

THE CUPRITE-LIKE FRAMEWORK OF OCu_4 TETRAHEDRA IN THE CRYSTAL STRUCTURE OF SYNTHETIC MELANOTHALLITE, Cu_2OCl_2 , AND ITS NEGATIVE THERMAL EXPANSION

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ABSTRACT

Crystals of synthetic melanothallite, Cu_2OCl_2 , have been prepared by chemical transport reactions. Its crystal structure (orthorhombic, $Fddd$, a 7.4691(15), b 9.5969(19), c 9.700(2) Å, V 695.3(2) Å³, $Z = 8$) has been refined to $R_1 = 0.028$ ($wR = 0.078$; $S = 1.180$) on the basis of 346 unique observed reflections ($|F_o| \geq 4\sigma_F$). There is one symmetrically independent Cu atom in the structure, coordinated by two O and four Cl atoms. The mixed-ligand CuO_2Cl_4 octahedron shows strong Jahn–Teller (4 + 2)-distortion, with two O and two Cl atoms located in the equatorial plane and two Cl atoms in apical positions. The structure may be described as a three-dimensional framework formed by the cross-linking of chains of edge-sharing CuO_2Cl_2 squares. The chains are parallel to $[110]$ and $[\bar{1}10]$, and are linked to each other through the sharing of O atoms. The structure can also be described as an array of OCu_4 oxocentered tetrahedra linked by the sharing of Cu corners into a cuprite-like three-dimensional framework, with cavities in the framework containing Cl anions. As established previously, melanothallite shows negative thermal expansion along the b axis of its unit cell ($\alpha_b = -26.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), whereas thermal expansion along the a axis is positive and large ($\alpha_a = 50.6 \times 10^{-6} + 25.2 \times 10^{-9}t \text{ }^\circ\text{C}^{-1}$). This thermal behavior is explained on the basis of a cross-linking of chains of edge-sharing CuO_2Cl_2 squares. In the room-temperature structure, two chains are inclined to each other by $\sim 76^\circ$. When the temperature increases, the angle tends toward 90° , and the change of the angle between the two chains is accompanied by an increase of the a unit-cell parameter and by a decrease in the b parameter. This hinge mechanism provides an explanation for the high anisotropy in the thermal behavior of melanothallite observed by X-ray powder-diffraction methods.

Keywords: melanothallite, crystal structure, cuprite, oxocentered tetrahedra..

SOMMAIRE

Nous avons synthétisé des cristaux de mélanothallite, Cu_2OCl_2 , par réaction de transfert chimique. Elle possède une structure cristalline orthorhombique [$Fddd$, a 7.4691(15), b 9.5969(19), c 9.700(2) Å, V 695.3(2) Å³, $Z = 8$], affinée jusqu'à un résidu R_1 de 0.028 ($wR = 0.078$; $S = 1.180$) en utilisant 346 réflexions uniques observées ($|F_o| \geq 4\sigma_F$). Il y a une position Cu symétriquement indépendante dans la structure, en coordination avec deux atomes d'oxygène et quatre atomes de chlore. L'octaèdre à ligands mixtes CuO_2Cl_4 fait preuve d'une forte distorsion (4 + 2) due à l'effet Jahn–Teller, deux atomes d'oxygène et deux atomes de chlore étant situés dans le plan équatorial et deux atomes de Cl dans les positions apicales. La structure est une trame tridimensionnelle contenant une interconnexion de chaînes de carrés CuO_2Cl_2 à arêtes partagées. Les chaînes sont parallèles à $[110]$ et $[\bar{1}10]$, et sont liées l'une à l'autre par partage d'atomes d'oxygène. On peut aussi considérer la structure comme un agencement de tétraèdres OCu_4 , et donc centrés sur l'oxygène, et liés par partage de coins Cu pour former une trame tri-dimensionnelle typique de la cuprite, avec des cavités dans la trame contenant des atomes de Cl. Selon les travaux antérieurs, la mélanothallite montre une expansion thermique négative le long de l'axe b de la maille réticulaire ($\alpha_b = -26.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), tandis que l'expansion thermique le long de l'axe a est importante et positive ($\alpha_a = 50.6 \times 10^{-6} + 25.2 \times 10^{-9}t \text{ }^\circ\text{C}^{-1}$). Nous pouvons rendre compte de ce comportement thermique par allusion aux chaînes interconnectées de carrés CuO_2Cl_2 à arêtes partagées. Dans cette structure à température ambiante, les deux chaînes sont inclinées $\sim 76^\circ$ l'une par rapport à l'autre. Quand la température augmente, l'angle tend vers 90° , et ce changement de l'angle entre les deux chaînes mène à une augmentation de la dimension a de la maille réticulaire, et une diminution du paramètre b . Ce mécanisme de charnière fournit l'explication de l'anisotropie marquée du comportement thermique de la mélanothallite tel qu'observé par spectres de diffraction X obtenus sur poudre.

(Traduit par la Rédaction)

Mots-clés: mélanothallite, structure cristalline, cuprite, tétraèdres centrés sur l'oxygène.

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INTRODUCTION

Melanothallite, Cu_2OCl_2 , was first described by Scacchi (1870) from fumaroles of the Vesuvius volcano, Italy, where it was found in association with eriochalcite, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, chalcocyanite, CuSO_4 , euchlorine, $\text{NaKCu}_3\text{O}(\text{SO}_4)_3$, and dolerophanite, $\text{Cu}_2\text{O}(\text{SO}_4)$. It is unstable under atmospheric conditions, and was found to change its color from black to green in a few days. Scacchi (1884) suggested the formula $\text{CuCl}(\text{OH})$ for melanothallite, but Zambonini (1910, 1935) criticized his conclusions and proposed that melanothallite is simply a cupric chloride, CuCl_2 . A mineral with this composition was described by Vergasova & Filatov (1983) as tolbachite.

The great fissure Tolbachik eruption (GFTE) that occurred in 1975–1976 on the Kamchatka Peninsula, Russia, provided a unique assemblage of exhalative minerals, and more than 25 new species have been discovered there to date. Vergasova & Filatov (1982) examined exhalative products of the GFTE, and isolated a mineral that occurs as black plates in association with tenorite, CuO , and tolbachite, CuCl_2 . The mineral is similar to melanothallite as described by Scacchi (1870, 1884) and Zambonini (1910, 1935). An X-ray powder-diffraction study indicated that the mineral is identical to the synthetic compound Cu_2OCl_2 (JCPDS, card # 23–954). These data, together with chemical data, were used to assign the formula of melanothallite as Cu_2OCl_2 . A single-crystal X-ray-diffraction study of natural crystals of melanothallite showed that it is orthorhombic, space group *Fddd*, *a* 7.461(3), *b* 9.595(3), *c* 9.693(3) Å, *V* 693.9(1) Å³. However, attempts to solve the structure using data collected from natural crystals were unsuccessful, probably owing to the instability of the mineral in air. Arpe & Müller-Buschbaum (1977) used chemical transport reaction (CTR) methods with a temperature range of 350–450°C to synthesize crystals of Cu_2OCl_2 . They solved the structure and refined it to *R* =

0.112 on the basis of 335 unique reflections. The relatively high value of the *R* index may be due to the instability of melanothallite.

A high-temperature X-ray powder-diffraction study of melanothallite was done by Filatov & Vergasova (1983; see also Filatov 1990), which provided the following thermal-expansion coefficients ($^{\circ}\text{C}^{-1}$): $\alpha_a = 50.6 \times 10^{-6} + 25.2 \times 10^{-9}t$, $\alpha_b = -26.7 \times 10^{-6}$, $\alpha_c = 8.47 \times 10^{-6} + 54.1 \times 10^{-9}t$. Thus the structure of melanothallite shows contraction (negative thermal expansion) along the *b* axis and large positive expansion along the *a* axis.

The purpose of this paper is to report results of a crystal-structure refinement of synthetic melanothallite, to discuss its relationships to other structures that are based on cuprite-like frameworks of oxocentered tetrahedra, and to suggest an explanation for the negative thermal expansion along the *b* axis.

EXPERIMENTAL

Synthesis

The crystals of synthetic melanothallite were prepared using CTR at the lower temperature of a gradient from 370 to 470°C, from stoichiometric amounts of CuO and CuCl_2 (Filatov *et al.* 1992a). The main product of synthesis consists of tabular, elongate crystals up to 5 mm in maximum dimension.

Data collection

A crystal was encased in epoxy and mounted on a Bruker three-circle X-ray diffractometer operated at 50 kV and 40 mA and equipped with an APEX CCD area detector. More than a hemisphere of data was collected over approximately 3 h using monochromatic $\text{MoK}\alpha$ X-radiation, with frame widths of 0.3° in ω , and with a 5 s count for each frame. The unit-cell parameters (Table 1) were refined from 1344 reflections using least-squares techniques. The intensity data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical absorption-correction was done based upon 957 intense reflections. The crystal was modeled as an ellipsoid, which lowered R_{int} from 0.189 to 0.077.

Structure solution and refinement

The Bruker SHELXTL Version 5 system of programs was used for determination and refinement of the crystal structure. Systematic absences of reflections indicated space group *Fddd*, in accord with Arpe & Müller-Buschbaum (1977) and Vergasova & Filatov (1982). The structure was solved by direct methods and refined to an R_1 value of 0.028, calculated for the 346 unique observed ($|F_o| \geq 4\sigma_F$) reflections. Final atom coordinates and anisotropic displacement parameters are given in Table 2, selected interatomic distances are in

TABLE 1. CRYSTALLOGRAPHIC DATA FOR SYNTHETIC MELANOTBALLITE

<i>a</i> (Å)	7.4691(15)	<i>c</i> (Å)	9.700(2)
<i>b</i> (Å)	9.5969(19)	<i>V</i> (Å ³)	695.3(2)
<i>Z</i>	8		
Space group	<i>Fddd</i>	<i>F</i> ₀₀₀	800
μ (cm ⁻¹)	135.18		
Crystal size (mm)	0.30 × 0.18 × 0.06	<i>D</i> _{calc} (g/cm ³)	4.09
Radiation	$\text{MoK}\alpha$	Total reflections	1770
Unique reflections	363	Unique <i>F</i> _o = 4 σ_F	346
<i>R</i> *	0.028		
<i>wR</i>	0.078		
<i>S</i>	1.180		

* $R = \sum(F_o - F_c) / \sum F_o$; $S = [\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$, for *m* observations and *n* parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 0.5152P]$, where $P = (F_o^2 + 2F_c^2)/3$

TABLE 2. ATOM COORDINATES AND DISPLACEMENT PARAMETERS FOR SYNTHETIC MELANOTHALLITE

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	0	0	½	0.0140(2)	0.0179(3)	0.0130(3)	0.0110(3)	-0.0006(1)	-0.0008(1)	-0.0026(1)
Cl	½	½	0.32431(7)	0.0213(2)	0.0289(4)	0.0220(4)	0.0131(4)	0	0	-0.0087(2)
O	½	½	¾	0.0127(5)	0.0167(10)	0.0119(10)	0.0094(11)	0	0	0

Table 3. Calculated and observed structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

RESULTS

Copper polyhedron

There is one symmetrically independent Cu^{2+} cation. It is octahedrally coordinated by two O and four Cl atoms. The two O atoms are in a *trans* arrangement with Cu^{2+} -O bond lengths of 1.9444(2) Å. Two Cu^{2+} -Cl bond lengths, corresponding to Cl atoms in a *trans* arrangement, are 2.2836(6) Å. The remaining Cu^{2+} -Cl bond lengths are much longer: 3.1311(5) Å. As noted by Burns & Hawthorne (1995), mixed-ligand $\text{Cu}^{2+}\phi_6$ octahedra (ϕ : unspecified ligand) are distorted owing to the Jahn-Teller effect (Jahn & Teller 1937), and this type of coordination is common for Cu oxyhalides. Although holosymmetric coordination about the Cu^{2+} cation is impossible where different types of ligands are involved, a pseudo-holosymmetric octahedral geometry can occur, and involves a near-degenerate electronic state. The expected Cu^{2+} -O and Cu^{2+} -Cl bond lengths, derived from sums of effective ionic radii, are 2.09 and 2.40 Å, respectively [$\text{Cu}^{2+} = 0.73$ Å, $\text{O}^{2-} = 1.36$ Å (Shannon 1976); $\text{Cl}^- = 1.67$ Å (Whittaker & Muntus 1970)]. It is therefore apparent that the $\text{Cu}^{2+}\phi_6$ octahedron in melanothallite is (4 + 2)-distorted, with two elongate apical Cu^{2+} -Cl bonds. Burns & Hawthorne (1995) noted that CuO_2Cl_4 octahedra with similar distortions occur in the structures of eriochalcite, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Engberg 1970, Brownstein *et al.* 1989) and chlorothionite, $\text{K}_2\text{Cu}(\text{SO}_4)\text{Cl}_2$ (Giacovazzo *et al.* 1976). Note that the long Cu-Cl interactions of 3.1311 Å are essential for a good agreement between bond-valence sums and expected formal valences.

Description of the structure

The structure of synthetic melanothallite is shown in Figure 1a. The Cu-O bond network, shown in Figure 1b, is of special interest. It may be described as an array of OCu_4 oxocentered tetrahedra linked by sharing of Cu corners, resulting in a three-dimensional framework. From the perspective of Cu polyhedra, the structure can

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF SYNTHETIC MELANOTHALLITE

Cu-O _a	1.9444(2) 2×	O-Cu _{d,e,f}	1.9444(2) 4×
Cu-Cl _a	2.2836(6) 2×	Cu...Cud	3.0402(4) 2×
Cu-Cl _{b,c}	3.1311(5) 2×	Cu...Cuf	3.0605(5) 2×
		Cu...Cue	3.4112(5) 2×
		<Cu...Cu>	3.171

a = -x, -y, -z + 1; b = -x - 1/4, y, -z + 3/4; c = x + 1/4, -y, z + 1/4; d = -x + 1/4, -y + 1/4, z; e = -x + 1/4, y, -z + 5/4; f = x, -y + 1/4, -z + 5/4

be described as a three-dimensional framework of cross-linked chains of edge-sharing CuO_2Cl_2 squares (Fig. 1c) (ignoring the long Cu-Cl bonds). The chains are parallel to [110] and $[\bar{1}\bar{1}0]$, and are linked through O atoms.

Geometry of OCu_4 tetrahedra

The average <O-Cu> bond length for the OCu_4 tetrahedron in melanothallite is 1.94 Å, in close agreement with the value of 1.92 Å usually observed for OCu_4 tetrahedra (Effenberger 1985, Filatov *et al.* 1992b). The OCu_4 tetrahedron is rather distorted, with four Cu-O-Cu angles in the range 102.9–103.8° and two Cu-O-Cu angles of 122.6°. The average <Cu...Cu> distance is 3.17 Å (Table 3), in agreement with the value of 3.14 Å given for OCu_4 tetrahedra by Krivovichev & Filatov (1999).

DISCUSSION

Comparison with related compounds: structures with cuprite-like frameworks

The structure of cuprite, Cu_2O , contains two interlocking frameworks of OCu_4 tetrahedra that are topologically identical to the framework of SiO_4 tetrahedra in cristobalite, SiO_2 (Fig. 2a). The $[\text{OCu}_2]$ framework in melanothallite is shown in Figures 1b and 2b; it is identical to one of the frameworks of OCu_4 tetrahedra in cuprite. To obtain the crystal structure of melanothallite from that of cuprite, the voids of the $[\text{OCu}_2]$ framework must be filled by Cl anions (Fig. 2c).

There are several inorganic compounds with structures based on cuprite-like frameworks of oxocentered OA_4 tetrahedra (A = cation) (Table 4). In two modifica-

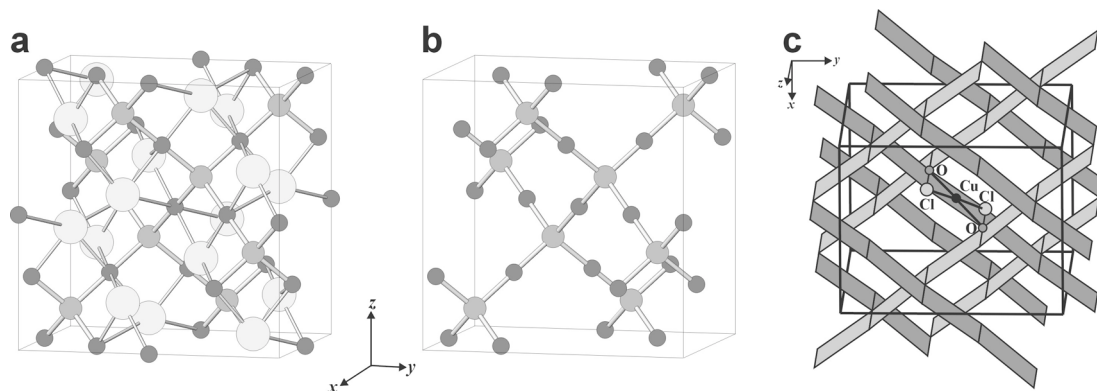


FIG. 1. The crystal structure of synthetic melanothallite in “ball-and-stick” representation (a), framework of Cu–O bonds in the structure (b), and the structure represented as a framework of chains of edge-sharing CuO_2Cl_2 squares (c).

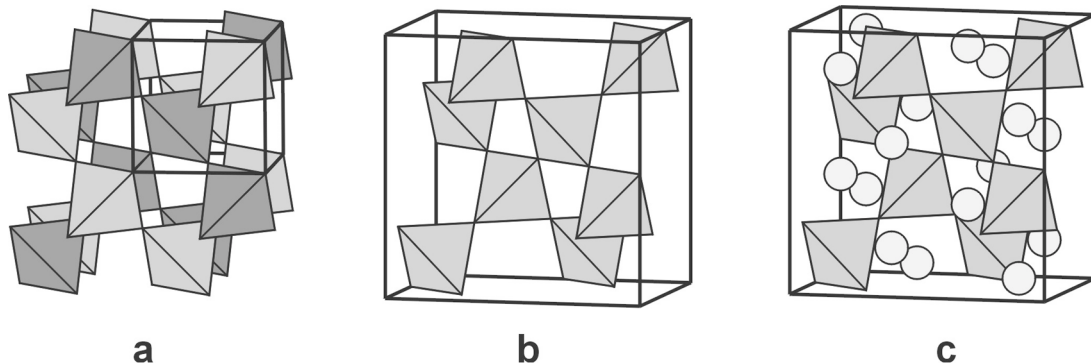


FIG. 2. Crystal structure of cuprite as based on two interpenetrating frameworks of OCu_4 oxocentered tetrahedra (a), cuprite-like framework of OCu_4 tetrahedra in melanothallite (b), and the structure of melanothallite represented as a cuprite-like framework filled by Cl anions (c).

tions of $\text{Cu}_2\text{O}(\text{SeO}_3)$, voids in $[\text{OCu}_2]$ cuprite-like frameworks contain SeO_3 groups. In monoclinic $\text{Cu}_2\text{O}(\text{SeO}_3)$ and Pd_2OCl_2 , the a and b cell parameters are related to the ideal subcell of the cuprite-like framework with a_c defined by $a = b = a_c/2^{1/2}$. The average $\langle a_c \rangle$ parameters for structures with cuprite-like frameworks are given in Table 4. It is interesting that, in structures with $[\text{OCu}^{2+}_2]^{2+}$ frameworks, the values of the $\langle a_c \rangle$ parameter are in the range of 4.455–4.463 Å (*i.e.*, slightly longer than the $\langle a_c \rangle$ parameter of cuprite, 4.267 Å). Note that Pd_2OCl_2 is not isostructural with melanothallite. The $[\text{NHg}_2]$ frameworks of NHg_4 tetrahedra in mosesite and gianellaite are cuprite-like (*i.e.*, they belong to the cristobalite structure-type), whereas the $[\text{NHg}_2]$ framework in kleinite, $\text{Hg}_2\text{N}(\text{SO}_4, \text{Cl}, \text{H}_2\text{O})$ (Giester *et al.* 1996), is of the tridymite type (Hawthorne *et al.* 2000).

Cuprite-like frameworks of OA_4 tetrahedra occur in the structures of oxide pyrochlores, $\text{A}_2\text{O}[\text{A}'_2\text{O}_6]$ (Sleight 1968). This description is especially appropriate for $\text{A} = \text{Pb}^{2+}, \text{Bi}^{3+}, \text{Hg}^{2+}$ or REE^{3+} , because these A –O bonds to “additional” O atoms (not bonded to A' high-valence cations) are shorter than A –O bonds to O atoms of $\text{A}'\text{O}_6$ octahedra ($\text{A}' = \text{Nb}, \text{Ti}, \text{Re}, \text{Ru}, \text{etc.}$) (see, for example, Tabira *et al.* 1999).

Thermal expansion of melanothallite: an interpretation

Melanothallite exhibits negative thermal expansion along the b axis ($\alpha_b = -26.7 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$), whereas thermal expansion along the a axis is much larger ($\alpha_a = 50.6 \times 10^{-6} + 25.2 \times 10^{-9}t \text{ } ^\circ\text{C}^{-1}$) (Filatov & Vergasova 1983). This thermal behavior can be explained on the

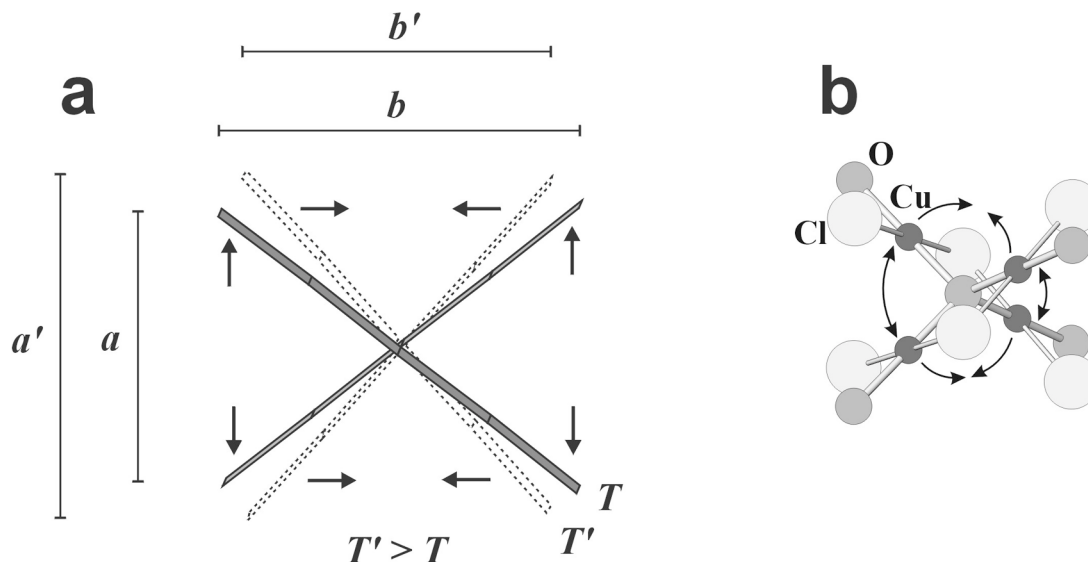


FIG. 3. An interpretation of negative thermal expansion of the structure of melanothallite along the b axis: (a) mechanism of thermal behavior of the structure represented as a hinge framework of chains of CuO_2Cl_2 squares (see Fig. 1c); (b) thermal behavior of the $\text{OCu}_4\text{O}_4\text{Cl}_6$ complex that has an OCu_4 tetrahedron as its core.

basis of a description of the structure as cross-linked chains of edge-sharing CuO_2Cl_2 squares (Fig. 1c). In the room-temperature structure, two chains are inclined at $\sim 76^\circ$ to each other. As the temperature increases, the angle tends toward 90° (Fig. 3a). Increase in the angle between the two chains is accompanied by an increase in the a cell parameter and by a decrease in the b parameter. As a result, thermal expansion along the b axis is negative, whereas that along the a axis is positive and large. This hinge-like mechanism can account for the high anisotropy of the thermal behavior of melanothallite. This hinge mechanism (involving two chains of edge-sharing CuO_4 squares) was recognized by Domnina *et al.* (1986) and Filatov (1990) during their study of the thermal expansion of tenorite. In tenorite, two chains of CuO_4 squares are parallel to $[110]$ and $[\bar{1}10]$ with an interchain angle of $\sim 72^\circ$ (*i.e.*, similar to that in melanothallite). Thermal expansion along the b axis of tenorite is negative above 650°C . This finding was explained by Domnina *et al.* (1986) using the same hinge model as suggested above for melanothallite. It should be noted that high anisotropy is common for hinge structures and has also been observed in borates (Filatov & Bubnova 2000).

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TABLE 4. MINERALS AND INORGANIC COMPOUNDS BASED ON CUPRITE-LIKE FRAMEWORKS OF ANION-CENTERED AX_4 TETRAHEDRA ($X = \text{O}^{2-}, \text{N}^{3-}, \text{A} = \text{Cu}^{2+}, \text{Pb}^{2+}, \text{Hg}^{2+}, \text{Pd}^{2+}$)

Compound	Space group	a (Å)	b (Å)	c (Å)	β (°)	$\langle a_c \rangle^*$ (Å)	Ref
Cuprite, Cu_2O	$Pn\bar{3}m$	4.267	-	-	-	4.267	1
Melanothallite, Cu_2OCl_2	$Fddd$	7.469	9.597	9.700	-	4.461	2
$\text{Cu}_2\text{O}(\text{SeO}_3)\text{-I}$	$P2_13$	8.925	-	-	-	4.463	3
$\text{Cu}_2\text{O}(\text{SeO}_3)\text{-II}$	$P2_1/n$	6.987	5.953	8.429	92.2	4.455	3
Pd_2OCl_2	$I4_1/amd$	6.313	-	9.872	-	4.621	4
Mosesite, $\sim [\text{Hg}_2\text{N}]_2(\text{H}_2\text{O})(\text{SO}_4)$	$F\bar{4}3m$	9.503	-	-	-	4.752	5
Gianellaite, $[\text{Hg}_2\text{N}]_2(\text{SO}_4)$	$F\bar{4}3m$	9.521	-	-	-	4.760	6

* Average parameter of the cubic subcell of cuprite-like framework.

References: (1) Restori & Schwarzenbach (1986), (2) this work, (3) Effenberger & Pertlik (1986), (4) Dannecker & Thiele (1986), (5) Airoldi & Magnano (1967), and (6) Gaines *et al.* (1997).

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