

Crystal-structure determination of pinalite

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ABSTRACT

The crystal structure of pinalite, $\text{Pb}_3\text{WO}_5\text{Cl}_2$, is orthorhombic *Amam*, with $a = 11.073(2)$, $b = 13.067(3)$, $c = 5.617(1)$ Å, $V = 812.81(3)$ Å³, and $Z = 4$. It has been refined to an R index of 0.049 on the basis of 593 unique, observed reflections. There are two crystallographically distinct Pb cations with different coordinations: Pb1 has eightfold-coordination with ligands of 4 Cl atoms, 4 O atoms, and one stereoactive lone-pair, whereas Pb2 has ninefold-coordination with ligands of 4 Cl atoms and 5 O atoms. The W cation has fivefold-coordination with 5 O ligands. The pinalite structure is layered parallel to (100) with Pb-O-Cl layers interleaved with Pb-W-O layers. Pinalite belongs to the bismuth oxychloride group of structures. The Pb-O-Cl layer of pinalite duplicates the basic structure of thorikosite and the Pb-W-O layer of pinalite is able to conform to this fundamental cell through differences in the two Pb coordinations and a unique W coordination. Similarly the structures of nadorite and kettnerite are also shown to replicate the basic bismuth oxychloride structure.

INTRODUCTION

Pinalite, $\text{Pb}_3\text{WO}_5\text{Cl}_2$, from the Mammoth mine, Pinal County, Arizona was first reported by Dunn et al. (1989). At the time the authors noted there was insufficient material to determine the crystal structure of the new mineral, but there was sufficient to collect the data necessary to define it as a new mineral species. To the best of our knowledge no additional material has been found, but with improved X-ray technology it became possible to solve the crystal structure. The present study does not in any way alter the basic data that originally defined the species.

EXPERIMENTAL METHODS

For the intensity-data measurements, a fragment of a crystal blade (010) ($0.2 \times 0.03 \times 0.01$ mm) of pinalite was used. The specimen was part of the type material stored at the Canadian Museum of Nature under catalogue number CMNMC 53775. Intensity data were collected on a Siemens *P4* four-circle diffractometer operated at 50 kV, 40 mA, with graphite-monochromated $\text{MoK}\alpha$ radiation. The setting angles of 33 reflections were used to determine the orientation matrix and refine the cell dimensions. Two asymmetric units of intensity data (assuming centrosymmetric orthorhombic symmetry) were collected (i.e., $+h \pm k + l$) up to $2\theta = 60^\circ$ using a $\theta:2\theta$ scan-mode with scan speeds inversely proportional to intensity, varying from 3.95 to 29.3°/minute. Reduction of the intensity data, structure determination, and structure refinement were done using the SHELX-93 (Sheldrick 1993) package of computer pro-

grams. For the plate absorption correction, 12 intense diffraction-maxima in the range $2\theta = 14$ to 53° were chosen for ψ diffraction-vector scans at 10° intervals of ψ (North et al. 1968). With reflections omitted within a 5° glancing angle of the plate, the converging R refinement for the ψ -scan data set (420 reflections) decreased from 0.087 before correction to 0.039 after the absorption correction. Information relevant to the data collection is given in Table 1.

STRUCTURE SOLUTION AND REFINEMENT

In the original description (Dunn et al. 1989) precession photographs with exposures of 2–4 d were used to establish possible space groups *A2aa* and *Amaa* from the systematic extinctions. With the experimental set-up described above, the improved sensitivity of the detector was sufficient to establish possible space groups *Ama2*, *A2₁am*, and *Amam*. This change in space group choices requires a mere addition of a few reflections of the type $hk0$. Assigning phases to a set of normalized structure factors gave a mean value $|E^2 - 1|$ of 0.938. This value is characteristic of centrosymmetric space groups. The E -map coordinates for the *Amam* model were assigned the appropriate scattering curves, and a model with two Pb, one W and two O atoms refined to $R = 0.12$. With the additional sites added from the Fourier map the structure refined to $R = 0.07$ with isotropic displacement parameters. This model refined to $R = 0.049$ with anisotropic-displacement parameters. The final residual electron-densities are $+3.65$ and $-4.01 e^-/\text{Å}^3$. Table 2 lists the final positional and anisotropic-displacement parameters and bond valences. Table 3 gives the selected interatomic distances and Table 4¹ the observed and calculated structure factors.

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TABLE 1. Data collection and structure refinement information for pinalite

Space Group: <i>Amam</i> (no. 63)	Reflections collected	1181	ψ -merge (before/after)	0.087/0.039	wR_2	0.127
Radiation: MoK α	Unique reflections	593	Transmission (min./max.)	0.449/0.779	Goof	1.047
Cell Parameters	Observed reflections ($F_o > 4\sigma$)	440	Reflection omission for plate $< 5^\circ$			
$a = 11.073(2)$ Å	ψ -scan reflections	420	R(equivalent reflections)	0.050		
$b = 13.067(3)$ Å	Unit-cell contents	$4 \times \text{Pb}_3\text{WO}_3\text{Cl}_2$	R_1 (observed data)	0.049		
$c = 5.617(1)$ Å	μ	76.7 mm^{-1}	R_1 (all data)	0.073		

Notes: $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$;
 $w = 1 / [\sigma^2(F_o^2) + (a \times P^2) + (b \times P)]$; a and b refine, $P = \{(\max(0, F_o^2)) + 2F_c^2\} / 3$.

TABLE 2. Atomic parameters and bond valence sums for pinalite

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}	BVS*
Pb1	0.4678(1)	0.3489(1)	0	187(5)	202(6)	131(5)	0	0	16(4)	174(4)	1.98
Pb2	$\frac{3}{4}$	0.4002(2)	$-\frac{1}{2}$	214(7)	216(8)	71(6)	0	0	0	167(4)	1.79
W	$\frac{3}{4}$	0.2350(1)	0	164(7)	190(8)	68(7)	0	0	0	141(4)	6.00
O1	0.632(1)	0.270(1)	0.232(3)	185(50)	235(63)	100(52)	22(5)	-15(43)	-44(48)	173(28)	2.11
O2	$\frac{3}{4}$	0.105(4)	0	324(107)	397(120)	370(120)	0	0	0	364(87)	2.15
Cl1	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	141(41)	474(75)	428(73)	0	0	61(50)	348(29)	0.81
Cl2	$\frac{3}{4}$	0.475(1)	0	251(48)	379(68)	155(50)	0	0	0	262(24)	0.90

Notes: U values are in $\text{Å}^2 \times 10^4$.

* Calculated from the constants of Brese and O'Keeffe (1991).

TABLE 3. Selected bond distances (Å) and angles ($^\circ$) for pinalite

Pb1-O1	$2.43(1) \times 4$	Pb2-O1	$2.62(1) \times 4$
Pb1-Cl1	$3.45(1) \times 2$	Pb2-O2	2.68(5)
Pb1-Cl2	3.34(1)	Pb2-Cl1	$3.06(1) \times 2$
Pb1-Cl2'	3.52(1)	Pb2-Cl2	$2.97(1) \times 2$
W-O1	$1.91(1) \times 4$	O2-W-O1	$103.9(4) \times 4$
W-O2	1.69(5)	O1-W-O1'	$86.4(8) \times 2$
		O1-W-O1''	$86.9(8) \times 2$
		O1'-W-O1''	$152.2(8) \times 2$
Shortest cation-cation and anion-anion distances			
Pb1-Pb2	4.051(2)	Cl1-Cl2	3.96(1)
W-Pb1	3.461(1)	Cl1-O1	3.66(2)
W-Pb1'	3.861(1)	O1-O1	3.01(3)

DESCRIPTION OF THE CRYSTAL STRUCTURE

Pinalite has two Pb-sites with similar but distinct polyhedra and a W-site having a unique coordination. The Pb polyhedra have similar geometries, a monocapped square anti-prism, but with differing coordinations. The Pb1 cation, has eight-fold-coordination. The Cl atoms define the corners of the cube, and the O atoms occur at the center of the cube edge (Fig. 1a); thus the Pb-O bond-lengths, $\langle \text{Pb-O} \rangle = 2.43$ Å, are considerably shorter than the Pb-Cl bonds, $\langle \text{Pb-Cl} \rangle = 3.43$ Å. The geometrical apex for the monocapped square anti-prism for Pb1 (Fig. 1a) is a stereochemically active lone-pair of electrons which is graphically shown as two dots in Figure 1a. The Pb2 cation has nine-fold coordination. As in the Pb1-site the Cl atoms define the corners of the cube, $\langle \text{Pb2-Cl} \rangle = 3.01$ Å, and the O atoms centre the cube edges, $\langle \text{Pb-O2} \rangle = 2.62$ Å. The ninth ligand in the Pb2 polyhedron is an O2 atom which aligns the monocapped square anti-prism along the **b**-axis. The stereochemically active lone-pair of electrons manifests itself by compressing the Pb1 cation into its base along the **b**-axis. This affects the bondlengths by decreasing the average Pb-O bond length in

the polyhedron base and increasing the average Pb-Cl bond length in the polyhedron top; i.e., $\langle \text{Pb1-O} \rangle = 2.43$ Å vs. $\langle \text{Pb2-O} \rangle = 2.62$ Å and $\langle \text{Pb1-Cl} \rangle = 3.44$ Å vs. $\langle \text{Pb2-Cl} \rangle = 3.02$ Å.

The W polyhedron has fivefold-coordination in a regular square pyramid compressed along the **b**-axis with four W-O1 bond lengths of 1.91 Å and the apical W-O2 bond length of 1.69 Å. This configuration is an unusual polyhedral geometry for W which normally has octahedral coordination in tungsten oxides and tetrahedral coordination in tungstates. Typically,

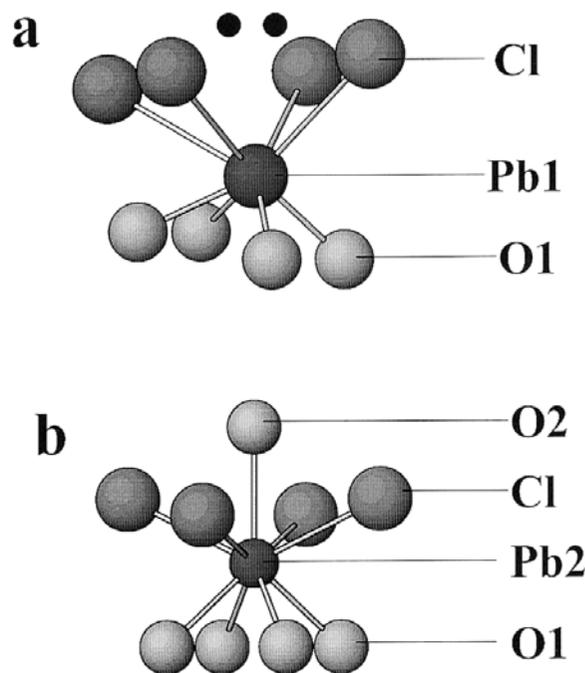


FIGURE 1. The Pb cation coordinations in pinalite in oblique projection with [010] vertical: (a) Pb1 with the stereochemically active lone-pair represented by two dots; (b) Pb2.

¹For a copy of Table 4, document item AM-00-042, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site (<http://www.minsocam.org> or current web address).

[WO₆] polyhedra have W-O bonds of 1.94 Å and [WO₄] polyhedra have W-O bonds of 1.78 Å. Thus, the W polyhedron in pinalite is unusual with the tetrahedral base having bond lengths similar to those of a regular [WO₆] octahedron while the fifth ligand has a much shorter bond length than even those observed in tungstate tetrahedra. This extreme shortening of the fifth ligand brings the bond valence into excellent agreement with the expected value (Table 2).

Pinalite is layered (Fig. 2) parallel to (100) with a distinct segregation of the cations into two fundamental layers. The Pb1-O-Cl layer (Fig. 3a) consists entirely of a network of Pb1 polyhedra comprised of Pb, O, and Cl atoms. The stereochemically active lone-pair leaves "apparent" gaps in the structure between adjacent Pb atoms. The second layer (Fig. 3b) consists of W and Pb2 polyhedra. As in the first layer the cations align themselves along [010]. The two layers are reinforced by cross-linkage through all polyhedra negating any cleavage (Dunn et al. 1989). The (010) plane defines the twin plane and the lamellar plane recorded by Dunn et al. (1989).

Dunn et al. (1989) remarked on the close relationship between the X-ray powder-diffraction pattern of pinalite and that of the bismuth oxychlorides or "Sillén phases" (Sillén 1942; Dunn and Rouse 1985). Now, with the crystal-structure analysis complete it is possible to explain this relationship. The basic unit cell of the bismuth oxyhalides is tetragonal with $a \sim 4$ Å and $c \sim 12$ or 24 Å. The group has been expanded considerably to include a number of Pb minerals such as thorikosite, (PbSb)O₂Cl (Rouse and Dunn 1985), parkinsonite, (Pb,Mo,□)₄O₄Cl (Symes et al. 1994), and asisite, Pb₇SiO₈Cl₂ (Rouse et al. 1988). Other members of the structural group are orthorhombic (pseudo-tetragonal) with $a \sim b \sim 4\sqrt{2} \sim 5.7$ Å. These include nadorite, PbSbO₂Cl (Giuseppetti and Tadani 1973); perite, PbBiO₂Cl; and blixite, Pb₂(O,OH)₂Cl. The closely interrelated minerals kettnerite, CaBi(CO₃)OF; beyerite, CaBi₂(CO₃)₂O₂; and bismutite, Bi₂(CO₃)O₂ are also structur-

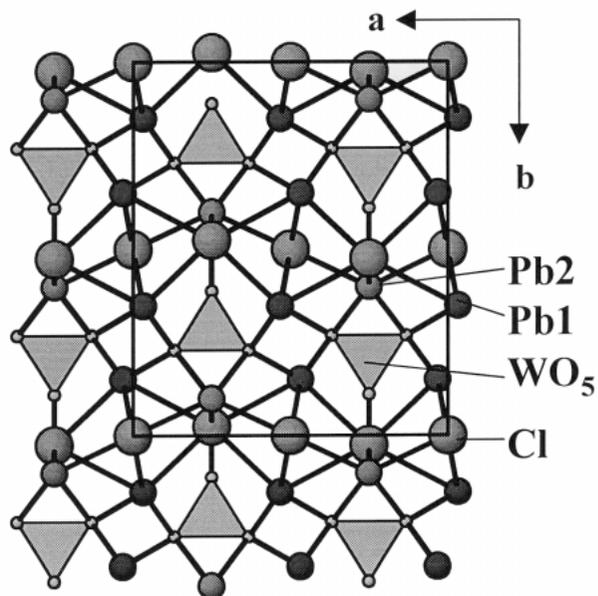


FIGURE 2. The structure of pinalite projected on (001), showing the layering in the structure parallel to (100). The unit cell is outlined.

ally related to the bismuth oxychlorides. The recent structure refinement of kettnerite (Grice et al. 1999) shows these three minerals are orthorhombic with merohedral twinning resembling tetragonal symmetry. Each have $a \sim b \sim 3.8$ Å and $c \sim 13$ or 21 Å.

This large and seemingly disparate group of chemical compounds all have a common structural template; that of the thorikosite structure (Rouse and Dunn 1985) with layers of PbO (litharge) interspersed with layers of Cl atoms (Fig. 4a). This is essentially one of the two basic layers described above for

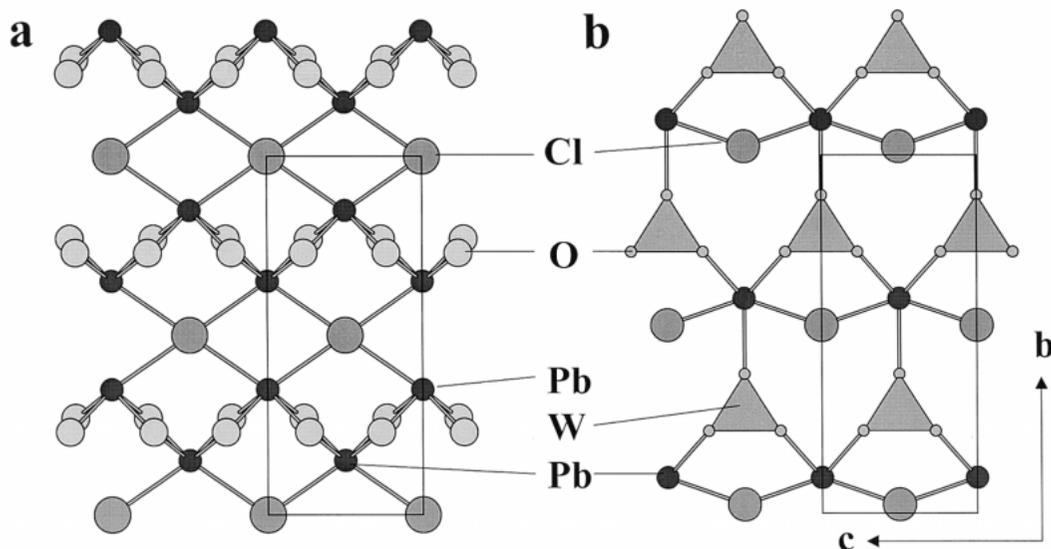


FIGURE 3. The (100) structure layers of pinalite: (a) the Pb1-O-Cl layer and (b) the Pb2-W-O-Cl layer.

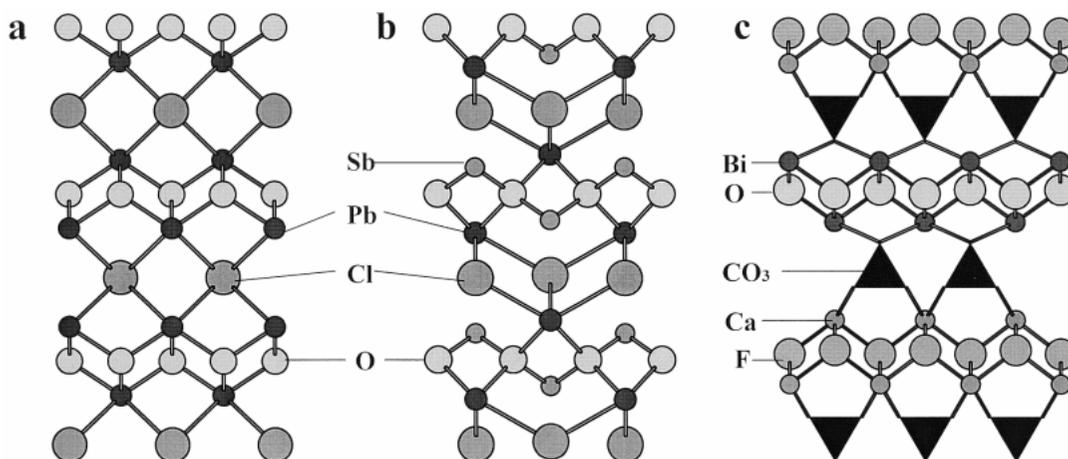


FIGURE 4. Comparison of bismuth oxychloride-type structures; (a) thorikosite structure projected on (100) with *c*-axis vertical, (b) nadorite structure projected on (100) with *b*-axis vertical and (c) kettnerite structure projected on (010) with *c*-axis vertical.

pinalite (Fig. 3a). The second layer in pinalite (Fig. 3b) “fits” this template by aligning the Cl- and O-layers and fitting one Pb-site to a Pb-site in the litharge layer and replacing the other Pb-site with W. This is spatially possible as a result of the “extra” O atom, which forms the apex of the [WO₅] tetragonal pyramid filling the “apparent” gap of the stereochemically active lone pair of the first layer.

Fitting the nadorite and kettnerite structures to the thorikosite template requires slightly different mechanisms. In the nadorite structure the Pb and Sb cations are ordered while in the thorikosite structure these cations are disordered. This ordering of cations lowers the symmetry from tetragonal to orthorhombic. It is interesting that in thorikosite the (PbSb)-site displays the effects of a stereochemically active lone pair, whereas in the nadorite structure only the Sb-sites display this phenomenon (Fig. 4b). In the kettnerite structure the Bi-O and Ca-F layers readily copy the PbO (litharge) unit (Fig. 4c) while the (CO₃) groups replace the Cl layer. The Bi-site in kettnerite has a stereochemically active lone pair, as does the (PbSb)-site of thorikosite. In kettnerite this lone pair “fits” between apices of the (CO₃) groups (Fig. 4c). In contrast the Ca-site does not have a stereochemically active lone pair so it fills the more regular, tighter position within the square anti-prism between the F anion layer and the O layer forming the base edges of the (CO₃) groups. The consistent cell parameters in this structural group are controlled by the square anti-prism co-ordination of these large cations. The corners of the cube are halogen or oxygen atoms with a typical anion-anion distance of ~4 Å (i.e., the *a* and *b* parameters outlined above). The basic *c* cell parameter consists of the litharge, PbO, unit of 2.5 Å sandwiched between two halogen layers, each adding 2 Å, for a total base unit of ~6.5 Å (Fig. 4a). Not surprisingly, the *c* cell parameter of kettnerite is slightly larger than that of thorikosite (13.57 vs. 12.85 Å).

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REFERENCES CITED

- Breese, N.E. and O’Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, B47, 192–197.
- Dunn, P.J. and Rouse, R.C. (1985) Freeditite and thorikosite from Långban, Sweden, and Laurion, Greece: two new species related to the synthetic bismuth oxyhalides. *American Mineralogist*, 70, 845–848.
- Dunn, P.J., Grice, J.D., and Bideaux, R.A. (1989) Pinalite, a new lead tungsten chloride mineral from the Mammoth mine, Pinal County, Arizona. *American Mineralogist*, 74, 934–935.
- Giuseppetti, G. and Tadini, C. (1973) Riesame della struttura cristallina della nadorite. *Periodico Mineralogia*, 42, 335–345.
- Grice, J.D., Cooper, M., and Hawthorne, F.C. (1999) Crystal-structure of twinned kettnerite. *Canadian Mineralogist*, 37, 923–927.
- North, A.C.T., Phillips, D.C., and Mathews, F.S. (1968) A semi-empirical method of absorption correction. *Acta Crystallographica*, A24, 351–359.
- Rouse, R.C. and Dunn, P.J. (1985) The structure of thorikosite, a naturally occurring member of the bismuth oxyhalide group. *Journal of Solid State Chemistry*, 57, 389–395.
- Rouse, R.C., Peacor, D.R., Dunn, P.J., Criddle, A.J., Stanley, C.J., and Innes, J. (1988) Asisite, a silicon-bearing lead oxychloride from the Kombat mine, South West Africa (Namibia). *American Mineralogist*, 73, 643–650.
- Sheldrick, G.M. (1993) *SHLXL-93*. Program for the refinement of crystal structures. University of Göttingen, Göttingen, Germany.
- Sillén, L.G. (1942) Ueber eine Familie von Oxyhalogeniden. *Die Naturwissenschaften*, 30, 318–324.
- Symes, R.F., Cressey, G., Criddle, A.J., Stanley, C.J., Francis, J.G., and Jones, G.C. (1994) Parkinsonite, (Pb,Mo,□)₈O₈Cl₂, a new mineral from Merehead quarry, Somerset. *Mineralogical Magazine*, 58, 59–68.

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