The Canadian Mineralogist
Vol. 33, pp. 1125-1129 (1995)

DIABOLEITE, $Pb_2Cu(OH)_4Cl_2$, A DEFECT PEROVSKITE STRUCTURE WITH STEREOACTIVE LONE-PAIR BEHAVIOR OF Pb^{2+}

MARK A. COOPER and FRANK C. HAWTHORNE

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

ABSTRACT

The crystal structure of diaboleite, $Pb_2Cu(OH)_4Cl_2$, tetragonal, *P4mm*, *a* 5.880(1), *c* 5.500(2) Å, *V* 190.1(1) Å^3, $Z = 1$, has been refined to an *R* value of 1.8% using 356 observed (5σ) reflections measured with Mo*K*α X-radiation. There is one unique Cu^{2+} position coordinated by four $(OH)^-$ and two Cl^- anions; the Cl^- anions occupy the apical positions, and the $Cu\phi_6$ octahedron (ϕ: unspecified ligand) shows the [4 + 2] distortion typical of $^{[6]}Cu^{2+}$ oxides and oxysalts. There is one unique Pb^{2+} position coordinated by four $(OH)^-$ and four Cl^- anions. The $(OH)^-$ anions all form short (2.46 Å) bonds with Pb^{2+}, and lie to one side of the cation, whereas the Cl^- anions all form long (3.22 and 3.40 Å) bonds with Pb^{2+}, and are on the other side of the cation; thus Pb^{2+} shows a one-sided coordination typical of stereoactive lone-pair behavior. There are two unique Cl^- positions; one is strongly bonded to Cu^{2+} and Pb^{2+} cations, whereas the other is primarily held in place by a network of hydrogen bonds emanating from the $(OH)^-$ groups. The $Cu\phi_6$ octahedra form corner-sharing $[M\phi_5]$ chains along the *c* axis, and these chains are cross-linked by Pb^{2+} cations and by hydrogen bonding. The structure may be described as a defect-perovskite arrangement of the form $Pb_2(Cu\square)\phi_6$ in which half of the octahedra are not occupied by cations.

Keywords: diaboleite, crystal-structure refinement, Cu^{2+}, Pb, stereoactive lone pair.

SOMMAIRE

Nous avons affiné la structure cristalline de la diaboléite, $Pb_2Cu(OH)_4Cl_2$, tetragonale, *P4mm*, *a* 5.880(1), *c* 5.500(2) Å, *V* 190.1(1) Å^3, $Z = 1$, jusqu'à un résidu *R* de 1.8% en utilisant 356 réflexions observées (5σ) et mesurées avec rayonnement Mo*K*α. La structure contient un seul site occupé par le Cu^{2+}, coordonné par quatre groupes $(OH)^-$ et deux atomes de Cl^-; les anions Cl^- occupent les positions apicales, et les octaèdres $Cu\phi_6$ (ϕ: ligand non spécifié) sont difformes et de type [4 + 2], ce qui est typique des oxydes and oxysels de $^{[6]}Cu^{2+}$. Le Pb^{2+} occupe une position unique; il est entouré de quatre groupes $(OH)^-$ et de quatre anions Cl^-. Les groupes $(OH)^-$ sont tous à une courte distance (2.46 Å) du Pb^{2+} et sont situés d'un côté du cation, tandis que les anions Cl^- sont tous situés à une plus grande distance (3.22 et 3.40 Å) de l'atome Pb^{2+}, de l'autre côté. Le Pb^{2+} montre donc une polarité dans sa coordinence, résultat typique d'un comportement stéréoactif d'une paire d'électrons isolés. La structure contient deux positions distinctes de l'anion Cl^-; une d'elles est fortement liée aux cations Cu^{2+} and Pb^{2+}, tandis que la position de l'autre est surtout régie par un réseau de liaisons hydrogène provenant des groupes $(OH)^-$. Les octaèdres $Cu\phi_6$ sont agencés en chaînes $[M\phi_5]$ le long de l'axe *c* par partage de coins; ces chaînes sont rattachées par les cations Pb^{2+} et par les liaisons hydrogène. On peut qualifier la structure comme étant une pérovskite à lacunes, de forme $Pb_2(Cu\square)\phi_6$, dans laquelle il ne se trouve aucun cation dans la moitié des octaèdres.

(Traduit par la Rédaction)

Mots-clés: diaboléite, affinement de la structure cristalline, Cu^{2+}, Pb, paire isolée d'électrons stéréoactifs.

INTRODUCTION

Diaboleite, $Pb_2Cu(OH)_4Cl_2$, was originally described from the Mendip Hills, Somerset, England (Spencer & Mountain 1923). A more detailed description was published by Palache (1941) on diaboleite from the Mammoth mine, Pinal County, Arizona. Palache (1941) confirmed the chemical composition, showed that diaboleite is tetragonal hemimorphic with point symmetry *4mm*, and determined the optical properties and cell dimensions. Diaboleite was synthesized (Winchell & Wenden 1968) between 25° and 100°C at atmospheric pressure, and the cell dimensions and hemimorphic character were confirmed on the synthetic material. Byström & Wilhelmi (1950) solved the crystal structure of diaboleite, and it was refined by Rouse (1971), who described it as a defect perovskite arrangement. Rouse (1971) also suggested that the formula might not be correct, as his model had one of the Cl sites only two-thirds occupied, and he proposed either the presence of significant Cu^+ or charge compensation by the presence of O^{2-} replacing OH^- (with the concomitant presence of some [5]-coordinated Cu^{2+}).

Diaboleite occurs as deep blue tabular crystals with perfect {001} cleavage, as aggregates of thin plates, and as massive finely crystalline material. At the Mammoth mine, it is associated with cerussite, wulfenite, quartz and hemimorphite, and is followed by boléite, linarite, pseudoboléite and other less common secondary minerals.

EXPERIMENTAL

Collection of X-ray data

The material used for this work is from the Mammoth mine, Arizona; it was obtained from the Royal Ontario Museum, sample number M24959. The crystal used for measurement of the cell dimensions and intensity-data collection was ground to a plate 18 μm thick and was mounted on a Nicolet *R*3*m* automated four-circle diffractometer. The cell dimensions and orientation matrix were derived by least-squares methods from the setting angles of 25 aligned reflections. Intensity data were collected according to the method of Hawthorne & Groat (1985). A total of 1212 intensities was collected over the range $4° \leq 2\theta \leq 60°$ and index ranges $0\,\bar{k}\,\bar{l}$ to $h\,k\,l$. The data were corrected for absorption (polyhedron correction by Gaussian-quadrature integration), Lorentz, polarization and background effects, and then reduced to structure factors, with averaging over four symmetry-related units; of the 372 reflections measured, 356 were classed as observed ($|F_0| > 5\sigma$). Experimental details are listed in Table 1.

Structure refinement

All calculations were done with the SHELXTL PC system of programs. The structure refinement was initiated in the space group *P4mm* using the coordinates of Rouse (1971), and converged rapidly to an *R* value of 3.0%. At this stage, a difference-Fourier map revealed the position of the H atom, which was inserted into the refinement with the soft constraint that the O–H bond-length must be approximately equal to 0.98 Å. Full-matrix least-squares refinement, including an isotropic extinction correction, converged to an *R* value of 1.8% and a *wR* value of 1.8%. Final parameters are given in Table 2, selected interatomic distances are listed in Table 3, and a bond-valence table is shown in Table 4. Observed and calculated structure-

TABLE 1. MISCELLANEOUS EXPERIMENTAL INFORMATION ABOUT DIABOLEITE AND THE STRUCTURE REFINEMENT

a (Å)	5.880(1)	Crystal size (mm)	0.220 x 0.190 x 0.018
c	5.500(2)	Radiation	Mo*Kα*/Graphite
V (Å^3)	190.1(1)	Total no. of *I*	1212
Space Group	*P4mm*	No. of $|F|$	372
μ (cm^{-1})	479	No. of $|F_0| > 5\sigma$	356
Min. transmission	0.005	*R* (merge) %	3.3
Max. transmission	0.411	*R* (obs) %	1.8
D_{calc} (g cm^{-3})	5.387	*wR* (obs) %	1.8

Cell content: $[Pb_2Cu(OH)_4Cl_2]$

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

$wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma F_0^2]^{½}$, $w = 1/\sigma^2F*[1-\exp(-1.6\{\sin\theta/\lambda\}^2)]$

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

Pb-O	x4	2.456(3)	Cu-Oe	x4	1.972(4)
Pb-Cl(1)	x2	3.218(3)	Cu-Cl(1)		2.550(7)
Pb-Cl(2)	x2	3.398(5)	Cu-Cl(1)f		2.950(7)
O-Pb-Oa	x2	116.1(2)	<Cu-Cl>		2.75
O-Pb-Ob	x2	79.3(2)			
O-Pb-Oc	x2	68.0(2)	Of-Cu-Oe	x4	88.3(1)
O-Pb-Cl(1)	x4	68.5(1)	Of-Cu-Cl(1)	x4	99.9(2)
O-Pb-Cl(1)d	x4	143.0(1)	Of-Cu-Cl(1)f	x4	80.1(2)
O-Pb-Cl(2)	x4	77.4(1)			
O-Pb-Cl(2)c	x4	138.5(1)	O-H		0.98(5)
Cl(1)-Pb-Cl(2)	x4	78.2(1)	H···Cl(2)g		2.39(6)
Cl(1)-Pb-Cl(1)d		132.0(2)			
Cl(2)-Pb-Cl(2)c		119.8(3)	O-H···Cl(2)g		162(6)
<O-Pb-O>		87.8			
<Cl-Pb-Cl>		94.1			

a: 1−x, −y, z; b: 1−x, y, z; c: x, −y, z; d: 1+x, y, z; e: −x, y, z−1; f: x, y, z−1; g: x, y, 1+z.

TABLE 4. BOND-VALENCE TABLE FOR DIABOLEITE

	Pb	Cu	H	
O	$0.39^{x4}{\downarrow}^{x2}{\rightarrow}$	$0.45^{x4}{\downarrow}$	0.80	2.03
Cl(1)	$0.16^{x2}{\downarrow}^{x4}{\rightarrow}$	0.23 0.08		0.95
Cl(2)	$0.10^{x2}{\downarrow}^{x4}{\rightarrow}$		$0.20^{x4}{\rightarrow}$	1.20
Σ	2.08	2.11	1.00	

* Parameters from Brese & O'Keeffe (1991)

TABLE 2. FINAL ATOMIC PARAMETERS FOR DIABOLEITE

Site	*x*	*y*	*z*	U_{eq}*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb	1/2	0	0.7298**	139(1)	100(2)	152(2)	165(2)	0	0	0
Cu	0	0	0.0282(9)	113(5)	92(5)	92(5)	157(14)	0	0	0
Cl(1)	0	0	0.492(1)	205(7)	234(9)	234(9)	146(15)	0	0	0
Cl(2)	1/2	1/2	0.420(2)	255(11)	287(12)	287(12)	193(29)	0	0	0
O	0.2336(5)	0.2336(5)	0.966(1)	155(9)	120(10)	120(10)	226(24)	−9(12)	−9(12)	−16(14)
H	0.291(9)	0.291(9)	0.122(8)	100**						

* *U* values x 10^4; ** fixed.

factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

DESCRIPTION OF THE STRUCTURE

Cation coordination

There is one unique Pb position surrounded by four OH groups and four Cl anions arranged at the vertices of a square antiprism (Fig. 1a); there are four equivalent Pb–OH distances of 2.46 Å and two sets of two Pb–Cl distances of 3.22 and 3.40 Å, respectively. The latter Pb–Cl distance is quite long (Table 3), and it is not clear from the bond-valence values (Table 4) whether or not these should be considered as bonds. However, what is clear from Figure 1a is that the coordination of Pb^{2+} is very asymmetrical; there are four short bonds to OH groups on one side of the central cation and four long bonds to Cl anions on the other side of the cation. This type of coordination geometry is characteristic of stereoactive lone-pair behavior by the central cation, with the lone-pair projecting toward the four Cl anions.

There is one unique *Cu* position; the Cu^{2+} is octahedrally coordinated by four OH groups and two Cl anions (Fig. 1b). The four OH groups constitute the usual four short equatorial bonds typical of $Cu\phi_6$, and the two Cl anions are in the apical positions, as is usually the case in Cl-containing mixed-ligand $Cu^{2+}\phi_6$ groups (Burns & Hawthorne 1995). Octahedral $Cu^{2+}\phi_6$ groups characteristically show a (4 + 2) distortion, in which the two apical bonds are significantly longer than the equatorial bonds. However, simple inspection of the bond lengths is not sufficient to decide the present case, as Cl^- is a significantly larger anion than $(OH)^-$, and hence cation–Cl bonds are intrinsically longer than cation–(OH) bonds. This effect may be evaluated from the structure of tolbachite (Burns & Hawthorne 1993), in which the $Cu^{2+}Cl_6$ octahedron has a <Cu–Cl> distance of 2.506 Å. This distance is shorter than the apical Cu–Cl distances in diaboleite; hence we may conclude that the apical Cu–Cl bonds in diaboleite are elongated, and that the $Cu^{2+}(OH)_4Cl_2$ octahedron does show the typical [4 + 2] Jahn–Teller distortion. The Cu^{2+} cation is actually displaced 0.34 Å from the plane of the equatorial anions in the direction of the nearer apical Cl atom. This indicates a Cu^{2+} coordination intermediate between octahedral and square pyramidal.

Hydrogen bonding

The H position was located and refined with the soft constraint that the O–H distance should be close to 0.98 Å. The resulting geometry (Table 3) shows that there is a hydrogen bond to the Cl(2) anion. There are four hydrogen bonds incident at the Cl(2) anion, providing most, if not all, of its incident bond-valence requirements. The OH group is bonded to one Cu and two Pb cations, and all the metal–OH bonds are quite short (Table 3). As a consequence of this, the metal–OH bonds are quite strong (Table 4), and contribute 0.39 × 2 + 0.45 = 1.23 *vu* (valence units) to the oxygen anion. This ensures that the resulting hydrogen-bond is strong enough (~0.20 *vu*) to satisfy the incident bond-valence requirements of the Cl(2) anion. The actual hydrogen-bond arrangement is

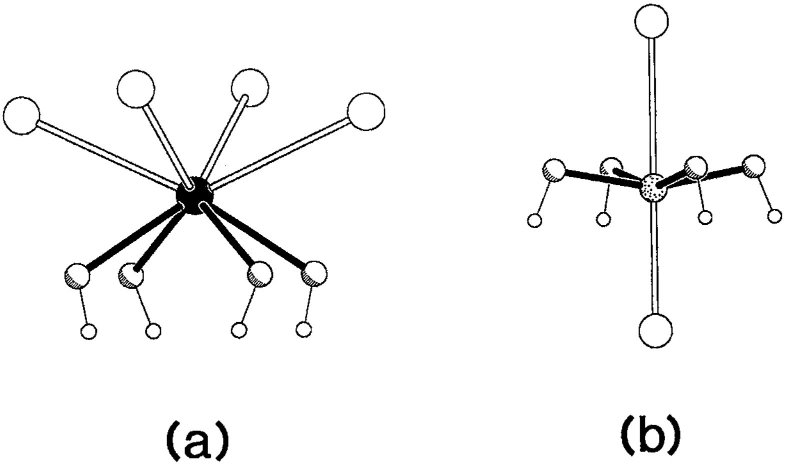

FIG. 1. Coordination of the cations in diaboleite; Pb is black, Cu is random-dot-shaded, oxygen atoms are shaded circles, Cl atoms are large unshaded circles, and H atoms are small unshaded circles, cation–oxygen bonds are shown as thick black lines, cation–chlorine bonds are shown as unshaded lines, and donor–H bonds are shown as narrow lines; (a) Pb; (b) Cu.

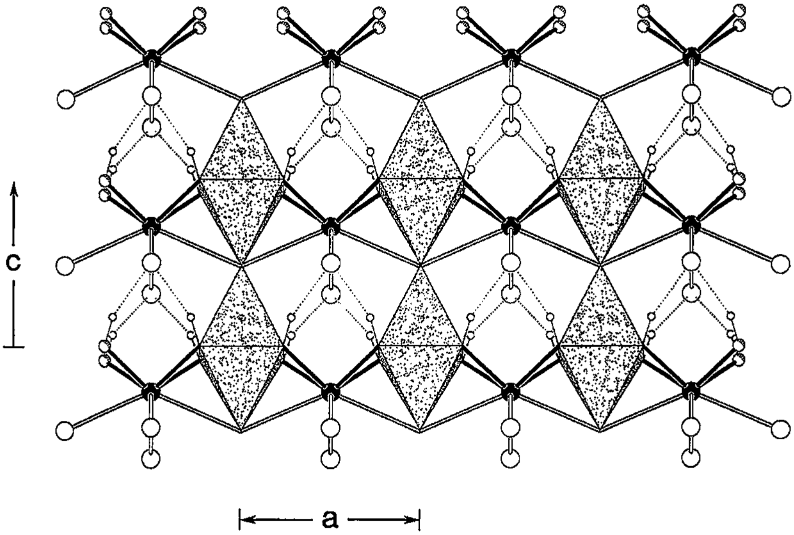

FIG. 2. The atomic arrangement in diaboleite projected down an axis 10° away from [010]; legend as in Fig. 1, with hydrogen bonds shown as dotted lines.

shown in Figure 2. The Cl(2) anion lies approximately in the plane of the Cl(1) anions, approximately 3 Å from the plane of the Cu^{2+} cations and O^{2-} anions. The H bonds to Cl(2) in the $[00\bar{1}]$ direction with an O–H–Cl(2) angle of 162°, giving Cl(2) a very unusual "one-sided" coordination.

Structure topology

The description of the diaboleite arrangement as a defect-perovskite structure (Rouse 1971) is an excellent approach. As shown in Figure 3a, the structure consists of a sheet of isolated $Cu^{2+}\phi_6$ octahedra at the

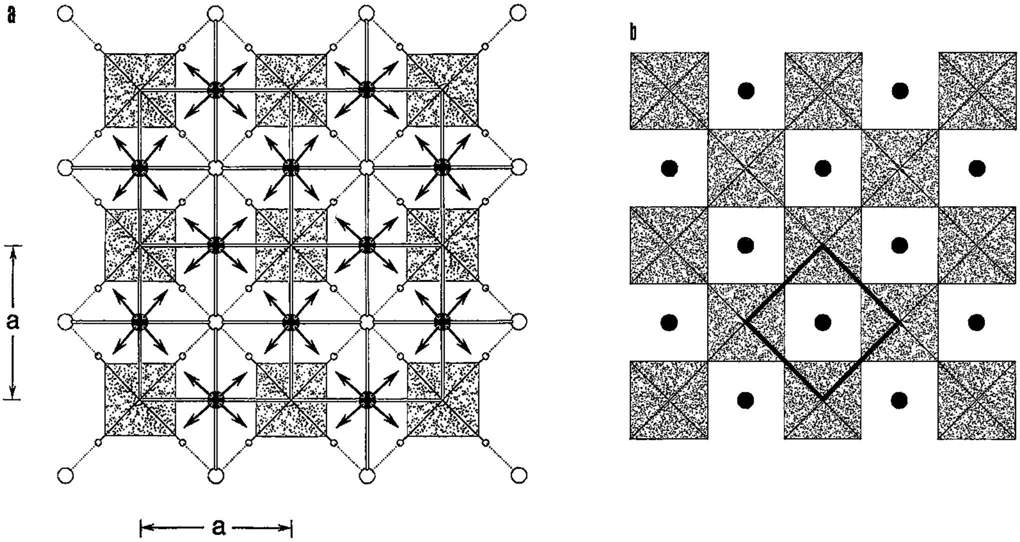

FIG. 3. (a) The atomic arrangement in diaboleite projected onto (001); legend as in Fig. 1. (b) The atomic arrangement in an ideal cubic perovskite; interstitial cations are filled circles, octahedra are random-dot-shaded, and the unit cell is outlined in thick lines.

nodes of a 4_4 net. This arrangement is repeated in the [001] direction by the lattice translation to form corner-sharing $[Cu^{2+}\phi_5]$ chains parallel to [001] (Fig. 2). The analogous arrangement in an idealized cubic perovskite is shown in Figure 3b. Comparison of the two structures shows that omission of half the octahedrally coordinated cations in perovskite can lead to the diaboleite arrangement. We can express this conceptual process as $CaTiO_3 \rightarrow Ca_2Ti_2O_6 \rightarrow Pb_2(Cu^{2+}\square)\phi_6^{1-} \rightarrow Pb_2Cu(OH)_4Cl_2$, with rearrangement of the unit cell such that *a*(diaboleite) = *a*(perovskite) √2 and *c*(diaboleite) = *c*(perovskite). The cooperative stereochemical interactions within this structure are extensive. The occurrence of Cl as the apical anions of the $Cu^{2+}\phi_6$ group cause strong extension of the octahedral chains along [001]. In turn, this provides additional space for the lone-pair stereoactivity of Pb^{2+}. The short Cu^{2+}–O(equatorial) bonds ensure strong H-bonding by the equatorial OH groups (Fig. 2), which provide additional bond-valence to the Cl anions, compensating for the long Cl–Cu^{2+} and Cu–Pb^{2+} bonds (Table 4). This type of cooperative interaction between Pb^{2+} and Cu^{2+} seems too common to be accidental, and may also be associated with strong ferroelastic behavior in minerals.

ACKNOWLEDGEMENTS

The crystals used in this work were obtained from the Department of Mineralogy, Royal Ontario Museum; we thank the Emerald Goddess for her cooperation. The manuscript benefitted from reviews by Yongshan Dai and Roland Rouse. The work was supported by the Natural Sciences and Engineering Research Council of Canada in the form of Operating, Infrastructure and Major Equipment grants to FCH.

REFERENCES

BRESE, N.E. & O'KEEFFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.

BURNS, P.C. & HAWTHORNE, F.C. (1993): Tolbachite, $CuCl_2$, the first example of Cu^{2+} octahedrally coordinated by Cl^-. *Am. Mineral.* **78**, 187-189.

________ & ________ (1995): Mixed-ligand $Cu^{2+}\phi_6$ octahedra in minerals. *Can. Mineral.* **33**,

BYSTRÖM, A. & WILHELMI, K.A. (1950): The crystal structure of diaboleite, $Pb_2Cu(OH)_4Cl_2$. *Ark. Kemi* **2**, 397-404.

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

PALACHE, C. (1941): Diaboleite from Mammoth mine, Tiger, Arizona. *Am. Mineral.* **26**, 605-612.

ROUSE, R.C. (1971): The crystal chemistry of diaboleite. *Z. Kristallogr.* **134**, 69-80.

SPENCER, L.J. & MOUNTAIN, E.D. (1923): New lead–copper minerals from the Mendip Hills (Somerset). *Mineral. Mag.* **20**, 67-92.

WINCHELL, R.E. & WENDEN, H.E. (1968): Synthesis and study of diaboleite. *Mineral. Mag.* **36**, 933-939.

Received January 11, 1995, revised manuscript accepted June 19, 1995.