

## THE CRYSTAL STRUCTURE OF CHOLOALITE

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### ABSTRACT

The crystal structure of choloalite,  $(\text{Cu}_{2.79}\text{Sb}_{0.21})\Sigma_{3.00}(\text{Pb}_{2.70}\text{Ca}_{0.30})\Sigma_{3.00}\text{Te}_{6.00}\text{O}_{18.00}\text{Cl}_{0.92}$ ,  $a$  12.520(4) Å,  $V$  1963(2) Å<sup>3</sup>, space group  $P4_132$ ,  $Z = 4$ , has been solved by Patterson and direct methods, and refined to an  $R$  index of 5.3% based on 956 unique reflections measured using  $\text{MoK}\alpha$  radiation on an automated four-circle diffractometer. The structure consists of distorted  $\text{TeO}_6$  octahedra,  $\text{Cu}\phi_5$  square pyramids (where  $\phi = \text{O}$  and  $\text{Cl}$ ),  $\text{Pb}(1)\text{O}_9$  triaugmented trigonal prisms, and  $\text{Pb}(2)\text{O}_{12}$  icosahedra. The  $\text{Pb}(1)\text{O}_9$  polyhedra polymerize to form a three-dimensional network, as do the  $\text{Cu}\phi_5$  square pyramids and  $\text{Pb}(2)\text{O}_{12}$  polyhedra. The two networks fit together in three-dimensional space, leaving voids that are filled by the  $\text{TeO}_6$  octahedra. It is likely that the ideal formula of choloalite is  $\text{CuPbTe}^{4+}_2\text{O}_6$ , with  $\text{CuO}_4$  square planes as opposed to  $\text{Cu}\phi_5$  square pyramids.

*Keywords:* choloalite, crystal structure, tellurite, lead, copper.

### SOMMAIRE

La structure cristalline de la choloalite,  $(\text{Cu}_{2.79}\text{Sb}_{0.21})\Sigma_{3.00}(\text{Pb}_{2.70}\text{Ca}_{0.30})\Sigma_{3.00}\text{Te}_{6.00}\text{O}_{18.00}\text{Cl}_{0.92}$ ,  $a$  12.520(4) Å,  $V$  1963(2) Å<sup>3</sup>, groupe spatial  $P4_132$ ,  $Z = 4$ , a été résolue par méthodes de Patterson et méthodes directes, et affinée jusqu'à un résidu  $R$  de 5.3% à la lumière de 956 réflexions uniques mesurées au moyen de rayonnement  $\text{MoK}\alpha$  avec un diffractomètre automatisé à quatre cercles. La structure contient des octaèdres difformes  $\text{TeO}_6$ , des pyramides carrées  $\text{Cu}\phi_5$  ( $\phi = \text{O}$  and  $\text{Cl}$ ), des prismes trigonaux triaugmentés  $\text{Pb}(1)\text{O}_9$ , et des icosaèdres  $\text{Pb}(2)\text{O}_{12}$ . Les polyèdres  $\text{Pb}(1)\text{O}_9$  sont polymérisés pour donner une trame tridimensionnelle, tout comme les pyramides carrées  $\text{Cu}\phi_5$  et les polyèdres  $\text{Pb}(2)\text{O}_{12}$ . Les deux trames sont agencées ensemble dans les trois dimensions, et les espaces vides qui en résultent sont remplis par les octaèdres  $\text{TeO}_6$ . Il semble probable que la formule idéale de la choloalite est  $\text{CuPbTe}^{4+}_2\text{O}_6$ , et que la structure contient des plans carrés  $\text{CuO}_4$  plutôt que des pyramides carrées  $\text{Cu}\phi_5$ .

(Traduit par la Rédaction)

*Mots-clés:* choloalite, structure cristalline, tellurite, plomb, cuivre.

### INTRODUCTION

The type specimen of choloalite was described by Williams (1981) from waste rock in the tunnel at the Mina La Oriental, Moctezuma, Mexico. The type material consists of a matrix of intensely altered rhyolite vitrophyre crossed by veins of crystalline crusts and choloalite crystals. Soon after the discovery of the type material, samples with tiny crystals of choloalite were found between the dumps of the Joe and Grand Central shafts at Tombstone, Arizona. Choloalite also was described by Roberts *et al.* (1994) from the McAlpine mine, Tuolumne County, California.

The structure of choloalite was solved as part of a long-term project on the crystal chemistry of the Te-oxysalt minerals.

### PREVIOUS WORK

Using powder X-ray-diffraction data, Williams (1981) showed that choloalite is isometric. The refined unit-cell dimensions were reported to be  $a$  12.519 Å for the type specimen and 12.576 Å for the Tombstone sample. The larger cell edge of the Tombstone specimen was attributed to the presence of minor amounts of antimony. Wet-chemical analysis of the type material (Table 1) gave the empirical formula  $\text{CuPb}(\text{Te}^{4+}\text{O}_3)_2\cdot\text{H}_2\text{O}$ .

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TABLE 1. CHEMICAL COMPOSITION OF CHOLOALITE

Oxides (wt.%)	Williams (1981)*	This study	Elements (apfu)	Williams (1981)*	This study
CaO	trace	0.50	Ca <sup>2+</sup>	trace	0.17
PbO	33.0	31.22	Pb <sup>2+</sup>	2.94	2.65
CuO	11.0	11.81	Cu <sup>2+</sup>	2.75	2.81
ZnO	—	0.37	Zn <sup>2+</sup>	—	0.09
Sb <sub>2</sub> O <sub>5</sub>	trace	1.10	Sb <sup>5+</sup>	trace	0.13
TeO <sub>2</sub>	50.7	51.81	Te <sup>4+</sup>	6.31	6.15
Cl	—	1.19	Cl <sup>-</sup>	—	0.64
H <sub>2</sub> O	3.4	—	H <sup>+</sup>	7.50	—
O=Cl	—	-0.27	O <sup>2-</sup>	22.06	18.03
TOTAL	98.1	97.73			

Note: Analyses are normalized on 12 cations per formula unit. \*Average of four wet chemical analyses for CuO, and three for PbO and TeO<sub>2</sub>. Water by the Penfield method.

The formula of choloalite was revised to CuPb(TeO<sub>3</sub>)<sub>2</sub> by Powell *et al.* (1994), who synthesized crystals with this formula by fusion of stoichiometric amounts of CuO, TeO<sub>2</sub>, and PbO. No weight loss was detected with heating to 400°C, and infrared spectroscopy was used to confirm the absence of H<sub>2</sub>O. Powder X-ray-diffraction spectra of the synthetic material were found to be similar to those obtained from type choloalite, with some additional weak reflections. Powell *et al.* (1994) concluded that choloalite is anhydrous, and that the H<sub>2</sub>O determined by Williams (1981), using only 156 µg of material, was adsorbed on the surface of the mineral particles. The cell dimension *a* obtained from the synthetic phase was 12.514 Å, and indexed reflections suggested possible space groups *P*2<sub>3</sub>, *P*m<sub>3</sub>, *P*4<sub>3</sub>2, *P*4<sub>3</sub>m, or *P*m<sub>3</sub>m (none of which would result in systematic absences).

Powell *et al.* (1994) also suggested an additional occurrence of choloalite. This was based on the original description of balyakinite (Spiridonov 1980), which occurs with teinite and two unnamed Cu, Pb tellurites with formulae CuPb(TeO<sub>3</sub>)O and CuPb(TeO<sub>3</sub>)<sub>2</sub> (as derived from electron-microprobe analyses). The latter formula is the same as that obtained by Powell *et al.* (1994) for their synthetic material.

## EXPERIMENTAL

An electron-microprobe analysis was obtained using a JEOL 733 electron microprobe with Tracor Northern 5500 and 5600 automation. The wavelength-dispersion mode was used. The operating conditions were as follows: voltage 15 kV, beam current 20 nA, and beam diameter 5 µm. Data for Ca, Cu, Sb, and Te were collected for 25 s; data for Cl, Zn and Pb were collected for 50 s. The following standards were used: scapolite (ClKα), CaTa<sub>4</sub>O<sub>11</sub> (CaKα), cuprite (CuKα), ZnWO<sub>4</sub> (ZnKα), stibiotantalite (SbLα), and Pb<sub>2</sub>Te<sub>3</sub>O<sub>8</sub> (TeLα and PbMα). Data were reduced using a PAP routine

(program XMAQNT by C. Davidson, CSIRO). The results of the analysis are given in Table 1, together with the data of Williams (1981).

An attempt was made to obtain an infrared spectrum of choloalite, using a Fourier-transform infrared spectrometer equipped with a diamond-anvil microsample cell. The results show considerably more H<sub>2</sub>O than could possibly be accommodated in the structure of choloalite. Since this is undoubtedly evidence of adsorbed H<sub>2</sub>O, the results of the infrared experiment were considered to be inconclusive.

The crystal used in this study is from the Mina La Oriental locality (Canadian Museum of Nature sample MI58777). The crystal is optically isotropic and shows no evidence of twinning. It was mounted on a Siemens P3 automated four-circle diffractometer, and cell dimensions (Table 2) and intensity data were collected according to the procedure of Lam *et al.* (1998). One octant of reflections (3186 measurements, exclusive of standards) was collected from 3 to 60° 2θ; 64 reflections were rejected because of asymmetrical backgrounds, and one because of peak asymmetry. Fifteen strong reflections uniformly distributed with regard to 2θ were measured at 5° intervals of Ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector) from 0 to 355°, after the method of North *et al.* (1968). These data (920 measurements) were used to calculate an absorption correction. The merging *R* index for the Ψ-scan data set decreased from 5.1% before the absorption correction to 2.1% after the absorption correction. This correction was then applied to the entire dataset; minimum and maximum transmissions were 0.88 and 0.68, respectively. The data were also corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors. Of the 956 unique reflections, 455 were classed as observed [*I* ≥ 3σ(*I*)].

## STRUCTURE SOLUTION AND REFINEMENT

The Siemens SHELXTL PC system of programs was used throughout this study. Scattering curves for neutral atoms together with anomalous dispersion coefficients were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). Miscellaneous data on the collection and refinement are given in Table 2.

TABLE 2. MISCELLANEOUS INFORMATION: CHOLOALITE

<i>a</i> (Å)	12.520(4)	Rad/mono	MoKα/graphite
<i>V</i> (Å <sup>3</sup> )	1963(2)	Total   <i>F</i> <sub>o</sub>	3186
Space group	<i>P</i> 4 <sub>3</sub> 2	[ <i>I</i> ≥ 3σ( <i>I</i> )]	455
<i>Z</i>	4	<i>R</i> (%)	5.3
Crystal size (mm)	0.04 × 0.04 × 0.05	<i>wR</i> (%)	5.9
μ (MoKα; mm <sup>-1</sup> )	35.6		
$R = \sum  F_o - F_c  / \sum F_o, \quad wR = \left[ \sum (w F_o - F_c )^2 / \sum w F_o^2 \right]^{0.5}, \quad w = 1$			

TABLE 3. ATOMIC PARAMETERS FOR CHOLOALITE

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub> <sup>*</sup>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>eq</sub>
Te	0.0812(2)	0.4406(2)	0.3401(2)	204(11)	265(11)	201(10)	34(9)	47(8)	-5(9)	224(6)
Cu	1/8	0.2321(3)	-0.3179(3)	193(33)	199(27)	199(27)	-11(15)	11(15)	91(22)	197(17)
Pb(1)	0.1927(1)	0.1927(1)	0.1927(1)	378(7)	378(7)	378(7)	-73(7)	-73(7)	-73(7)	378(4)
Pb(2)	3/8	3/8	3/8	265(17)	265(17)	265(17)	-76(9)	-76(9)	-76(9)	265(10)
O(1)	0.0261(23)	0.1205(23)	0.2682(24)							413(65)
O(2)	0.1759(18)	0.3274(18)	0.3738(17)							232(48)
O(3)	0.1857(19)	0.5200(18)	0.2613(18)							248(50)
Cl	7/8	7/8	7/8	548(128)	548(128)	548(128)	24(92)	24(92)	24(92)	548(74)

\**U*<sub>11</sub> and *U* values are listed × 10<sup>4</sup> Å<sup>2</sup>.

The mean value of  $[E^2 - 1]$  was found to be 0.85, indicative of a non-centrosymmetric space-group. Systematic absences in the original dataset suggested the space groups  $P4_332$  and  $P4_132$ . The structure was solved by Patterson and direct methods and refined in  $P4_332$  to an *R* index of 6.9% for an isotropic displacement model. The refined atomic positions were used in the normalization program STRUCTURE TIDY (Gelato & Parthé 1987), which suggested the enantiomorphic space-group  $P4_132$ . Accordingly, the structure was refined in  $P4_132$  to an *R* index of 6.9% for an isotropic displacement model. Conversion to anisotropic displacement factors for all cations and Cl resulted in convergence at *R* and *wR* indices of 5.3 and 5.9%, respectively (13.0 and 28.4% for all 956 data). Conversion to anisotropic displacement factors for the oxygen atoms resulted in convergence at an *R* index of 5.1% (due to "smearing" of the electron density), but did not improve the model. Addition of an isotropic extinction correction did not improve the results. The program MISSYM (Le Page 1987) was used to search for additional elements of symmetry; none were indicated. Positional coordinates and anisotropic and equivalent isotropic displacement factors are given in Table 3. Interatomic distances and angles are given in Table 4, and a bond-valence analysis in Table 5. Initially, bond-valence values were calculated using the curves of Brese & O'Keeffe (1991), but the sums were poor. Bond-valence values calculated using the "correction" terms given by Wang & Liebau (1996) for Te<sup>4+</sup> were consistently too high. The curves of Brown (1981) were found to give the best sums for bonds to oxygen atoms (if the correct *R*<sub>0</sub> value of 1.951 is used for Te<sup>4+</sup>, as shown by Back 1990). Structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

#### DESCRIPTION OF THE STRUCTURE

Coordination polyhedra of cations in the choloalite structure are shown in Figure 1. There are four distinct cation positions in the structure. The *Te* site is completely occupied by Te<sup>4+</sup>, as shown by results of the electron-microprobe analysis, refined site-occupancy, and bond-valence analysis. The atom at the *Te* position is

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR CHOLOALITE

Te-O(1)a	1.87(3)	O(2)e-Cu-O(3)f	× 2	94.0(1.0)
-O(1)b	2.95(3)	O(2)e-Cu-O(3)h	× 2	85.7(1.0)
-O(2)	1.90(2)	O(2)e-Cu-Cl	× 2	93.4(7)
-O(3)	1.92(2)	O(3)f-Cu-Cl	× 2	92.3(7)
-O(3)c	2.71(2)	<O-Cu-O>		90
-O(3)d	3.05(2)	<O-Cu-O, Cl>		91.4
<Te-O>	2.40			
		O(1)-Pb(1)-O(1)i	× 3	98.9(9)
Cu-O(2)e	1.92(2) × 2	O(1)-Pb(1)-O(1)j	× 3	65.1(1.0)
-O(3)f	1.86(2) × 2	O(1)-Pb(1)-O(1)a	× 3	67.9(6)
-Cl	2.531(6)	O(1)-Pb(1)-O(2)	× 3	81.3(8)
<Cu-O>	1.89	O(1)-Pb(1)-O(2)j	× 3	115.0(8)
<Cu-O, Cl>	2.02	O(1)g-Pb(1)-O(1)j	× 3	119.4(1.0)
		O(1)g-Pb(1)-O(2)	× 3	122.3(7)
Pb(1)-O(1)	2.46(3) × 3	O(1)g-Pb(1)-O(2)j	× 3	81.7(7)
-O(1)g	3.14(3) × 3	O(1)g-Pb(1)-O(2)k	× 3	55.1(7)
-O(2)	2.83(2) × 3	O(2)-Pb(1)-O(2)j	× 3	68.1(7)
<Pb(1)-O>	2.81	<O-Pb(1)-O>		87.4
		O(2)-Pb(2)-O(2)j	× 6	76.5(8)
Pb(2)-O(2)	2.56(2) × 6	O(2)-Pb(2)-O(2)d	× 3	116.9(1.0)
-O(3)	3.21(2) × 6	O(2)-Pb(2)-O(2)l	× 3	93.8(1.0)
<Pb(2)-O>	2.94	O(2)-Pb(2)-O(3)	× 6	55.1(6)
		O(2)-Pb(2)-O(3)j	× 6	54.4(6)
O(1)a-Te-O(1)b	79.0(6)	O(2)-Pb(2)-O(3)k	× 6	115.4(6)
O(1)a-Te-O(2)	94.9(1.1)	O(2)-Pb(2)-O(3)d	× 6	68.6(6)
O(1)a-Te-O(3)	97.5(1.1)	O(2)-Pb(2)-O(3)m	× 6	142.5(6)
O(1)a-Te-O(3)c	78.1(1.0)	O(2)-Pb(2)-O(3)l	× 6	107.2(6)
O(1)b-Te-O(3)	71.2(9)	O(3)-Pb(2)-O(3)j	× 6	108.7(4)
O(1)b-Te-O(3)c	127.6(7)	O(3)-Pb(2)-O(3)d	× 3	53.0(8)
O(1)b-Te-O(3)d	99.8(7)	O(3)-Pb(2)-O(3)m	× 3	92.3(8)
O(2)-Te-O(3)	94.3(1.0)	<O-Pb(2)-O>		90.7
O(2)-Te-O(3)c	65.1(8)			
O(2)-Te-O(3)d	82.1(8)			
O(3)-Te-O(3)d	68.6(9)			
O(3)c-Te-O(3)d	113.0(9)			
<O-Te-O>	89.3			

Note: <M-φ> denotes the mean metal-ligand distance (Å). Equivalent positions: a = z + 3/4 - 1, y + 1/4, x̄ + 1/4; b = x̄, y + 1/2, z̄ + 1/2; c = z̄ + 1/4, y + 3/4 - 1, x + 1/4; d = ȳ + 3/4, x̄ + 3/4, z̄ + 3/4; e = x, y, z - 1; f = z, x, y - 1; g = y + 1/4, x̄ + 1/4, z + 3/4 - 1; h = z̄ + 1/4, y + 3/4 - 1, x + 1/4 - 1; i = z, x, y; j = x̄ + 1/4, z + 3/4 - 1, y + 1/4; k = y, z, x; l = z̄ + 3/4, ȳ + 3/4, x̄ + 3/4; m = x̄ + 3/4, z̄ + 3/4, ȳ + 3/4.

coordinated by at least four O atoms at distances of 1.87, 1.90, 1.92, and 2.71 Å. In accordance with Zemann (1968, 1971), Galy *et al.* (1975), and Effenberger *et al.* (1978), these can be described as forming a trigonal

TABLE 5. BOND-VALENCE\* ARRANGEMENT IN CHOLOALITE

	Te	Cu	Pb(1)	Pb(2)	Total
O(1)	1.21		0.36 × 3 ↓		1.82
	0.16		0.09 × 3 ↓		
O(2)	1.13	0.55 × 2 ↓	0.17 × 3 ↓	0.26 × 6 ↓	2.11
O(3)	1.07	0.66 × 2 ↓		0.07 × 6 ↓	2.16
	0.23				
	0.13				
Cl		0.26 × 3 →			0.78
Total	3.93	2.68	1.86	1.98	

\*Calculated from the curves of Brown (1981), as modified by Back (1990) for Te, and those of Bressé & O'Keeffe (1991) for bonds to Cl.

dipyramid, with a lone pair of electrons occupying one corner of the equatorial triangle. Brown (1974), however, assumed that the coordination environment of  $\text{Te}^{4+}$  (and  $\text{Sn}^{2+}$ ,  $\text{Sb}^{3+}$ ,  $\text{I}^{5+}$ , and  $\text{Xe}^{6+}$ ) is an octahedron distorted by a lengthening of some of the bonds on one side. Back (1990) showed that  $\text{Te}^{4+}$  can be coordinated by up to eight anions, and Rossell *et al.* (1992) demonstrated that the coordination polyhedra of the four  $\text{Te}^{4+}$  atoms in the

structure of  $\text{Bi}_2\text{Te}_4\text{O}_{11}$  can be described as distorted octahedra. In the crystal structure of choloalite, two additional O atoms, at distances of 2.95 and 3.05 Å, can be considered to form bonds with the atom at the *Te* position (contributing 0.16 and 0.13 valence units, *vu*, respectively). The resulting polyhedron is a distorted octahedron, with three weak bonds occurring opposite three strong bonds. As suggested by Brown (1974), the bond-valence sum of each *trans* pair is approximately equal. The environment corresponds to type "C" of Brown (1974), although the valence ratio suggests configuration "A" (with two strong, two intermediate, and two weak bonds). The mean Te–O distance is 2.40 Å, and the O–Te–O angles range from 65.1 to 127.6°, with a mean value of 89°. The variance of the octahedron angle is 354.14, the mean quadratic elongation of the octahedron (Robinson *et al.* 1971) is 1.2296, and the polyhedron volume is 14.47 Å<sup>3</sup>. The lone pair of electrons is most likely located on the side of the Te atom opposite the three closest O atoms, and within the volume defined by the Te atom and the three O atoms with the largest Te–O distances and O–Te–O angles. It is unlikely that the atom at the *Te* position forms a bond with the atom at the nearest Cl site, given the distance

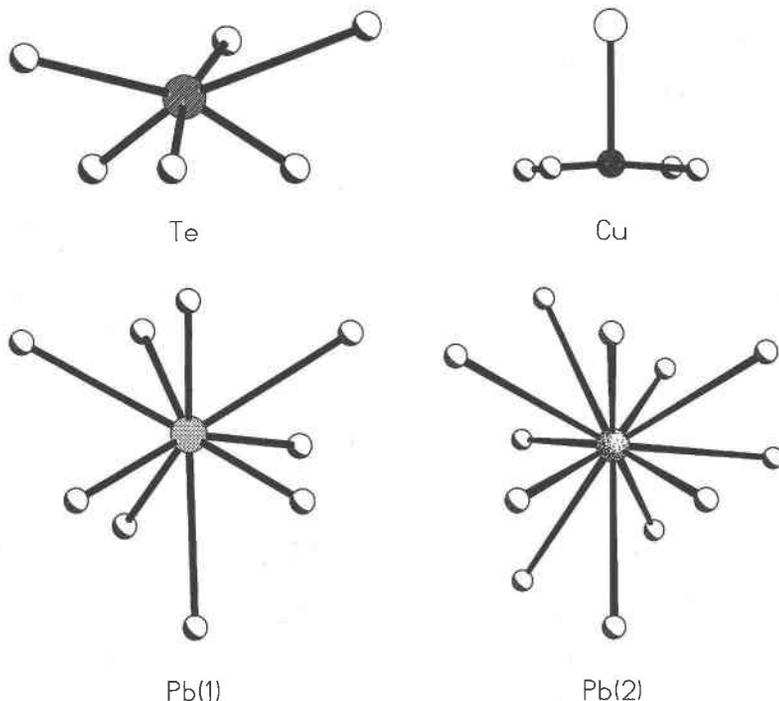


FIG. 1. Coordination polyhedra of cations in the structure of choloalite. O atoms are shown as shadowed spheres, the Cl atom as an open, larger sphere.

(3.701 Å), the possible bond-valence contribution (0.03 *vu*), and the presence of Cu atoms at a distance of 3.206 and 3.330 Å.

The atom at the *Cu* site, special position 12*d* (1/8, *x*, 1/4+*x*), is bonded to four oxygen atoms in approximate square-planar coordination (the oxygen atoms deviate from a common plane by  $\pm 0.02$  Å). The Cu–O distances are 1.86 and 1.92 Å (both  $\times 2$ , mean 1.89 Å) and the O–Cu–O angles are 86 and 94° (both  $\times 2$ , mean 90°). If the Cu site is assumed to be fully occupied by Cu<sup>2+</sup>, the resulting bond-valence sum is 2.26 *vu*. However, the electron-microprobe data suggest 92.7% Cu, 4.3% Sb, and 3.0% Zn at the *Cu* site (resulting in bond-valence sums of 2.33 and 2.34 *vu* for Sb<sup>3+</sup> and Sb<sup>5+</sup>, respectively). The structure refinement shows 93(4)% Cu and 7(4)% Sb at the *Cu* position (resulting in bond-valence sums of 2.40 for both Sb<sup>3+</sup> and Sb<sup>5+</sup>). Assuming no vacancies, the results show that the atom at the *Cu* site is overbonded by a minimum 0.26 *vu*. However, there is an additional site (labeled *Cl*) at a distance of 2.531 Å from the *Cu* position. The structure refinement shows that the *Cl* site is predominately occupied by Cl<sup>−</sup>; refinement of the site occupancy shows 92(12)% Cl at the *Cl* position, although the electron-microprobe data suggest only 0.64 Cl atoms per formula unit. There is no evidence for any other atom or molecule at the *Cl* position; as noted previously, the results of the infrared spectroscopy experiment were inconclusive as to the presence of OH or H<sub>2</sub>O. If the atom at the *Cu* position is considered to be bonded to one Cl atom in addition to four oxygen atoms, the resulting sphere of coordination is almost a square pyramid (actually a very distorted trigonal dipyramid), with a mean Cu– $\phi$  ( $\phi$ : unspecified anion) distance of 2.02 Å, a mean O–Cu– $\phi$  angle of 91.4°, and a polyhedron volume of 6.3 Å<sup>3</sup>.

It is likely that the Cl in choloalite serves to balance the excess positive charge introduced by Sb. Is the Sb at the *Cu* position trivalent or pentavalent? According to Shannon (1976), the ionic radii of Cu<sup>2+</sup> and Sb<sup>3+</sup> in fivefold coordination, and of Sb<sup>5+</sup> in sixfold coordination, are 0.65, 0.80, and 0.60 Å, respectively. This suggests that the Sb at the *Cu* position is pentavalent. In addition, the chemical formulae obtained from both the electron-microprobe and crystal-structure analyses (see below) are only (approximately) charge-balanced with pentavalent Sb.

It is entirely possible that if the *Cu* site was only occupied by Cu, the bond distances would be slightly longer, resulting in lower bond-valence sums. In this case, there would be no need for additional negative charge at the *Cl* position, and the true coordination would be square-planar. However, it is interesting to note that of the 94 Cu-oxysalt minerals listed in the compendium by Eby & Hawthorne (1993), only three show Cu in fourfold coordination, and 11 in fivefold coordination.

The atom at the *Pb(1)* site, special position 8*c* (*x*, *x*, *x*), is coordinated by nine O atoms, forming a triangulated trigonal prism. The Pb(1)–O distances are 2.46, 2.83,

and 3.14 Å (all  $\times 3$ ; mean 2.81 Å), and the O–Pb(1)–O angles range from 55.1 to 122.3° (mean 87.4°). The lengths of the polyhedron edges are 2.78, 3.07, 3.17, 3.18, 3.46, 3.74, and 3.92 Å (all  $\times 3$ ). The polyhedron volume is 40.6 Å<sup>3</sup>. The coordination polyhedron is somewhat distorted, suggesting the presence of a lone pair of electrons. The results of the crystal-structure refinement show that the *Pb(1)* site is completely occupied by Pb<sup>2+</sup>.

The atom at the *Pb(2)* site, special position 4*a* (3/8, 3/8, 3/8), is coordinated by twelve O atoms, forming a distorted icosahedron. The Pb(2)–O distances are 2.56 and 3.31 Å (both  $\times 6$ ; mean 2.94 Å), and the O–Pb(2)–O angles range from 53.0 to 142.5° (mean 90.7°). The lengths of the polyhedron edges are 2.95 and 4.77 Å (both  $\times 3$ ), and 2.76, 2.80, 3.17, and 3.37 Å (all  $\times 6$ ). The polyhedron volume is 57.9 Å<sup>3</sup>. The structure refinement shows 70(2)% Pb and 30(2)% Ca at the *Pb(2)* position, which is in good agreement with the electron-microprobe results (79% Pb and 21% Ca). Other minerals with twelve-coordinated Pb<sup>2+</sup> include osarizawaite (Giuseppetti & Tadini 1980), plumbojarosite (Szymański 1985) and senaite (Grey & Lloyd 1976). All show six equal short and six equal longer Pb–O distances, with mean values of 2.82 to 2.92 Å. Although the Pb(2)–O distances in choloalite show a larger range, the mean value is close to those for the other minerals.

It is difficult to describe a crystal structure as complicated as that of choloalite. We begin by assuming full occupancy of the *Cl* position and a square-pyramidal coordination sphere around the atom at the *Cu* site (the alternate description, of a structure with a vacant *Cl* site and Cu with square-planar coordination, is only slightly different). We may consider the polymerization of coordination polyhedra by simple rotation around an atom (generally a central cation) at a special position. The *Cl* site, at special position 4*b* (7/8, 7/8, 7/8), lies at the intersection of one axis of twofold and one axis of threefold rotation. The atom at this site forms bonds with atoms at three *Cu* positions (each of which is on an axis of twofold rotation). Because of this, each Cu $\phi_5$  square pyramid is attached to two others by corner-sharing of the atom or molecule at the *Cl* site, forming a “pinwheel” (Fig. 2a). In addition, each Cu $\phi_5$  polyhedron shares two *trans* O(2)–O(3) edges (length 2.57 Å) with two TeO<sub>6</sub> octahedra, and the other *trans* O(2)–O(3) edges (length 2.76 Å) with two Pb(2)O<sub>12</sub> polyhedra. The lengths of the unshared O(2)–Cl and O(3)–Cl edges are 3.26 and 3.20 Å, respectively. In addition, each Cu $\phi_5$  polyhedron is linked by corner-sharing to additional TeO<sub>6</sub> octahedra ( $\times 4$ ) and Pb(1)O<sub>9</sub> polyhedra ( $\times 2$ ).

The *Pb(1)* sites lie on axes of threefold rotation. Each Pb(1)O<sub>9</sub> polyhedron shares edges with three others, forming an additional “pinwheel” (Fig. 2b). The “pinwheels” polymerize to form a three-dimensional network (Fig. 3).

Like the *Cl* sites, the *Pb(2)* positions lie at intersections of one axis of twofold and one axis of threefold

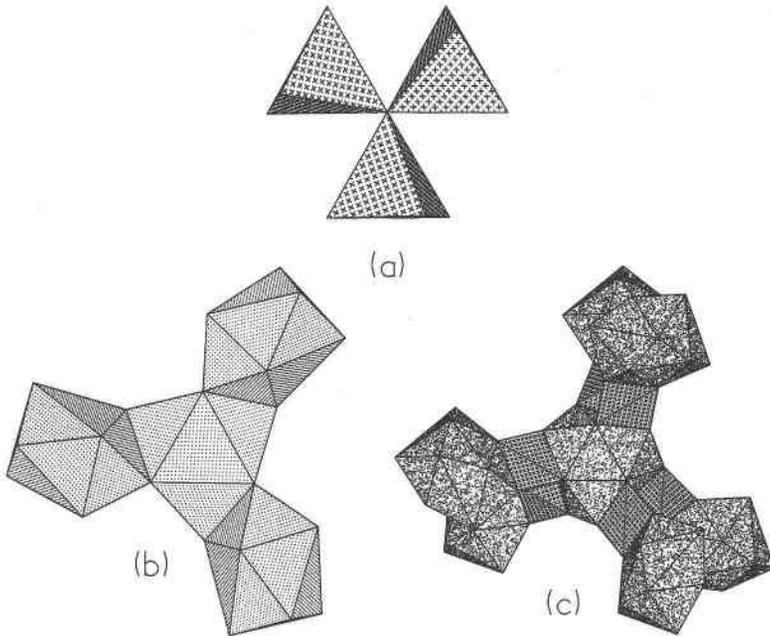


FIG. 2. "Pinwheels" in the crystal structure of choloalite: (a) three  $\text{Cu}\phi_5$  polyhedra; (b) four  $\text{Pb}(1)\text{O}_9$  polyhedra; (c) seven  $\text{Pb}(2)\text{O}_{12}$  polyhedra linked by six  $\text{Cu}\phi_5$  polyhedra.

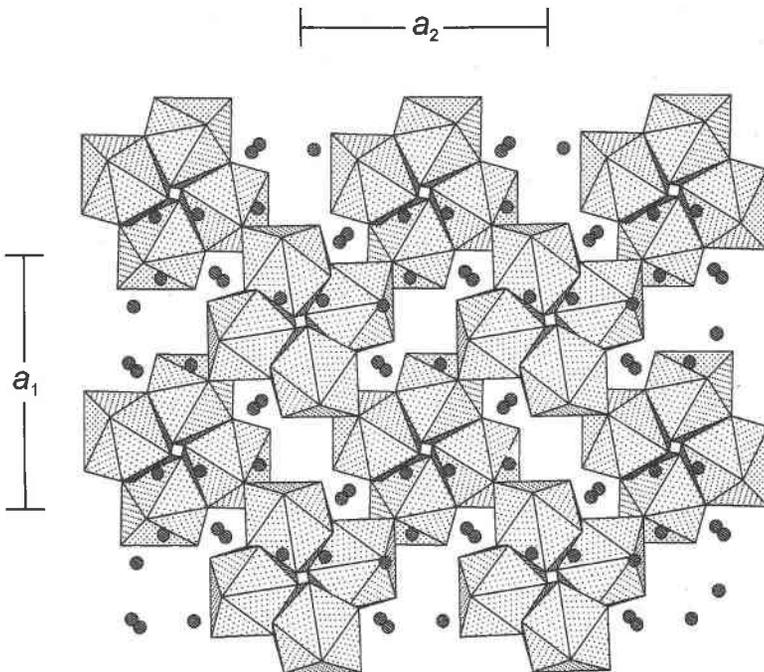


FIG. 3. Three-dimensional network of  $\text{Pb}(1)\text{O}_9$  polyhedra. The Te atoms are shown as spheres. The positions of the  $4_1$  axes are evident.

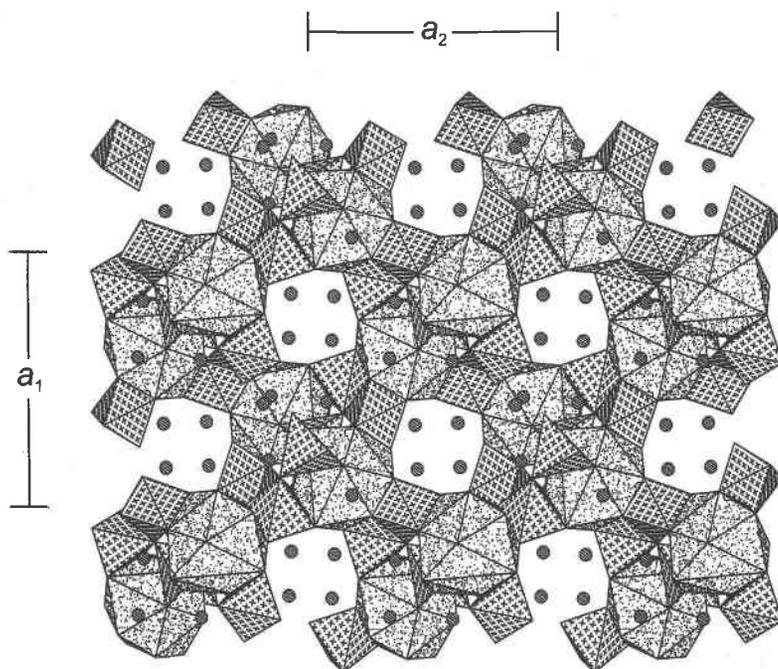


FIG. 4. Three-dimensional network of  $\text{Cu}\phi_5$  and  $\text{Pb}(2)\text{O}_{12}$  polyhedra. The Te atoms are shown as spheres.

rotation. Individual  $\text{Pb}(2)\text{O}_{12}$  polyhedra are not joined; however, each is linked by the shared  $\text{O}(2)\text{--O}(3)$  edges to six  $\text{Cu}\phi_5$  polyhedra. Each  $\text{Cu}\phi_5$  polyhedron is then joined through the *trans*  $\text{O}(2)\text{--O}(3)$  edge to an additional  $\text{Pb}(2)\text{O}_{12}$  polyhedron. The result is yet another "pin-wheel" (Fig. 2c). These polymerize to form an additional three-dimensional network (Fig. 4).

The two three-dimensional networks are linked by the two *trans*  $\text{O}(2)\text{--O}(2)\text{--O}(2)$  faces (edge length  $3.17 \text{ \AA}$ ,  $\times 3$ ) of each  $\text{Pb}(2)\text{O}_{12}$  icosahedron, which are shared with adjacent  $\text{Pb}(1)\text{O}_9$  polyhedra. The spaces are filled with  $\text{TeO}_6$  octahedra (note that the Te atom, alone among the cations in the choloalite structure, does not lie on an axis of rotation). The linkage of the  $\text{TeO}_6$  polyhedra with neighboring polyhedra is shown in Figure 5. Each  $\text{TeO}_6$  octahedron shares one triangular  $\text{O}(2)\text{--O}(3)\text{--O}(3)$  face with a  $\text{Pb}(2)\text{O}_{12}$  polyhedron; the lengths of the shared edges are  $2.80$ ,  $2.95$ , and  $3.37 \text{ \AA}$ . In addition, each  $\text{TeO}_6$  polyhedron shares one  $\text{O}(2)\text{--O}(3)$  edge ( $2.57 \text{ \AA}$ ) with an adjacent  $\text{Cu}\phi_5$  square pyramid, and one  $\text{O}(3)\text{--O}(3)$  ( $2.95 \text{ \AA}$ ) and two  $\text{O}(1)\text{--O}(3)$  edges ( $2.96 \times 2 \text{ \AA}$ ) with three different  $\text{TeO}_6$  octahedra. Furthermore, one  $\text{O}(1)\text{--O}(1)$  edge ( $3.18 \text{ \AA}$ ) and one  $\text{O}(1)\text{--O}(2)$  edge ( $2.78 \text{ \AA}$ ) are shared with adjacent  $\text{Pb}(1)\text{O}_9$  polyhedra. The three unshared edges have lengths of  $4.60$ ,  $4.81$ , and  $5.08 \text{ \AA}$ . Finally, each  $\text{TeO}_6$  polyhedron is linked by corner-

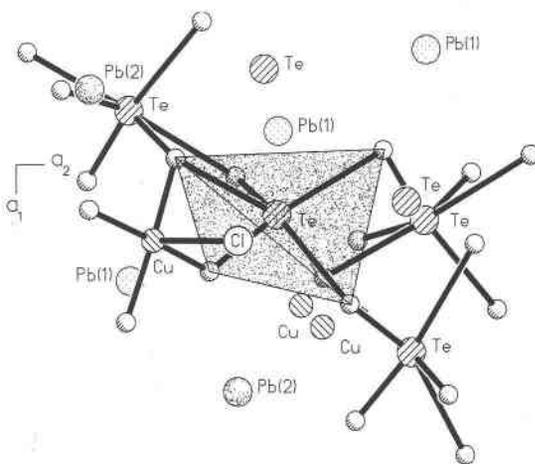


FIG. 5. Linkage of adjacent polyhedra to the  $\text{TeO}_6$  octahedron. Bonds are shown for the central  $\text{TeO}_6$  octahedron and those adjacent polyhedra linked to it by shared edges. Only the central cation is shown for those polyhedra that link by shared corners. The O atoms are shown as shadowed spheres with no labels.

sharing to additional  $\text{Cu}\phi_5$  ( $\times 2$ ),  $\text{TeO}_6$  ( $\times 2$ ),  $\text{Pb}(1)\text{O}_9$ , and  $\text{Pb}(2)\text{O}_{12}$  polyhedra.

#### DISCUSSION

The empirical formula of choloalite, based on the electron-microprobe results, and calculated on the basis of 12 cations per formula unit, is  $(\text{Cu}_{2.81}\text{Sb}_{0.13}\text{Zn}_{0.09})_{\Sigma 3.03}(\text{Pb}_{2.65}\text{Ca}_{0.17})_{\Sigma 2.82}\text{Te}_{6.15}\text{O}_{18.03}\text{Cl}_{0.64}$ . This is similar to the formula based on the structure analysis, which is  $(\text{Cu}_{2.79}\text{Sb}_{0.21})_{\Sigma 3.00}(\text{Pb}_{2.70}\text{Ca}_{0.30})_{\Sigma 3.00}\text{Te}_{6.00}\text{O}_{18.00}\text{Cl}_{0.92}$ . The empirical formula calculated from the chemical data in Williams (1981) (on the basis of 12 cations per formula unit) is  $\text{Cu}_{2.75}\text{Pb}_{2.9}\text{Te}_{6.31}\text{O}_{18.31} \cdot (\text{H}_2\text{O})_{3.75}$ . Our results show a Cl position that is approximately 64 to 92% occupied by Cl, which presumably is there to balance the excess positive charge introduced by  $\text{Sb}^{3+}$  in the Cu site, and would not be present but for the Sb. Since there is no evidence to suggest that choloalite is normally a hydrous mineral, the ideal formula is likely  $\text{CuPbTe}^{4+}_2\text{O}_6$ , as suggested by Powell *et al.* (1994).

Choloalite is one of five cubic Te-oxysalt minerals; the others are cliffordite, mc Alpineite, winstanleyite, and yafsoanite. Only the structures of cliffordite and yafsoanite are known. Brandstätter (1981) showed that there are three distinct cation sites in the structure of cliffordite. The atom at the Te position, which is completely occupied by  $\text{Te}^{4+}$ , is coordinated by five (Brandstätter 1981) or more (Back 1990) O atoms. There are also two U positions in the crystal structure of cliffordite; each is coordinated by eight O atoms forming hexagonal bipyramids. The crystal structure of yafsoanite was most recently studied by Jarosch & Zemmann (1989), who showed that it is a garnet-type oxide with Ca,  $\text{Te}^{6+}$ , and Zn atoms coordinated by eight, six and four O atoms, respectively.

As noted previously, Williams (1981) derived the following paragenetic sequence from textural evidence: rodalquilarite  $\rightarrow$  choloalite  $\rightarrow$  emmonsite  $\rightarrow$  cerussite. The first three are all tellurites, suggesting that the oxidation potentials at the type locality were not high enough to produce  $\text{Te}^{6+}$ . The formula and crystal structure of choloalite are very different from those of the other tellurites. However, the crystal structures of rodalquilarite and emmonsite are similar; both contain  $\text{Fe}^{3+}$  (suggesting some degree of oxidation) in octahedral coordination. In rodalquilarite, the octahedra share edges to form chains parallel to the *b* axis. The chains join with Te polyhedra to form planes approximately parallel to (100), and these are held together by Te-Cl-Te and hydrogen bonds. In emmonsite, isolated pairs of  $\text{Fe}^{3+}\phi_6$  octahedra share edges, and are in turn connected into a three-dimensional array by Te polyhedra. Comparison of the structures with the paragenetic sequence of Williams (1981) shows a depolymerization of  $\text{Fe}^{3+}\phi_6$  octahedra with progressive crystallization.

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#### REFERENCES

- BACK, M.E. (1990): *A Study of Tellurite Minerals: their Physical and Chemical Data Compatibility, and Structural Crystallography*. M.Sc. thesis, Univ. Toronto, Toronto, Ontario.
- BRANDSTÄTTER, F. (1981): Non-stoichiometric, hydrothermally synthesized cliffordite. *Tschermaks Mineral. Petrogr. Mitt.* **29**, 1-8.
- BRESE, N.E. & O'KEEFFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.
- BROWN, I.D. (1974): Bond valence as an aid to understanding the stereochemistry of O and F complexes of Sn(II), Sb(III), Te(IV), I(V) and Xe(VI). *J. Solid State Chem.* **11**, 214-233.
- \_\_\_\_\_ (1981): The bond-valence method: an empirical approach to chemical structure and bonding. *In Structure and Bonding in Crystals II* (M. O'Keeffe & A. Navrotsky, eds.). Academic Press, New York, N.Y. (1-30).
- CROMER, D.T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X rays. *J. Chem. Phys.* **53**, 1891-1898.
- \_\_\_\_\_ & MANN, B.J. (1968): X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallogr.* **A24**, 321-324.
- EBY, R.K. & HAWTHORNE, F.C. (1993): Structural relations in copper oxysalt minerals. I. Structural hierarchy. *Acta Crystallogr.* **B49**, 28-56.
- EFFENBERGER, H., ZEMANN, J. & MAYER, H. (1978): Carl-friesite: crystal structure, revision of chemical formula, and synthesis. *Am. Mineral.* **63**, 847-852.
- GALY, J., MEUNIER, G., ANDERSSON, S. & ÅSTRÖM, A. (1975): Stéréochimie des éléments comportant des paires non liées: Ge (II), As (III), Se (IV), Br (V), Sn (II), Sb (III), Te (IV), I (V), Xe (VI), Tl (I), Pb (II), et Bi (III) (oxydes, fluorures et oxyfluorures). *J. Solid State Chem.* **13**, 142-159.
- GELATO, L.M. & PARTHÉ, E. (1987): STRUCTURE TIDY - a computer program to standardize crystal structure data. *J. Appl. Crystallogr.* **20**, 139-143.

- GIUSEPPE, G. & TADINI, C. (1980): The crystal structure of osarizawaite. *Neues Jahrb. Mineral., Monatsh.*, 401-407.
- GREY, I.E. & LLOYD, D.J. (1976): The crystal structure of senaite. *Acta Crystallogr.* **B32**, 1509-1513.
- JAROSCH, D. & ZEMANN, J. (1989): Yafsoanite: a garnet type calcium – tellurium (VI) – zinc oxide. *Mineral. Petrol.* **40**, 111-116.
- LAM, A.E., GROAT, L.A. & ERCIT, T.S. (1998): The crystal structure of dugganite,  $Pb_3Zn_3Te^{6+}As_2O_{14}$ . *Can. Mineral.* **36**, 823-830.
- LE PAGE, Y. (1987): Computer derivation of the symmetry elements implied in a structure description. *J. Appl. Crystallogr.* **20**, 264-269.
- NORTH, A.C.T., PHILLIPS, D.C. & MATHEWS, F.S. (1968): A semi-empirical method of absorption correction. *Acta Crystallogr.* **A24**, 351-359.
- POWELL, D.W., THOMAS, R.G., WILLIAMS, P.A., BIRCH, W.D. & PLIMER, I.R. (1994): Choloalite: synthesis and revised chemical formula. *Mineral. Mag.* **58**, 505-508.
- ROBERTS, A.C., ERCIT, T.S., CRIDDLE, A.J., JONES, G.C., WILLIAMS, R.S., CURETON, F.F., II & JENSEN, M.C. (1994): Mcalpineite,  $Cu_3TeO_6 \cdot H_2O$ , a new mineral from the McAlpine mine, Tuolumne County, California, and from the Centennial Eureka mine, Juab County, Utah. *Mineral. Mag.* **58**, 417-424.
- ROBINSON, K., GIBBS, G.V. & RIBBE, P.H. (1971): Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. *Science* **172**, 567-570.
- ROSSELL, H.J., LEBLANC, M., FÈREY, G., BEVAN, D.J.M., SIMPSON, D.J. & TAYLOR, M.R. (1992): On the crystal structure of  $Bi_2Te_4O_{11}$ . *Aust. J. Chem.* **45**, 1415-1425.
- SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751-767.
- SPIRIDONOV, E.M. (1980): Balyakinite,  $CuTeO_3$ , a new mineral from the zone of oxidation. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **253**, 200-202.
- SZYMAŃSKI, J.T. (1985): The crystal structure of plumbojarosite  $Pb[Fe_3(SO_4)_2(OH)_6]_2$ . *Can. Mineral.* **23**, 659-668.
- WANG, X. & LIEBAU, F. (1996): Influence of lone-pair electrons of cations on bond-valence parameters. *Z. Kristallogr.* **211**, 437-439.
- WILLIAMS, S.A. (1981): Choloalite,  $CuPb(TeO_3)_2 \cdot H_2O$ , a new mineral. *Mineral. Mag.* **44**, 55-57.
- ZEMANN, J. (1968): The crystal chemistry of the tellurium oxide and tellurium oxosalt minerals. *Z. Kristallogr.* **127**, 319-326.
- \_\_\_\_\_ (1971): Zur Stereochemie des Te(IV) gegenüber Sauerstoff. *Monatsh. Chem.* **102**, 1209-1216.

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