

NEW Cu²⁺ COORDINATION POLYHEDRA IN THE CRYSTAL STRUCTURE OF BURNSITE, KCdCu₇O₂(SeO₃)₂Cl₉

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ABSTRACT

The crystal structure of burnsite, KCdCu₇O₂(SeO₃)₂Cl₉, a new mineral species from fumaroles of the Tolbachik volcano, Kamchatka, Russia, has been solved by direct methods and refined on the basis of F^2 for all unique data collected with monochromatic MoK α X-radiation and a CCD (charge-coupled device) detector to an agreement factor ($R1$) of 1.9%, calculated using the 460 unique observed reflections ($|F_o| = 4\sigma_F$). The mineral is hexagonal, space group $P6_3/mmc$, a 8.7805(8), c 15.521(2) Å, V 1036.3(2) Å³, $Z = 2$. There are two non-equivalent Cu²⁺ cations in the structure of burnsite. The Cu(1) cation is coordinated by three atoms of O and three of Cl; this is the first example of this type of mixed-ligand Cu²⁺ ϕ_6 (ϕ : O²⁻, Cl⁻) octahedron in a mineral. The octahedron is (2 + 4)-distorted owing to the Jahn–Teller effect, in contrast to the vast majority of Cu²⁺ oxysalt minerals that contain (4 + 2)- distorted Cu²⁺ octahedra. The Cu(2) cation is coordinated by two O and three Cl anions arranged at the vertices of a trigonal bipyramid; this is the first occurrence of a mixed-ligand Cu²⁺O₂Cl₃ trigonal bipyramid in a mineral. The single symmetrically independent Cd²⁺ cation is coordinated by six Cl anions located at the vertices of a regular octahedron. The structure contains one symmetrically independent K cation that is coordinated by six Cl anions in a trigonal prismatic arrangement. There is one unique Se⁴⁺ cation that is strongly bonded to three O anions on one side of the cation, owing to the presence of a s^2 lone-electron pair. The structure is described both in terms of cation-centered polyhedra and oxocentered OCu₄ tetrahedra. The structure of burnsite is closely related to the structures of other natural copper oxide chloride selenites discovered in the Tolbachik fumaroles (chloromenite, georgbokiite, ilinskite).

Keywords: burnsite, crystal structure, copper selenites, oxocentered tetrahedra.

SOMMAIRE

Nous avons résolu la structure cristalline de la burnsite, KCdCu₇O₂(SeO₃)₂Cl₉, nouvelle espèce minérale provenant des fumaroles du volcan Tolbachik, péninsule de Kamchatka, en Russie, par méthodes directes, et nous l'avons affiné en utilisant les facteurs F^2 des réflexions uniques prélevées avec rayonnement monochromatique MoK α et un détecteur CCD à couplage de charges, jusqu'à un facteur de concordance ($R1$) de 1.9%, calculé pour les 460 réflexions uniques observées ($|F_o| = 4\sigma_F$). Il s'agit d'un minéral hexagonal, groupe spatial $P6_3/mmc$, a 8.7805(8), c 15.521(2) Å, V 1036.3(2) Å³, $Z = 2$. La structure contient deux cations non équivalents de Cu²⁺. Le cation Cu(1) est coordonné à trois atomes de O et trois de Cl; c'est en fait le premier exemple de ce type de ligand mixte Cu²⁺ ϕ_6 (ϕ : O²⁻, Cl⁻) octaédrique dans un minéral. L'octaèdre montre une distortion (2 + 4) due à l'effet Jahn–Teller, contrairement à la grande majorité d'oxysels de Cu²⁺, minéraux qui contiennent des octaèdres à Cu²⁺ montrant la distortion (4 + 2). Le cation Cu(2) est coordonné à deux atomes de O et trois anions de Cl aux coins d'une bipyramide trigonale. C'est le premier exemple d'un ligand mixte Cu²⁺O₂Cl₃ en bipyramide trigonale dans un minéral. Le cation unique Cd²⁺ est symétriquement indépendant et coordonné à six anions de Cl situés aux coins d'un octaèdre régulier. La structure contient un cation K symétriquement indépendant, coordonné par six anions Cl dans un agencement prismatique trigonal. Il y a un cation Se⁴⁺ unique avec fortes liaisons à trois atomes O d'un côté du cation, à cause de la présence d'une paire isolée d'électrons s^2 . Nous décrivons la structure à la fois en termes de polyèdres entourant un cation et de tétraèdres OCu₄ ayant un atome d'oxygène au centre. La structure de la burnsite montre des ressemblances étroites avec la structure d'autres sélénites chlorurés naturels de cuivre découverts dans les fumaroles à Tolbachik (chloromérite, georgbokiite, ilinskite).

(Traduit par la Rédaction)

Mots-clés: burnsite, structure cristalline, sélénites de cuivre, tétraèdres oxo-centrés.

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INTRODUCTION

Burnsite, $\text{KCdCu}_7\text{O}_2(\text{SeO}_3)_2\text{Cl}_9$, is a new potassium cadmium copper oxide chloride selenite mineral species that was recently described by Krivovichev *et al.* (2002) from the fumaroles of the Tolbachik volcano, Kamchatka, Russia. It forms aggregates of dark red transparent isometric grains up to 0.1 mm in maximum dimension. The crystal structure, which provides the first mineral examples of two new Cu^{2+} coordination polyhedra, is reported herein.

EXPERIMENTAL

X-ray diffraction

A single crystal of burnsite was selected by optical examination and mounted on a Bruker PLATFORM three-circle goniometer equipped with a 1K SMART CCD (charge-coupled device) detector and a crystal-to-detector distance of 5 cm. More than a hemisphere of three-dimensional intensity data was collected using monochromatic $\text{MoK}\alpha$ X-radiation and frame widths of 0.3° in ω . The unit-cell dimensions (Table 1) were refined from 2697 reflections using least-squares techniques. The data were integrated and corrected for Lorentz, polarization and background effects using the

Bruker program SAINT. A semi-empirical correction for absorption was done using 2003 intense reflections with the crystal modeled as an ellipsoid; the R_{int} was lowered from 8.36 to 3.97%. Additional information pertinent to the data collection is given in Table 1.

Structure solution and refinement

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from International Tables for X-Ray Crystallography, Vol. IV (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the structure. It was solved by direct methods and refined on the basis of F^2 for all unique data. The final refinement included all atomic positional parameters not restricted by symmetry, with an allowance for anisotropic displacement of all atoms, and a weighting scheme of the structure factors. The refinement converged to an agreement index ($R1$) of 1.9%, calculated for the 460 unique observed reflections ($F_o > 4\sigma_F$). Final atomic parameters and selected interatomic distances are presented in Tables 2 and 3, respectively. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

DESCRIPTION OF THE CATION POLYHEDRA

The coordination environments of the various cations in the structure of burnsite are illustrated in Figure 1. The coordination polyhedra about the two symmetrically distinct Cu^{2+} cations are most unusual. The Cu(1) site is coordinated by three O and three Cl anions arranged at the vertices of a distorted octahedron. Burns & Hawthorne (1995b) examined the geometries of mixed-ligand $\text{Cu}^{2+}\phi_6$ (ϕ : O^{2-} , OH^- , H_2O , Cl^-) octahedra, with an emphasis on the stereochemical details of observed octahedra and prediction of the polyhedron geometries using Hartree-Fock calculations. The Cu(1) ϕ_6 octahedron in burnsite is the first example in a mineral of a mixed-ligand $\text{Cu}^{2+}\phi_6$ octahedron that con-

TABLE 1. CRYSTALLOGRAPHIC DATA FOR BURNSITE

a (Å)	8.7805(8)	c (Å)	15.521(2)
V (Å ³)	1036.3(2)	Space group	$P6_3/mmc$
F_{000}	1110		
Crystal size (mm)	$0.09 \times 0.08 \times 0.04$	Radiation	$\text{MoK}\alpha$
Total reflections	6211	Unique reflections	532
Unique $F_o \geq 4\sigma_F$	460		
$R1$	0.019	$wR2$	0.046
S	0.99		
Formula	$\text{KCdCu}_7\text{O}_2(\text{SeO}_3)_2\text{Cl}_9$		
Z	2	μ (cm ⁻¹)	129.4
D_{calc} (g/cm ³)	3.85		
$R1 = \sum (F_o - F_c) / \sum F_o \times 100$			
$wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$			
$w = 1 / [\sigma^2(F_o^2) + (0.0314 \times P)^2]$, $P = [\max(F_o, 0) + 2 \times F_c^2] / 3$			
$S = [\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$, for 532 observations and 36 parameters			

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR BURNSITE

	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cd	0	0	0	0.0205(2)	0.0212(2)	0.0212(2)	0.0192(3)	0	0	0.0106(1)
Se	$-\frac{2}{3}$	$-\frac{1}{3}$	0.09730(4)	0.0131(2)	0.0147(2)	0.0147(2)	0.0099(3)	0	0	0.0073(1)
Cu(1)	-0.45264(3)	-0.54736(3)	0.09057(3)	0.0157(2)	0.0200(2)	0.0200(2)	0.0137(2)	0.0013(1)	-0.0013(1)	0.0150(2)
Cu(2)	$-\frac{1}{2}$	$-\frac{2}{3}$	$\frac{1}{4}$	0.0134(2)	0.0169(3)	0.0169(3)	0.0063(5)	0	0	0.0085(2)
K	0	0	$\frac{1}{4}$	0.0609(9)	0.080(1)	0.080(1)	0.023(1)	0	0	0.0398(7)
Cl(1)	-0.13697(8)	-0.2739(1)	0.10178(7)	0.0402(3)	0.0571(6)	0.0221(5)	0.0299(6)	0.0041(5)	0.0020(2)	0.0110(3)
Cl(2)	-0.4945(1)	-0.5055(1)	$\frac{1}{4}$	0.0352(4)	0.0433(7)	0.0433(7)	0.0370(8)	0	0	0.0350(8)
O(1)	$-\frac{1}{2}$	$-\frac{2}{3}$	0.1267(2)	0.0112(8)	0.012(1)	0.012(1)	0.010(2)	0	0	0.0058(6)
O(2)	-0.5696(2)	-0.1392(3)	0.0447(2)	0.0210(6)	0.026(1)	0.011(1)	0.021(1)	-0.001(1)	-0.0005(5)	0.0053(6)

$$* U_{eq} = (1/3) \sum U_{ij} a_i^* a_j^* a_i a_j$$

tains three Cl anions; such an octahedron occurs in the synthetic compound $\text{Cu}(\text{OH})\text{Cl}$ (Effenberger 1981). Examples of $\text{Cu}\phi_6$ octahedra with one, two and four Cl are listed in Burns & Hawthorne (1995b).

The distribution of bond lengths in the $\text{Cu}(1)\phi_6$ octahedron is worthy of comment. The expected $\text{Cu}^{2+}\text{-O}$

and $\text{Cu}^{2+}\text{-Cl}$ bond lengths 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)]. However, as noted by Burns & Hawthorne (1995b), mixed-ligand $\text{Cu}^{2+}\phi_6$ octahedra invariably involve bond-length distortion owing to the Jahn-Teller effect (Jahn & Teller 1937). Although a holosymmetric coordination about the Cu^{2+} cation is impossible because the ligands are mixed, a pseudo-holosymmetric octahedral geometry would involve a near-degenerate electronic state, and either an elongation [(4 + 2) distortion] or a compression [(2 + 4) distortion] of the ligand geometry will likely occur, removing the near-degenerate electronic state and resulting in a net stabilization of the octahedron. The $\text{Cu}(1)\phi_6$ octahedron involves two compressed $\text{Cu}^{2+}\text{-O}$ bond lengths of 1.899(1) and 1.916(3) Å, with the corresponding ligands in a *trans* arrangement. There is also one $\text{Cu}^{2+}\text{-O}$ bond-length of 2.126(3) Å, which is longer than the expected distance for an undistorted octahedron. The three $\text{Cu}(1)\text{-Cl}$ bond lengths range from 2.5554(6) to 2.612(1) Å, and are thus longer than the expected distance for an undistorted octahedron. The four elongate $\text{Cu}^{2+}\text{-}\phi$ bonds extend to ligands in the equatorial posi-

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

$\text{Cd-Cl}(1, \text{a,b,e,d,e})$	2.614(1) 6x	$\text{K-Cl}(1, \text{i,d,k,l,e})$	3.104(1) 6x
$\text{Se-O}(2), \text{f,g}$	1.687(3) 3x	$\text{O}(1)\text{-Cu}(1), \text{h,j}$	1.899(1) 3x
$\text{Cu}(1)\text{-O}(1)$	1.899(1)	$\text{O}(1)\text{-Cu}(2)$	1.914(4)
$\text{Cu}(1)\text{-O}(2)\text{g}$	1.916(3)	$\langle \text{O}(1)\text{-Cu} \rangle$	1.90
$\text{Cu}(1)\text{-O}(2)\text{e}$	2.126(3)	$\text{Cu}(1)\text{-Cu}(1), \text{h,j}$	3.1426(8) 2x
$\text{Cu}(1)\text{-Cl}(2)$	2.5554(6)	$\text{Cu}(1)\text{h-Cu}(1)\text{j}$	3.1426(8)
$\text{Cu}(1)\text{-Cl}(1), \text{h}$	2.612(1) 2x	$\text{Cu}(2)\text{-Cu}(1), \text{h,j}$	3.0685(5) 3x
$\text{Cu}(2)\text{-O}(1), \text{i}$	1.914(4) 2x	$\langle \text{Cu-Cu} \rangle$	3.106
$\text{Cu}(2)\text{-Cl}(2), \text{h,j}$	2.452(2) 3x		

a = $-y+1, x+y, z$; b = $-x-y, -x-1, z$; c = $-y-1, x, -z$; d = $x, y, -z+1/2$; e = $-y-1, x+y+1, -z+1/2$; f = $-y-1, x+y-1, z$; g = $-y, x+y, z$; h = $-x-1, -y-1, -z$; i = $-x(y-1), x-1, z$; j = $-y, x+y, z$; k = $-x+y, x-1, -z+1/2$; l = $-x, y, -z$

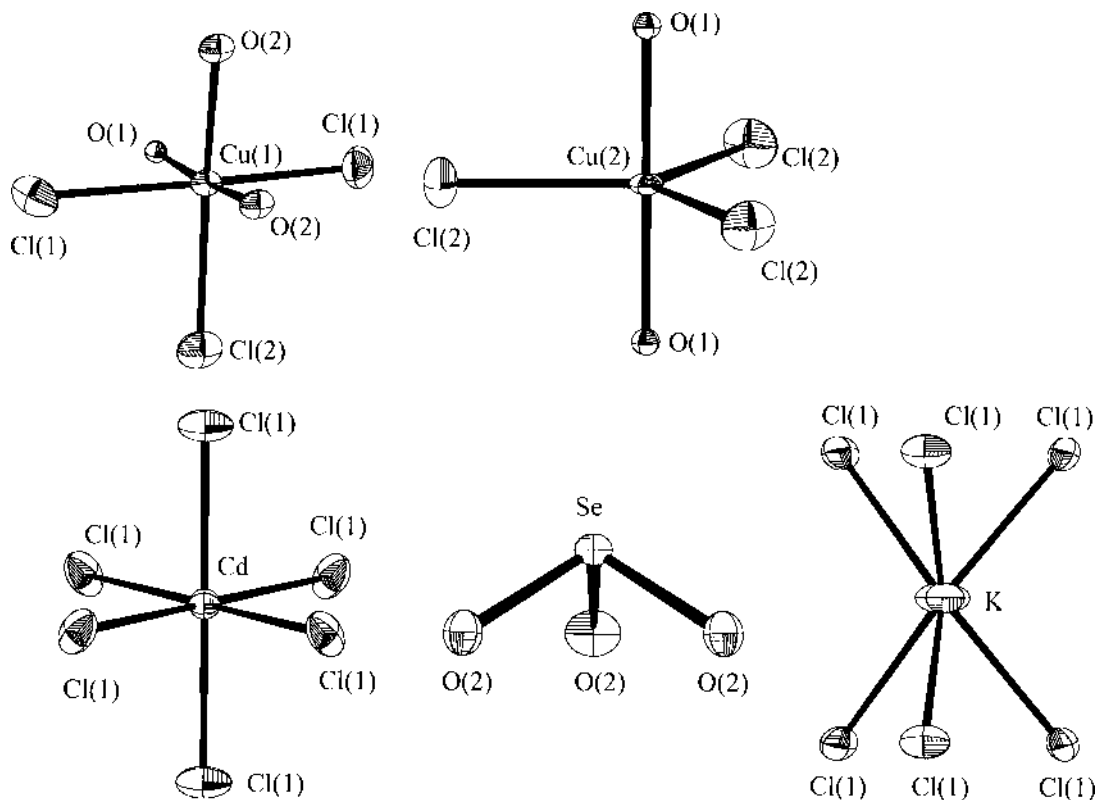


FIG. 1. Cation coordination polyhedra in the structure of burnsite.

tions of the octahedron, with the compressed bonds extending to the two apical ligands of the octahedron. The $\text{Cu}(1)\phi_6$ octahedron may therefore be described as (2 + 4)-distorted, which is extremely unusual in Cu^{2+} oxysalt minerals (Burns & Hawthorne 1996).

Burns & Hawthorne (1996) proposed that some Cu^{2+} octahedra in minerals may involve a dynamic Jahn–Teller distortion, in which case the structure determined by X-ray diffraction reveals coordination polyhedra with time-averaged geometries. Given the rarity of (2 + 4)-distorted Cu^{2+} octahedra in minerals, is it possible that the $\text{Cu}(1)\phi_6$ octahedron in burnsite involves a dynamic distortion? If this is the case, the dynamic interchange of elongation directions of (4 + 2)-distorted octahedra may result in an apparent (2 + 4)-distorted octahedron. Dynamic Jahn–Teller distortion of an octahedron involves movement of the ligands approximately parallel to the bond lengths, and thus should be reflected by anisotropic displacement ellipsoids that are elongate (sub)parallel to the bond direction. Inspection of the displacement ellipsoids for the ligands of the $\text{Cu}(1)$ octahedron (Fig. 1) shows that they are somewhat elongate (sub)perpendicular to the bond direction, which is inconsistent with a dynamic distortion of the octahedron. The $\text{Cu}(1)\phi_6$ octahedron thus appears to be a persuasive example of a (2 + 4)-distorted octahedron.

The $\text{Cu}(2)$ cation is coordinated by five ligands in a symmetric trigonal bipyramidal arrangement. The coordination polyhedron contains two O anions located in the apical positions, and three of Cl in the equatorial positions. Although Cu^{2+} occurs in trigonal prismatic coordination in several minerals (Burns & Hawthorne 1995a), burnsite is the first mineral to contain a mixed-ligand $\text{Cu}^{2+}\text{O}_2\text{Cl}_3$ trigonal bipyramid.

There is a single symmetrically distinct Cd^{2+} cation that is coordinated by six Cl(1) anions arranged at the

vertices of an octahedron. The K cation is coordinated by six Cl(1) anions in a trigonal prismatic arrangement. The structure contains one symmetrically distinct Se^{4+} cation, which is coordinated by three atoms of O that are arranged at the vertices of a trigonal pyramid. Note that all of the O atoms are located on the same side of the Se^{4+} cation, owing to the presence of a s^2 lone-electron pair on the other side of the cation.

DESCRIPTION OF THE STRUCTURE

The structure of burnsite is complex in that it involves five different types of cation coordination polyhedra. Here we provide two alternative descriptions of the structure, one based upon cation-centered polyhedra, and the other involving anion-centered tetrahedra. We consider each of these approaches to be of merit; both emphasize important structural features and facilitate comparison with related structures.

Description of the structure using cation-centered polyhedra

The structure of burnsite is shown projected along [001] in Figure 2a, and onto (100) in Figure 2b, with cation polyhedra shown in each case. From these projections, it is apparent that burnsite possesses a complex framework structure. Description of the structure is facilitated by considering first the $\text{Cu}(1)\phi_6$ octahedra. As illustrated in Figure 3a, $\text{Cu}(1)\phi_6$ octahedra occur as trimers of octahedra formed by the sharing of edges, with all three octahedra sharing the O(1) vertex. Each trimer is linked to three identical trimers by the sharing of O(2)–O(2) octahedron edges, resulting in layers of octahedra that are parallel to (001) that involve linkages only by the sharing of octahedron edges. The

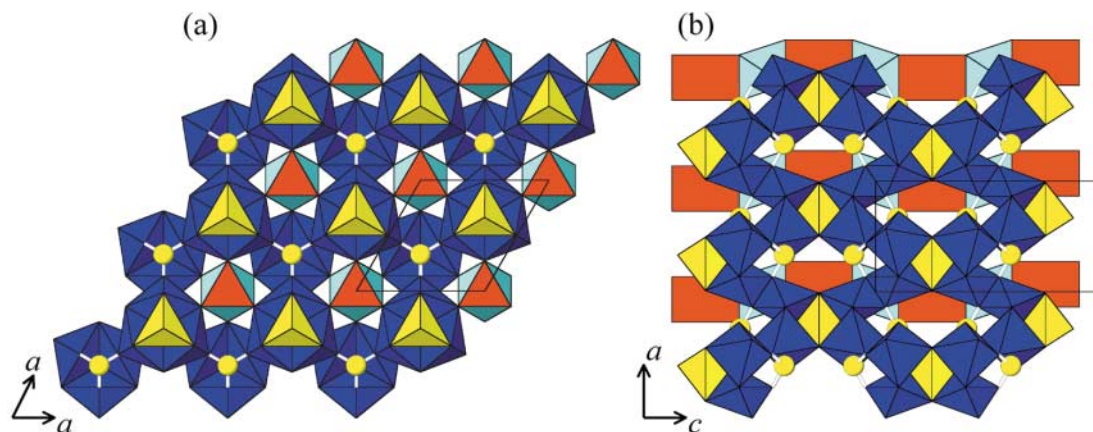


FIG. 2. Polyhedral representations of cation-centered polyhedra in the structure of burnsite. Legend: $\text{Cu}(1)\phi_6$ octahedra: dark blue, $\text{Cu}(2)\text{O}_2\text{Cl}_3$ triangular bipyramids: yellow, CdCl_6 octahedra: light blue, KCl_6 trigonal prisms: red, and Se atoms: yellow balls.

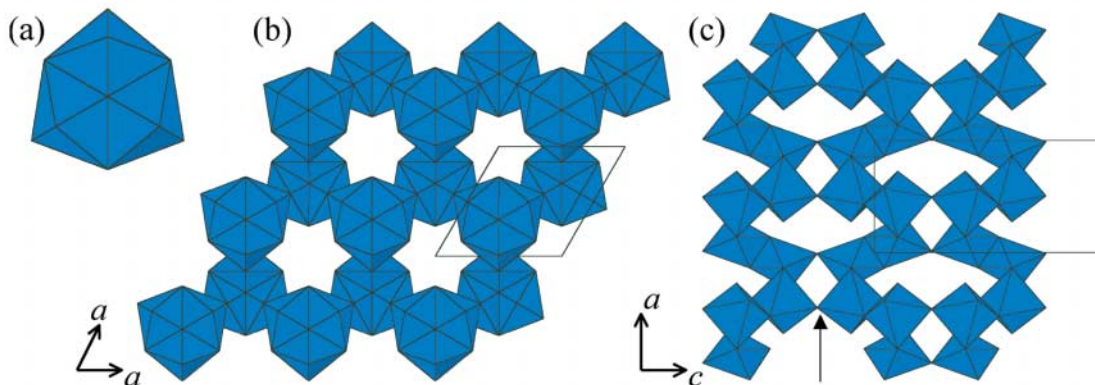


FIG. 3. The framework of $\text{Cu}(1)\phi_6$ octahedra in the structure of burnsite. (a) The trimer of edge-sharing $\text{Cu}(1)\phi_6$ octahedra, (b) the layer of edge-sharing octahedra parallel to (001), (c) linkage of layers of edge-sharing octahedra to form a framework. The $\text{Cl}(2)$ vertex, which is shared between adjacent layers, is indicated by the arrow. The unit cell is outlined in each case.

layers of $\text{Cu}(1)\phi_6$ octahedra are stacked along [001], and are connected by sharing the $\text{Cl}(2)$ vertex (shown by an arrow in Fig. 3c), resulting in a framework of $\text{Cu}(1)\phi_6$ octahedra that share vertices and edges.

The $\text{Cu}(2)\text{O}_2\text{Cl}_3$ trigonal bipyramid is located between two translationally equivalent trimers of $\text{Cu}(1)\phi_6$ octahedra, which belong to adjacent layers of edge-sharing $\text{Cu}(1)\phi_6$ octahedra (Figs. 2a, b). The $\text{Cl}(2)$ vertices shared between adjacent layers of $\text{Cu}(1)\phi_6$ octahedra constitute the equatorial ligands of the trigonal bipyramid, with the apical ligands corresponding to $\text{O}(1)$, which are shared between the three $\text{Cu}(1)\phi_6$ octahedra of each trimer. The SeO_3 trigonal pyramids are linked to the trimers of $\text{Cu}(1)\phi_6$ octahedra by sharing the $\text{O}(2)$ vertices, but on the side opposite the $\text{Cu}(2)\text{O}_2\text{Cl}_3$ trigonal bipyramid. The SeO_3 trigonal pyramid is located toward the center of individual layers of $\text{Cu}(1)\phi_6$ octahedra (Fig. 2b).

The KCl_6 trigonal prisms and CdCl_6 octahedra are linked to form columns that are parallel to [001] by the sharing of triangular faces (Fig. 2b). The columns extend through the framework of $\text{Cu}(1)\phi_6$ octahedra, and are linked to the framework by the sharing of each of their ligands with the $\text{Cu}(1)\phi_6$ octahedra (Figs. 2a, b).

Description of the structure using anion-centered tetrahedra

The two symmetrically distinct atoms of O in the structure of burnsite assume very different chemical roles. The $\text{O}(2)$ atom is strongly bonded to a Se^{4+} cation, as well as to two $\text{Cu}(1)$ cations. The $\text{O}(1)$ atom is tetrahedrally coordinated by three $\text{Cu}(1)$ and one $\text{Cu}(2)$ atoms, thus forming an OCu_4 oxocentered tetrahedron. The OCu_4 tetrahedron is common in structures of Cu^{2+} oxysalts that also contain O atoms that are not part of

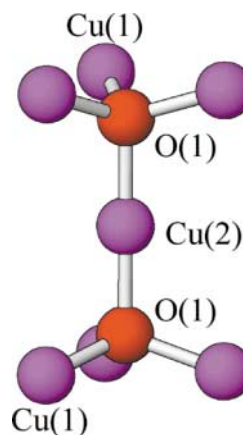


FIG. 4. The O_2Cu_7 finite clusters in the structure of burnsite.

the oxocentered tetrahedra (Effenberger 1985, Filatov *et al.* 1992, Starova *et al.* 1991, 1997, 1998, Gorskaya *et al.* 1992, Krivovichev *et al.* 1998a, 1999b). The mean $\langle\text{O}(1)\text{-Cu}\rangle$ bond length in burnsite is 1.90 Å, which is in accord with the typical $\langle\text{O-Cu}\rangle$ bond length in OCu_4 tetrahedra (Effenberger 1985, Filatov *et al.* 1992). The mean $\langle\text{Cu-Cu}\rangle$ distance in the OCu_4 tetrahedron in burnsite is 3.106 Å, in good agreement with the average value of 3.14 Å for such tetrahedra given by Krivovichev & Filatov (1999a).

In the structure of burnsite, two OCu_4 tetrahedra are linked by a common vertex, resulting in the O_2Cu_7 unit shown in Figure 4. The connectivity of this unit is analogous to the Si_2O_7 group in silicates, except that the cations and anions are inverted.

The bond valences associated with cation–anion bonds in the structure of burnsite may be grouped according to their approximate strengths (Table 4): Se^{4+} –O bonds [1.40 valence units (*vu*)], Cu^{2+} –O bonds [except the $\text{Cu}(1)$ – $\text{O}(2)$ bond; 0.53–0.55 *vu*] and other bonds (0.19–0.35 *vu*). The structure may be described on the basis of the polymerization of those polyhedra of higher bond-valence (Hawthorne 1983). The SeO_3 trigonal pyramid involves the strongest bonds, followed by the Cu^{2+} –O bonds. The Cu^{2+} –O bonds are of two types, those that are incident upon the $\text{O}(1)$ atom (bonds within the OCu_4 tetrahedron), and those that link OCu_4 tetrahedra and SeO_3 trigonal pyramids. The OCu_4 tetrahedra and SeO_3 pyramids are linked to each other according to the “face-to-face” principle (Krivovichev *et al.* 1999b); their Cu–Cu–Cu and O–O–O triangular

faces are parallel to each other and have the same orientation. The Cu^{2+} –O and Se^{4+} –O bonds thus form an extended three-dimensional $[\text{O}_2\text{Cu}_7](\text{SeO}_3)_2$ framework, which is illustrated in Figure 5a. The columns formed by the sharing of triangular faces of CdCl_6 octahedra and KCl_6 trigonal prisms (Fig. 5b) are located within large channels in the $[\text{O}_2\text{Cu}_7](\text{SeO}_3)_2$ framework (Fig. 6).

DISCUSSION

Burnsite, $\text{KCdCu}_7\text{O}_2(\text{SeO}_3)_2\text{Cl}_6$, was found in close association with other rare copper oxide selenite chlorides that have been described from the Tolbachik fumaroles: georgbokiite, $\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$, chloromenite, $\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$, ilinskite, $\text{NaCu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_3$, and an unnamed selenite with the ideal formula $[\text{Cu}^+\text{Cl}_2]\text{PbCu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_3$. Each of these minerals involve structures based upon structural units composed of oxo-centered tetrahedra. However, the coordination polyhedra about Cu^{2+} are variable in these structures, and include square planar arrangements, triangular bipyramids and octahedra.

The OCu_4 oxo-centered tetrahedra combine in a variety of ways in the structures of Tolbachik minerals. In burnsite, two OCu_4 tetrahedra form O_2Cu_7 finite clusters, whereas in chloromenite, OCu_4 tetrahedra are

TABLE 4. BOND-VALENCE* (*vu*) ANALYSIS FOR BURNSITE

Atom	Cd	K	Cu(1)	Cu(2)	Se(1)	Σ
Cl(1)	0.35 ⁶¹	0.21 ⁶¹	0.19 ²¹			0.75
Cl(2)			0.22 ^{2*}	0.30 ³¹		0.74
O(1)			0.55 ^{3*}	0.53 ²¹		2.18
O(2)					1.40 ¹⁴	2.23
Σ	2.10	1.26	1.98	1.96	4.20	

*calculated using parameters from Brese & O'Keeffe (1991)

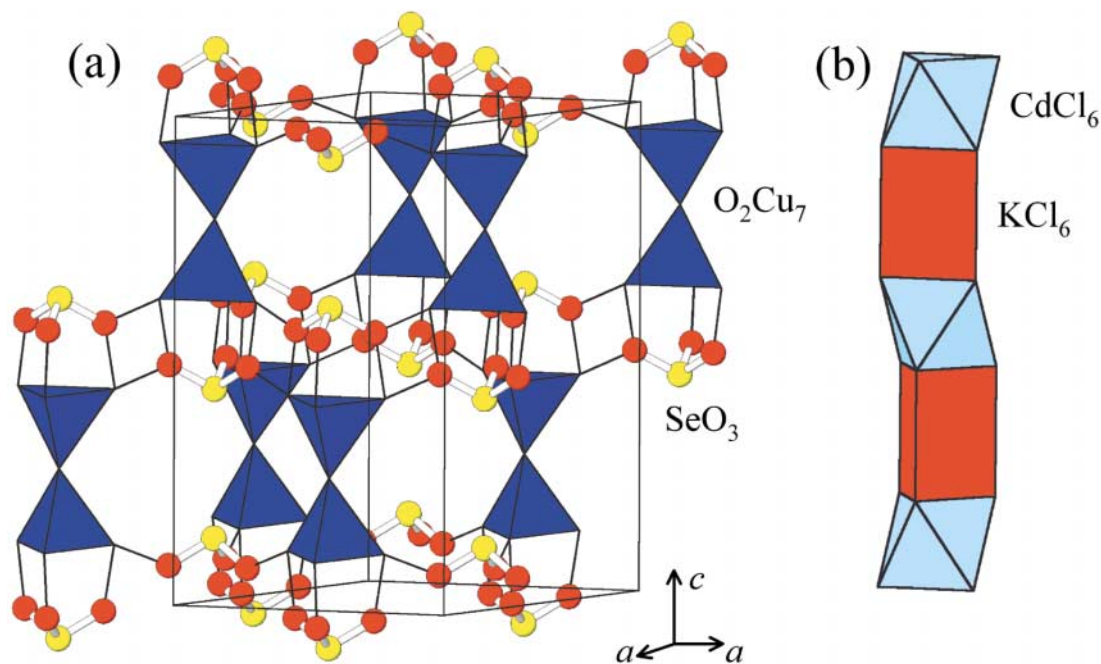


Fig. 5. Framework of O_2Cu_7 units and SeO_3 groups (a) and column of face-sharing CdCl_6 octahedra and KCl_6 trigonal prisms (b) in the structure of burnsite.

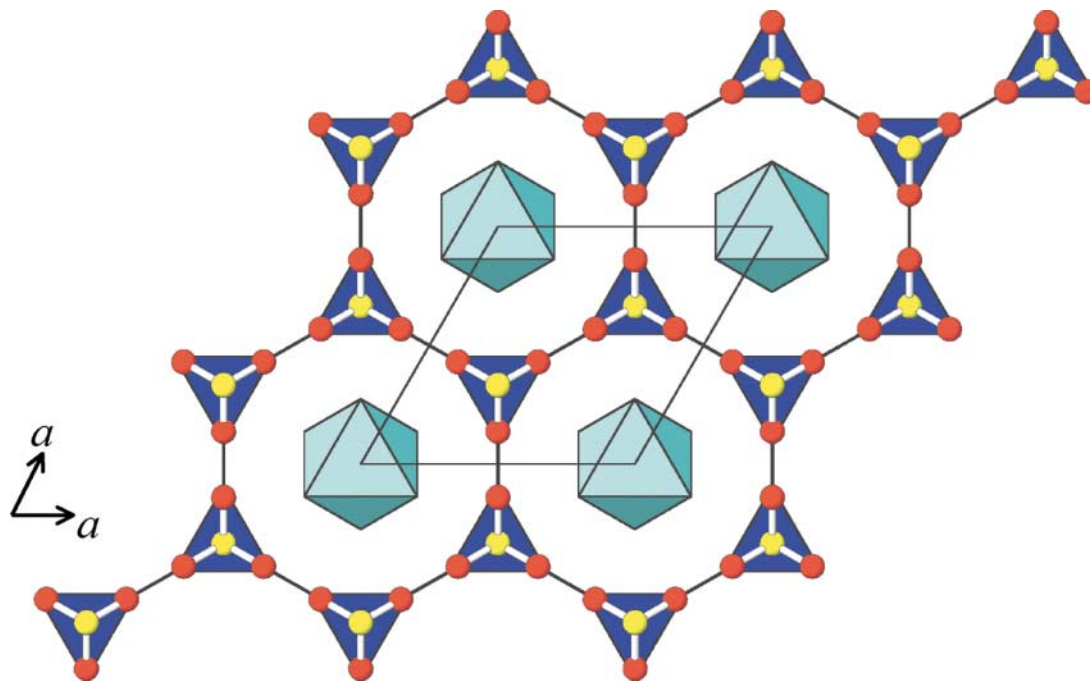


FIG. 6. Projection of the crystal structure of burnsite along the c axis showing the framework of O_2Cu_7 units and SeO_3 groups and the column of face-sharing $CdCl_6$ octahedra and KCl_6 trigonal prisms. The legend is the same as in Figure 5.

linked by corner-sharing into O_2Cu_6 chains (Krivovichev *et al.* 1998a). Identical chains with a formula O_2Cu_5Pb occur in the structure of $[Cu^+Cl_2]PbCu_5O_2(SeO_3)_2Cl_3$ (unpublished results). In georgbokiite, OCu_4 tetrahedra are linked by sharing vertices and edges, resulting in O_2Cu_5 chains (Krivovichev *et al.* 1999a). The structure of ilinskite is based upon O_2Cu_5 sheets of corner-sharing OCu_4 tetrahedra. Note that with the sole exception of $[Cu^+Cl_2]PbCu_5O_2(SeO_3)_2Cl_3$, this assemblage of minerals can be synthesized using chemical transport reactions (Galy *et al.* 1979, Shuvalov *et al.* 2000a, b, c, Bastide *et al.* 2000). In these experiments, crystals of the mineral analogues are formed directly from the gas phase. As noted by Filatov *et al.* (1992), the ability to synthesize these compounds by vapor transport provides evidence that oxocentered complexes may exist in gas phases, and they may play an important role in the transport of Cu and other metals involved in mineral-forming processes within fumaroles.

The description of structures of minerals and inorganic compounds in terms of anion-centered tetrahedra provides a useful tool for understanding occurrences of complex minerals such as those in the fumaroles of the Tolbachik volcano. For further references on anion-centered tetrahedra, see Krivovichev *et al.* (1998b, 2001),

Krivovichev & Burns (2000a, b, 2001a, b, 2002), Li *et al.* (2000, 2001), Hawthorne *et al.* (2000) and Krivovichev & Filatov (2001).

ACKNOWLEDGEMENTS

This research was supported by the Russian Foundation for Basic Research (RFBR), which supports SKF and SVK (grants 01–05–64883 and 01–05–06195). Collaboration between PCB and SVK is supported by the NATO Science program (grant EST.CLG.977834). We are grateful to Dr. H. Effenberger and an anonymous referee for their detailed comments, and to Dr. R.F. Martin for his editorial work. PCB thanks SVK and SKF for the invitation to join them in writing this manuscript describing the structure of burnsite.

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Received August 8, 2001, revised manuscript accepted October 29, 2002.