne 1993), we here report a structure refinement of mottramite, and examine the way in which the descloizite structure-type accommodates the Jahn–Teller distortion associated with Cu^{2+} in octahedral coordination.

EXPERIMENTAL

The material used in this work is from the Ford mine, Pinal County, Arizona, and was purchased from a mineral dealer. A flattened dipyramidal crystal was mounted on a Nicolet *R*3*m* automated four-circle

TABLE 1. MISCELLANEOUS INFORMATION FOR MOTTRAMITE

a (Å)	7.667(4)	crystal size (mm)	0.08 x 0.08 x 0.05
b	6.053(2)	Radiation	Mo$K\alpha$/Graphite
c	9.316(4)	Total no. of I	1453
V (Å^3)	432.3(3)	No. of $\|F\|$	688
Sp. Gr.	*Pnma*	No. of $\|F_o\| > 5\sigma$	550
μ (cm^{-1})	460	R(azimuthal) %	12.6 → 2.4
D_{calc} (g cm^{-3})	6.187	R(obs) %	3.6
		wR(obs) %	3.7

Cell content: 4[PbCuVO$_4$OH]

$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$

$wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2]^{\frac{1}{2}}$, $w = 1/\sigma^2 F^*[1-\exp(-1.8\{\sin\theta/\lambda\}^2)]$

diffractometer. Twenty-eight reflections over the range $8° < 2\theta < 30°$ were centered using graphite-monochromated Mo$K\alpha$ X-radiation. The unit-cell dimensions (Table 1) were derived from the setting angles of the twenty-eight automatically aligned reflections by least-squares techniques. Data were collected using the θ–2θ scan method, with a scan range of 3.0°. A variable scan-rate inversely proportioned to the peak intensity was used, with maximum and minimum scan-rates of 29.3°2θ/min and 1.5°2θ/min, respectively. A total of 1453 reflections was measured over the range $4° \le 2\theta \le 60°$, with index ranges $-10 \le h \le 10$, $-8 \le k \le 0$, $-13 \le l \le 0$. Two standard reflections were measured every fifty-eight reflections; there were no significant changes in their intensities during data collection. An empirical absorption-correction based on 36 psi-scans of each of 12 reflections over the range $10 \le 2\theta \le 60°$ was applied, with the crystal modeled as an ellipsoid. The absorption correction reduced R(azimuthal) from 12.6 to 2.4%. The data were merged and corrected for Lorentz, polarization and background effects; of the 688 unique reflections, 550 were classed as observed [$|F_0| > 5\sigma|F_0|$].

Structure Refinement

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. R indices are of the form given in Table 1 and are expressed as percentages. The Siemens SHELXTL PLUS (PC version) system of programs was used throughout this study.

Refinement of the positional and anisotropic displacement parameters converged to an R index of 3.6%. A three-dimensional difference-Fourier map was calculated at this stage of the refinement, and the single hydrogen atom was found at the 4c position. Subsequent cycles of refinement gave hydrogen coordinates that were not realistic, as indicated by an anomalously short donor–hydrogen bond-length, a common feature of hydrogen positions refined using X-ray data. The "soft" constraint that the donor–hydrogen distance should be ~0.98 Å was imposed by adding extra weighted observational equations to the least-squares matrix. Only the donor–hydrogen distance is constrained, and the hydrogen position is free to seek its optimum position around the donor atom. Refinement of all parameters gave a final R index of 3.6% and a wR index of 3.7%. Final positional and displacement parameters are given in Table 2, selected interatomic distances and angles in Table 3,

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN MOTTRAMITE

V–O(1)	1.750(8)	x2	Pb–O(1)b	2.501(8)	x2
V–O(2)a	1.682(12)		Pb–O(1)d	2.700(8)	x2
V–O(3)	1.704(10)		Pb–O(2)e	2.798(12)	
<V–O>	1.722		Pb–O(2)	3.195(4)	x2
			Pb–O(3)f	2.689(10)	
Cu–O(1)b	2.102(7)	x2	Pb–OHg	2.452(10)	
Cu–O(3)c	2.298(8)	x2			
Cu–OH	1.935(7)	x2	OH–H	0.98(15)	
<Cu–O>	2.112		H···O(2)h	1.90(16)	
O(1)b–Cu–O(3)c	88.5(3)	x2	OH–H···O(2)h	143(10)	
O(1)b–Cu–O(3)f	91.5(3)	x2			
O(1)b–Cu–OH	88.2(4)	x2	O(1)–V–O(1)j	114.5(5)	
O(1)b–Cu–OHi	91.8(4)	x2	O(1)–V–O(2)a	107.5(3)	x2
O(3)c–Cu–OH	92.7(3)	x2	O(1)–V–O(3)	111.0(3)	x2
O(3)c–Cu–OHi	87.3(3)	x2	O(2)a–V–O(3)	104.7(5)	
<O–Cu–O>	90.0		<O–V–O>	109.4	

a: x+1, y, z; b: x–½, ½–y, ½–z; c: x, y–1, z; d: x–1, y, z; e: $\bar{x}$, 1–y, $\bar{z}$; f: 1–x, 1–y, $\bar{z}$; g: x–½, y, ½–z; h: $\bar{x}$+1, $\bar{y}$+1, $\bar{z}$; i: 1–x, $\bar{y}$, $\bar{z}$; j: x, 1½–y, z

TABLE 2. FINAL POSITIONAL AND DISPLACEMENT PARAMETERS FOR MOTTRAMITE

Site	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	1/2	0	0	162(4)	161(7)	177(8)	127(6)	–11(6)	13(6)	1(7)
Pb	0.13186(7)	1/4	0.17374(6)	196(2)	188(2)	276(3)	142(2)	0	2(2)	0
V	0.8778(3)	3/4	0.1939(2)	138(6)	150(8)	148(11)	118(9)	0	9(9)	0
O(1)	0.8847(9)	0.507(1)	0.2954(7)	195(17)	199(27)	172(33)	216(27)	11(24)	–13(28)	–54(27)
O(2)	0.053(1)	3/4	0.086(1)	232(34)	170(50)	299(74)	228(46)	0	53(46)	0
O(3)	0.703(1)	3/4	0.081(1)	158(27)	131(39)	184(57)	159(41)	0	–11(36)	0
OH	0.637(2)	1/4	0.063(1)	136(24)	211(42)	52(44)	147(38)	0	–16(39)	0
H	0.71(2)	1/4	–0.02(1)	200						

* $U_{ij} = U_{ij} \times 10^4$

TABLE 4. BOND-VALENCE* TABLE FOR MOTTRAMITE

	Cu	Pb	V	H	Σ
O(1)	$0.32^{\times2}\downarrow$	$0.36^{\times2}\downarrow$ $0.20^{\times2}\downarrow$	$1.16^{\times2}\downarrow$		2.02
O(2)		0.16 $0.05^{\times2}\downarrow\rightarrow$	1.39	0.38	2.03
O(3)	$0.19^{\times2}\downarrow\rightarrow$	0.21	1.31		1.90
OH	$0.50^{\times2}\downarrow\rightarrow$	0.40		0.62	2.02
Σ	2.02	1.97	5.00	1.00	

* calculated from the curves of Brown & Altermatt (1985)

and a bond-valence analysis in Table 4. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

Chemical Composition

The crystal used in the collection of the X-ray intensity data was subsequently mounted in epoxy, ground, polished and analyzed by electron microprobe using a CAMECA SX–50 according to the procedure of Hawthorne *et al.* (1993). The results (mean of 10 points) are given in Table 5. The unit formula, based on 5(O,OH) with OH = 1 *apfu* (atom per formula unit), is $Pb_{1.04}(Cu_{0.81}Zn_{0.12})(VO_4)(OH)$, ignoring minor components. The crystal was found to be full of very small inclusions (usually < 1 μm). The composition of the largest inclusion (~5 μm) is given in Table 5. When reduced on the basis of 13 anions, the formula corresponds fairly closely to that of vanadinite, ideally $Pb_5(VO_4)_3Cl$, although the presence of some Cu^{2+} and Zn suggests analytical contamination from the host mottramite. This accounts for the slightly low (Cu+Zn) sum of 0.93 *apfu* relative to Pb and V derived from the composition of mottramite (Table 5).

TABLE 5. CHEMICAL COMPOSITION* AND UNIT FORMULAE OF MOTTRAMITE AND AN INCLUSION IN MOTTRAMITE

	**MOTTRAMITE	INCLUSION
V_2O_5	21.70	17.81
As_2O_5	0.29	0.30
CuO	15.49	1.29
ZnO	2.31	0.31
FeO	0.15	0.07
CaO	0.18	–
PbO	56.24	76.14
H_2O	2.18	--
Cl	–	1.83
O≡Cl	–	-0.41
Sum	98.54	97.34
V^{5+}	0.99	2.88
As	0.01	0.05
Σ	1.00	2.93
Cu	0.81	0.24
Zn	0.12	0.06
Fe	0.01	0.01
Σ	0.94	–
Pb	1.04	5.02
Ca	0.01	–
Σ	1.05	5.02
OH	1.00	
Cl	–	0.76

* – = not detected; Sr, S, Ni, Ti, Mn, Co, P not detected

** mean of 10 values

Cation Coordination

The Cu site is coordinated by four oxygen anions and two hydroxyl groups (Table 3) in a distorted octahedral arrangement (Fig. 1a). Nearly all $Cu\phi_6$ (ϕ: O^{2-}, OH, H_2O) octahedra in minerals and synthetic inorganic solids are strongly distorted away from holosymmetric symmetry owing to Jahn–Teller relaxation associated with the electronic degeneracy of a d^9 electron configuration in a holosymmetric octahedral field. Usually, this distortion results in an axially elongated octahedron (Eby & Hawthorne 1993), designated as a [4 + 2] distortion. However, such a pattern of distortion is not always the case. There are a significant number of instances where the $Cu\phi_6$ octahedron has two short bonds, two intermediate-length bonds, and two long bonds (Burns 1994). Mottramite is one such structure; the intermediate-length bonds (2.102 Å) are very close to the mean of the long and short bonds (2.117 Å), a [2 + 2 + 2]-coordination.

The V^{5+} is coordinated by four oxygen anions in a distorted tetrahedral arrangement. The <V–O> bond-length, 1.722 Å, lies in the range of <V–O> distances observed in inorganic vanadate structures (Hawthorne & Faggiani 1979), and the O–V–O angular range is also typical of other well-refined vanadates.

As is commonly the case for large cations, there is some ambiguity about the coordination number for Pb^{2+} in mottramite. There are seven bonds in the range 2.45–2.80 Å, and the next-nearest anions occur at 3.195 Å (the dashed lines in Fig. 1b); are these latter two distances to be considered as bonds? The bond-valence sum around the central Pb^{2+} is 1.87 *vu* without the two long distances and 1.97 *vu* including the two long distances. Although the latter value is closer to the ideal value of 2.0 *vu*, the value of 1.87 *vu* lies well within the range of bond-valence sums around Pb^{2+} observed in inorganic structures; thus the incident bond-valence sum around the Pb^{2+} cation does not resolve this point. The two long Pb–O distances involve the O(2) anion, and the bond-valence sums at

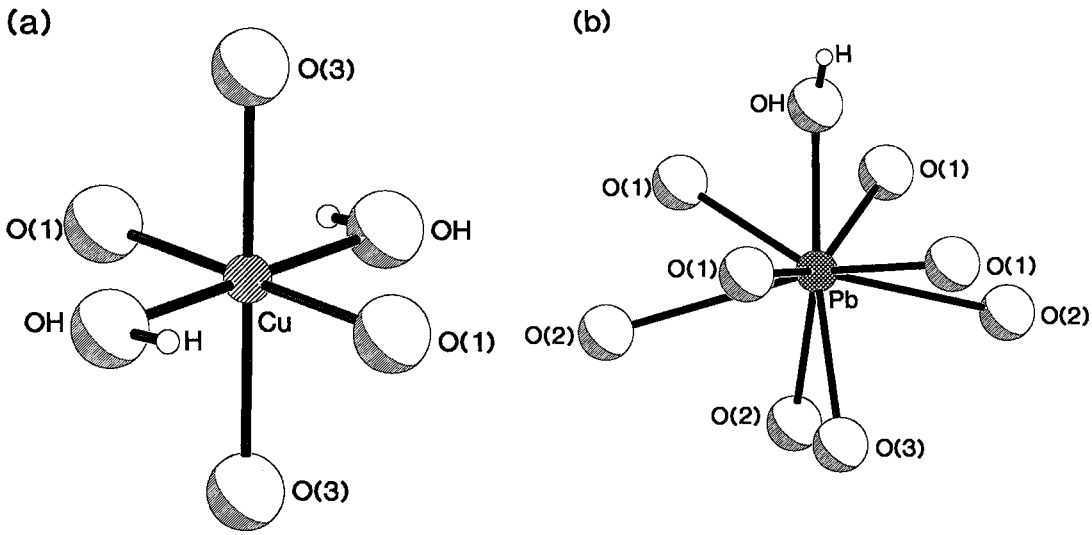

FIG. 1. Oblique views of selected coordination polyhedra in mottramite: (a) the $Cu\phi_6$ polyhedron; (b) the $Pb\phi_9$ polyhedron. Oxygen atoms are large highlighted circles, H atoms are small unshaded circles, Cu^{2+} is the diagonal-line shaded circle, and Pb is the cross-hatched circle.

O(2) with and without this long distance as a bond are 1.65 and 1.55 *vu*, respectively, not considering the contribution from the H-bond. Again, this situation is rather inconclusive, as if the bond-valence from the H-bond is included in the sum around O(2), the values are close to being ideal, both with (2.03 *vu*) and without (1.93 *vu*) this interaction. The same situation holds for the analogous distance in descloizite (Table 6).

The H atom is bonded to the OH oxygen atom, with the distance constrained by the refinement to be close to 0.98 Å. There is a H-bond with the O(2) anion, as suggested by the arrangement of non-H bond-valences in the structure (Table 4). The H...O(2) distance, 1.90 Å, suggests a strong H-bond, in accord with the low bond-valence sum around the O(2) anion when the H-bond is omitted from consideration. In this regard, it is important to note the different behavior of the O(2) anion in descloizite (Table 6): the H-bond is weaker in the latter mineral, a consequence of the different electronic structures of Zn and Cu^{2+}.

TABLE 6. BOND-VALENCE* TABLE FOR DESCLOIZITE

	Zn	Pb	V	H	Σ
O(1)	$0.26^{\times 2}\downarrow$	$0.40^{\times 2}\downarrow$ $0.19^{\times 2}\downarrow$	$1.19^{\times 2}\downarrow$		2.04
O(2)		0.16 $0.05^{\times 2}\downarrow\rightarrow$	1.53	0.29	2.08
O(3)	$0.27^{\times 2}\downarrow\rightarrow$	0.21	1.12		1.87
OH	$0.48^{\times 2}\downarrow\rightarrow$	0.41		0.71	2.08
Σ	2.02	2.06	5.03	1.00	

* calculated from the curves of Brown & Altermatt (1985)

STRUCTURE TOPOLOGY

The structural unit of mottramite is shown in Figure 2. Chains of edge-sharing octahedra of the general form $[M\phi_4]$ (*M*: octahedrally coordinated cation) extend along the *Y* axis, the double repeat of the *trans* edge-sharing octahedra defining the *b* dimension as ~6.1 Å (Hawthorne 1990). These chains are cross-linked by VO_4 tetrahedra that also link along the length of each chain, forming a fairly open framework. The interstitial Pb^{2+} cations occur in the interstices of this framework (Fig. 3) and play a key role in satisfying the local bond-valence requirements of all anions in the structure. Hawthorne (1990) gave details of isostructural minerals and other $MT\phi_n$ minerals with related structures based on $[M\phi_4]$ chains.

SOLID SOLUTION ALONG THE MOTTRAMITE–DESCLOIZITE JOIN

The question of solid solution between Cu^{2+} and other divalent cations in inorganic crystals is very interesting. There are three distinct situations: (1) no solid-solution, (2) complete solid-solution, or (3) complete solid-solution with a phase transition at some intermediate composition. The structural constraints on

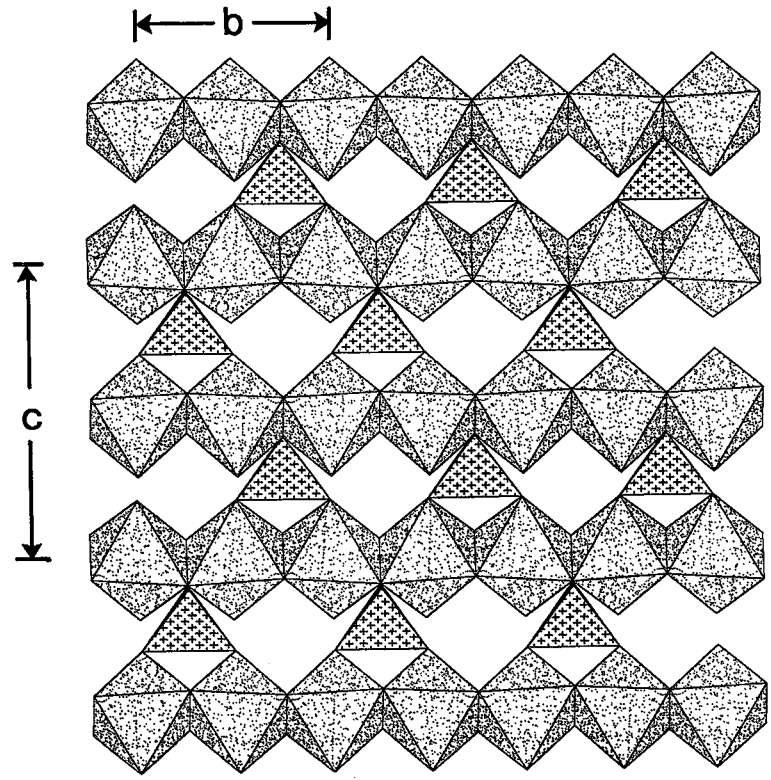

FIG. 2. The structural unit in mottramite projected down [100]; $Cu\phi_6$ polyhedra are random-dot-shaded, VO_4 polyhedra are cross-shaded.

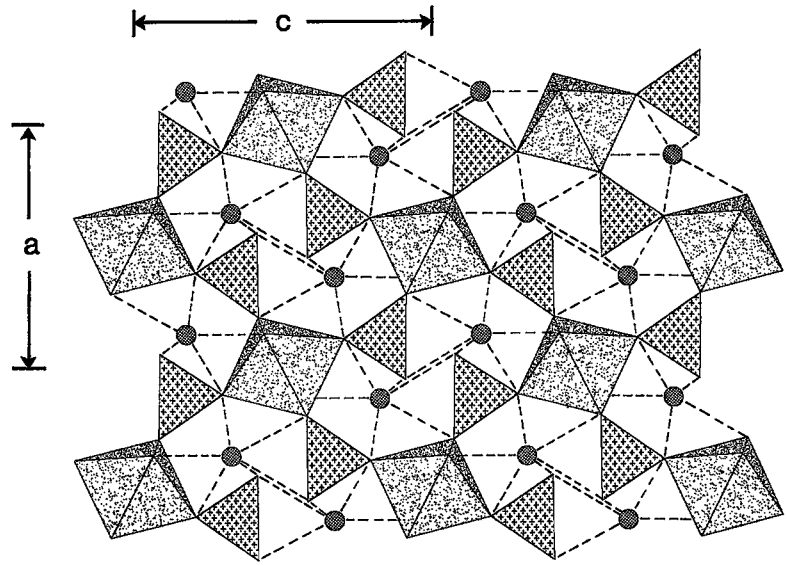

FIG. 3. The structure of mottramite projected down [010]; legend as in Figs. 1 and 2.

this type of solid solution have not been examined, in general. The fact that there is complete $Cu^{2+} \rightleftharpoons Zn$ solid-solution across the mottramite–descloizite join (Van der Westhuizen *et al.* 1986), together with the availability of structural data on near-end-member compositions (Hawthorne & Faggiani 1979, this study), gives us the opportunity to examine how the descloizite structure-type accommodates the geometrical requirements of relaxation associated with the degenerate or near-degenerate e_g state in holosymmetrically or regularly coordinated $^{[6]}Cu^{2+}$.

In descloizite (Table 6), the ZnO_6 octahedron has four long bonds [*bv* (bond valence) ≈ 0.27 *vu*] and two short bonds (*bv* = 0.48 *vu*), with the latter in a *trans* orientation. The four long bonds are to the O(1) and O(3) anions. O(1) is [4]-coordinated, with an incident bond-valence sum of 2.04 *vu*, and O(3) is [4]-coordinated, with an incident bond-valence sum of 1.87 *vu* (Table 6); note that in mottramite (Table 4), the same bond-valence sums occur, although the individual incident bond-valences are different. The two short bonds are to OH, the oxygen anion of which is [4]-coordinated (Cu^{2+},Pb,H). The O(2) anion is [4]-coordinated, but is not linked to the Zn cation; excluding the H bond, its incident bond-valence sum is 1.79 *vu*, and thus it needs a H-bond of average strength (~0.21 *vu*) to complete its bond-valence requirements.

If Zn is replaced by Cu^{2+}, as in mottramite, the structure has to change around the Cu^{2+} site to accommodate the geometrical requirements associated with the (pseudo-) Jahn–Teller instability of Cu^{2+} in regular octahedral coordination. Octahedrally coordinated Cu^{2+} is usually coordinated by a [4 + 2]-arrangement of anions, whereas Zn in descloizite has a [2 + 4]-arrangement of coordinating anions, a configuration that is energetically less favorable for Cu^{2+} (Burns & Hawthorne 1995). The anion arrangement around Cu^{2+} adjusts by shortening one pair of long bonds [to the O(1) anion] and lengthening the other pair of long bonds [to the O(3) anion], thus producing a [2 + 2 + 2]-coordination, a reasonably common type of coordination of Cu^{2+} in oxysalt minerals. Comparison of the bond-valence tables of descloizite and mottramite (Tables 4, 6) shows how this change is accommodated. The Cu^{2+}–O(3) bond in mottramite is lengthened relative to that in descloizite, reducing the bond-valence incident at O(3); this is compensated by a corresponding shortening of the V–O(3) bond in mottramite relative to descloizite. In turn, the bond-valence sum around the V^{5+} cation in mottramite is maintained close to its ideal value by lengthening the V–O(2) bond, hence reducing the incident bond-valence at the O(2) anion; this is compensated by an increase in the strength of H-bonding to the O(2) anion in mottramite (Table 4). Thus a [2 + 2 + 2]-distortion occurs around the Cu^{2+} cation in mottramite, and this is accommodated by further cooperative bond-valence adjustments in the structure.

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