THE CRYSTAL STRUCTURE OF AN ANTHROPOGENIC
Cu–K–Na–HYDRO-HYDROXYL–CARBONATE–CHLORIDE
FROM JOHANNGEORGENSTADT, SAXONY, GERMANY

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ABSTRACT

The Cu–K–Na–hydroxy-hydroxyl–carbonate–chloride, K₁ Na₃ Cu²⁺₂₄ (CO₃)₁₆ Cl₁ (OH)₂₀ (H₂O)₁₂, has been found on a museum specimen labeled Johanngeorgenstadt, Saxony, Germany. It occurs as blue transparent cubes 0.2 mm across on massive maucherite, and the unusual mineralogical and geochemical associations suggest that this phase may be of anthropogenic origin.

The crystal structure of this material, cubic, space group F23, a = 15.463(1) Å, V = 3697.5(1.6) Å³, Z = 2, was solved by direct methods and refined to an R1 index of 4.3% based on 409 observed (> 4σF) reflections measured with MoKα X-radiation. Electron-microprobe analysis gave the following empirical formula: K₆.₉₇ Na₂.₂₂ (Cu²⁺₂₂.₄₆ Ni₀.₁₂ As₀.₁₅ )Cl₁.₉₇ (H₂O)₁₂ Cl₁.₉₇ based on 83 (Cl + O) atoms.

Four of these clusters connect through common vertices to form a 12-membered cluster of point symmetry 23. In this cluster, every three trimeric clusters are linked by a (CO₃) group, resulting in a [Cu²⁺₁₂ C₄ O₂₄ (OH)₈ ]⁺⁺ cluster. These large cluster. Four of these clusters connect through common vertices to form a 12-membered cluster of point symmetry 23. In this cluster, every three trimeric clusters are linked by a (CO₃) group, resulting in a [Cu²⁺₁₂ C₄ O₂₄ (OH)₈ ]⁺⁺ cluster. These large clusters link through (CO₃) groups to form cages that accommodate the Na, K and Cl(2) sites. There is extensive hydrogen bonding between (OH) groups and Cl atoms and between (H₂O) groups and O atoms.

The Cu–K–Na–hydroxy-hydroxyl–carbonate–chloride, K₁ Na₃ Cu²⁺₂₄ (CO₃)₁₆ Cl₁ (OH)₂₀ (H₂O)₁₂, was discovered on a museum specimen labeled Johanngeorgenstadt, Saxony, Germany. It occurs as blue transparent cubes 0.2 mm across on massive maucherite, and the unusual mineralogical and geochemical associations suggest that this phase may be of anthropogenic origin. The crystal structure of this material, cubic, space group F23, a = 15.463(1) Å, V = 3697.5(1.6) Å³, Z = 2, was solved by direct methods and refined to an R1 index of 4.3% based on 409 observed (> 4σF) reflections measured with MoKα X-radiation. Electron-microprobe analysis gave the following empirical formula: K₆.₉₇ Na₂.₂₂ (Cu²⁺₂₂.₄₆ Ni₀.₁₂ As₀.₁₅ )Cl₁.₉₇ (H₂O)₁₂ Cl₁.₉₇ based on 83 (Cl + O) atoms.

Keywords: anthropogenic carbonate, crystal structure, copper clusters, Saxony, Germany.

Sommaire

Un carbonate–chlorure de Cu–K–Na hydroxy-hydroxylé, K₁ Na₃ Cu²⁺₂₄ (CO₃)₁₆ Cl₁ (OH)₂₀ (H₂O)₁₂, a été découvert sur un échantillon de musée provenant de Johanngeorgenstadt, Saxe, Allemagne. Ce composé forme des cubes bleus transparents 0.2 mm de taille sur la maucherite massive. D’après l’association minéralogique et géochimique inhabituelle, cette phase pourrait bien s’avérer d’origine anthropogénique. La structure cristalline de ce matériau, cubique, groupe spatial F23, a = 15.463(1) Å, V = 3697.5(1.6) Å³, Z = 2, a été résolue par méthodes directes et affinée jusqu’à un résidu R1 de 4.3% en utilisant 409 réflexions observées (>4σF), mesurées avec rayonnement MoKα. Une analyse à la microsonde électronique a donné la formule empirique suivante: K₆.₉₇ Na₂.₂₂ (Cu²⁺₂₂.₄₆ Ni₀.₁₂ As₀.₁₅ )Cl₁.₉₇ (H₂O)₁₂ Cl₁.₉₇ sur une base de 83 atomes de (Cl + O) par unité formérale. Il y a un site Cu entouré de trois atomes O et deux groupes (OH), avec <Cu–O,(OH)> = 2.025 Å. Il y a deux sites d’ions alcalins; le site Na possède une coordinence octaédrique régulière, assurée par six groupes (H₂O), avec <Na–H₂O> = 2.414 Å, et le site K est coordonné par trois atomes d’oxygène, 1.5 groupes (OH) et un atome de Cl, avec <K–Cl> = 2.998 Å. La structure contient deux sites C, chacun coordonné par trois atomes d’oxygène, avec <C–O> = 1.283 et 1.245 Å, respectivement. Elle contient deux types de site Cl: Cl(1) est un ligand du potassium, et Cl(2) reçoit quatre liaisons hydrogène de groupes OH dans un agencement tétraédrique. Trois polyèdres [Cu²⁺₁₂ O₁₂ (OH)₁₂ ]⁺⁺ sont liés par partage d’arêtes pour donner un groupe trimérique de stoechiométrie [Cu²⁺₃ O₆ (OH)₁₄ ]⁺⁺. Quatre de ces groupes sont connectés à un sommet commun pour donner une agglomération à 12 membres ayant une symétrie ponctuelle de 23. Dans cette agglomération, chaque trois groupes trimériques sont liés à un groupe (CO₃), ce qui mène à une agglomération de stoechiométrie [Cu²⁺₁₂ C₄ O₂₄ (OH)₈ ]⁺⁺. Ces agglomérations volumineuses sont liées grâce à des groupes (CO₃) pour former des cages où sont situés les sites Na, K et Cl(2).

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INTRODUCTION

The phase described here was discovered on a museum specimen (catalogue number 199.239) from the mineral collection at the Muséum National d’Histoire Naturelle, Paris, France. The specimen originated from Johanngeorgenstadt, Saxony, Germany, measures 3.5 × 2.5 × 2.0 cm, and is labelled “bunsenite”. The bulk of the specimen is a massive sulfide that has been identified as maucherite by X-ray powder diffraction, and has fine-grained green material on the surface; this is presumably the “bunsenite” of the label, but X-ray diffraction showed it to be almost X-ray amorphous, with some weak lines of aerugite. There are also crusty aggregates of quartz and arsenite, and scattered across the surface of the specimen are dark-blue subhedral to euhedral cubes of a phase that could not be identified by powder X-ray diffraction. The chemical composition of this blue phase was determined by solution and refinement of the crystal structure and electron-microprobe analysis: ideally K₅ Na₂ Cu²⁺₂₄ (CO₃)₁₆ Cl₃ (OH)₂₀ (H₂O)₁₂. The presence of near-amorphous aerugite is suggestive of high temperature, whereas the presence of the blue phase is incompatible with this origin. This feature, together with the unusual association of chemical compositions, convinced us that this sample is probably of anthropogenic origin, and we decided not to submit the blue phase as a new mineral. In this regard, the crystal structure of another anthropogenic copper compound, Cu²⁺ (C₄H₄O₄)·H₂O, was reported by Rastsvetaeva et al. (1996). It was obtained by treating azurite with detergent containing succinic acid. The crystal structure of the blue phase is extremely interesting, and we report our results here.

PHYSICAL PROPERTIES

The compound is dark blue with a medium blue streak, brittle with an uneven fracture, has a vitreous to adamantine to somewhat resinous luster, and is devoid of cleavage. Single crystals are translucent to transparent, whereas masses appear almost opaque when viewed against the metallic matrix. The compound does not fluoresce under short- or long-wave ultraviolet radiation. There is no evidence of twinning on single-crystal precession films. Subhedral to euhedral cubes generally do not exceed 0.2 mm in longest dimension; forms are {100} dominant and {110} rare.

X-RAY DIFFRACTION

Examination of the blue crystals by precession photography indicated cubic symmetry with a face-centered lattice and a cell parameter of 15.567 Å. The X-ray powder-diffraction pattern was obtained with a 114.6 Debye–Scherrer camera and CuKα radiation (Table 1). The cell parameter was refined with seventeen reflections between 3.541 and 1.492 Å; the indexing was based on single-crystal precession films, and the resulting refined unit-cell dimension is 15.436(4) Å. A small crystal (0.06 × 0.08 × 0.10 mm) previously used for precession photography was attached to a glass fiber and mounted on a Siemens P4 automated four-circle diffractometer equipped with a serial detector and MoKα X-radiation. Sixteen reflections over the range 8.7 ≤ 2θ ≤ 18.9° were centered, and the unit-cell dimension (Table 2) was refined by least-squares from the resultant setting angles. Intensity data were collected in 0–20 scan-mode at a fixed scan-rate of 1.0° 20/min. A total of 1518 reflections was measured over the range 4 ≤ 2θ ≤ 60.1°. Psi-scan data were measured on seven reflections out to 60°20 at increments of 5°, and an ab-
the phase contains Cu, K and Cl. In the course of structure solution, a site with a scattering of 11 e was located in the structure. It is octahedrally coordinated by (H₂O) groups at a distance of 2.41 Å. We assumed that this site contains Na, and subsequent electron-microprobe analysis confirmed this assumption. During the course of the refinement, it became apparent that the K site and the anion sites Cl(2), O(2A), O(2B) and O(4) are partly occupied. Attempts to refine all occupancies simultaneously were unsuccessful, the refinement becoming unstable. Successive cycles of refinement with occupancies refined in series indicated that all anion sites are half-occupied within two standard deviations. Hence these sites were subsequently fixed at half-occupancy, and refinement proceeded with the occupancy of the K site allowed to vary. Three unique H atoms were located in a difference-Fourier map at the final stages of refinement. Disorder of K and several O atoms made it difficult to refine both positional and displacement parameters for H atoms. DFIX constraints were used for the refinement, setting the isotropic-displacement parameter of the H atom as 1.5 times larger than the displacement parameter of the corresponding donor O atom. An extinction correction was also refined, but is negligible. The highest and lowest residuals in the final difference-Fourier map is 0.93 and −0.80 e/Å³. Positional and displacement parameters are given in Table 3, selected interatomic distances in Table 4, bond-valences in Table 5, and geometric characteristics of hydrogen bonding are given in Table 6. Observed and calculated structure-factors are available from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

**TABLE 2. MISCELLANEOUS DATA FOR K₃Na₃Cu₂(PO₄)₃Cl₂(OH)₁₀(H₂O)₁₂**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>15.6633 (13)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>3697.5 (16)</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Dₐ₀ (g/cm³)</td>
<td>3.044</td>
</tr>
<tr>
<td>Axial absorption coefficient (mm⁻¹)</td>
<td>7.28</td>
</tr>
<tr>
<td>F(000)</td>
<td>3288.0</td>
</tr>
<tr>
<td>ρ(θ) (%)</td>
<td>4.5</td>
</tr>
<tr>
<td>No. of unique reflections</td>
<td>1518</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>514</td>
</tr>
<tr>
<td>F(0) &gt; 4σ(F)</td>
<td>409</td>
</tr>
</tbody>
</table>

**TABLE 3. ATOMIC POSITIONS AND ANISOTROPIC-DISPLACEMENT FACTORS FOR K₃Na₃Cu₂(PO₄)₃Cl₂(OH)₁₀(H₂O)₁₂**

<table>
<thead>
<tr>
<th>Wyck. Sym. Occ.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U₁₁</th>
<th>U₂₂</th>
<th>U₃₃</th>
<th>U₁₂</th>
<th>U₁₃</th>
<th>U₂₃</th>
<th>U₁₄</th>
<th>U₂₄</th>
<th>U₃₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu 48h 1 1.0</td>
<td>0.92670(8)</td>
<td>0.92681(8)</td>
<td>0.78545(7)</td>
<td>0.0427(7)</td>
<td>0.0426(7)</td>
<td>0.0207(5)</td>
<td>-0.0003(5)</td>
<td>0.0005(5)</td>
<td>-0.0222(6)</td>
<td>0.0353(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na 4c 23 1.0</td>
<td>0.6205(7)</td>
<td>0.3838(3)</td>
<td>0.5162(3)</td>
<td>0.060(2)</td>
<td>0.060(2)</td>
<td>0.050(2)</td>
<td>-0.010(2)</td>
<td>0.010(2)</td>
<td>0.010(2)</td>
<td>0.050(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K 16e 3 1.0</td>
<td>0.6205(7)</td>
<td>0.3838(3)</td>
<td>0.5162(3)</td>
<td>0.060(2)</td>
<td>0.060(2)</td>
<td>0.050(2)</td>
<td>-0.010(2)</td>
<td>0.010(2)</td>
<td>0.010(2)</td>
<td>0.050(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(1) 16e 3 1.0</td>
<td>0.6205(7)</td>
<td>0.3838(3)</td>
<td>0.5162(3)</td>
<td>0.060(2)</td>
<td>0.060(2)</td>
<td>0.050(2)</td>
<td>-0.010(2)</td>
<td>0.010(2)</td>
<td>0.010(2)</td>
<td>0.050(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2) 16e 3 1.0</td>
<td>0.639(3)</td>
<td>0.465(2)</td>
<td>0.267(2)</td>
<td>0.057(2)</td>
<td>0.057(2)</td>
<td>0.037(1)</td>
<td>-0.003(1)</td>
<td>0.003(1)</td>
<td>0.003(1)</td>
<td>0.003(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(3) 36e 3 1.0</td>
<td>0.852(2)</td>
<td>0.852(2)</td>
<td>0.852(2)</td>
<td>0.014(2)</td>
<td>0.014(2)</td>
<td>0.014(2)</td>
<td>-0.002(2)</td>
<td>0.002(2)</td>
<td>0.002(2)</td>
<td>0.002(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(4) 48h 1 1.0</td>
<td>0.039(3)</td>
<td>0.14(4)</td>
<td>0.45(5)</td>
<td>0.055(5)</td>
<td>0.055(5)</td>
<td>0.055(5)</td>
<td>-0.018(5)</td>
<td>0.018(5)</td>
<td>0.018(5)</td>
<td>0.018(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(1) 16e 3 1.0</td>
<td>0.816(1)</td>
<td>0.816(1)</td>
<td>0.816(1)</td>
<td>0.022(3)</td>
<td>0.022(3)</td>
<td>0.022(3)</td>
<td>-0.007(5)</td>
<td>0.007(5)</td>
<td>0.007(5)</td>
<td>0.007(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(2) 24f 2 1.0</td>
<td>0.667(9)</td>
<td>0.667(9)</td>
<td>0.667(9)</td>
<td>0.00(2)</td>
<td>0.00(2)</td>
<td>0.00(2)</td>
<td>-0.00(2)</td>
<td>0.00(2)</td>
<td>0.00(2)</td>
<td>0.00(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(3) 48h 1 1.0</td>
<td>0.050</td>
<td>0.210</td>
<td>0.220</td>
<td>0.081(9)</td>
<td>0.081(9)</td>
<td>0.081(9)</td>
<td>-0.018(9)</td>
<td>0.018(9)</td>
<td>0.018(9)</td>
<td>0.018(9)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*These occupancies were considered fixed in the final refinement (see text).
ELECTRON-MICROPROBE ANALYSIS

Two crystals were analyzed with a Cameca SX–50 electron microprobe operating in wavelength-dispersion mode, with an accelerating voltage of 15 kV, a specimen current of 20 nA, a beam size of 5 μm and counting times on peak and background of 2 and 10 s, respectively. The crystals were very unstable during analysis. The following standards and crystals were used for K or L X-ray lines: F: fluorine-rich riebeckite; Na: albite; Al: andalusite; Si: diopside; K: orthoclase; Cl: tugtupite; As: cobaltite; Ni: pararammelsbergite.

Data were reduced using the \( \phi(pZ) \) procedure of Pouchou & Pichoir (1985). The chemical composition of the crystals is given in Table 7 and is the mean of 12 determinations. The empirical formula was calculated on the basis of 83 anions, with \( O = 48, (H_2O) = 12, OH = 20, Cl = 3 \) and \( C = 16 \) app: \( K_6.97 \) Na_1.22 \((Cu^{2+})_{22.46}Ni_{0.12}As_{0.15}\) _A_16.57_\(Cl_{1.97}(OH)_{20}(H_2O)_{12}\). The ideal composition from the crystal structure is \( K_5Na_2Cu^{2+}{_{24}}(CO_3)_{16}Cl_1(OH)_{20}(H_2O)_{12}\). We regard this agreement as reasonable, considering that the crystals decrepitated severely in the electron beam.

CRYSTAL STRUCTURE

Coordination of cations

There is one \( Cu \) site occupied by \( Cu^{2+} \) with minor (less than 1%) amounts of \( Ni \) and \( As \). The \( Cu^{2+} \) atom is surrounded by seven anion sites. \( O(1), O(2), O(3) \) (Table 4) have full occupancy (Table 3) and represent the coordinating anions \( O(OH) \). \( O(2A), O(2B), O(4) \) have only 50% occupancy (Table 3) and represent the coordinating anions \( O(OH) \). There are short distances equal to 0.856(17) Å between the \( O(2A) \) and \( O(2B) \) anions that are related by a pseudo-mirror plane parallel to \( (110) \) (see Table 3), and to 0.884(26) Å between \( O(4) \) \((x, y, z)\) and \( O(4)' \) \((-x, -y, z)\) that are related by a two-fold axis, \( 2_2 \). The \( [5]-coordinated polyhedron,\n
\[\begin{align*}
\text{Cu} & - O(1a) & 2.18(3) & K - O(2A)^* & x/2 & 3.17(1) \\
\text{Cu} - O(1b) & 2.19(3) & K - O(2B)^* & x/2 & 3.18(2) \\
\text{Cu} - O(2A)^* & x/2 & 1.92(1) & K - O(3) & x/2 & 2.69(1) \\
\text{Cu} - O(2B)^* & x/2 & 1.91(1) & K - O(5) & x/2 & 2.94(6) \\
\text{Cu} - O(3) & 1.92(5) & K - O(1) & 3.11(3) \\
\text{Cu} - O(4)^* & x/2 & 1.90(1) & <K-O> & 3.00(1) \\
\text{Cu} - O(4)^* & x/2 & 1.91(1) & <K-O> & 3.00(1) \\
\text{Cu} - O(5) & 2.02(5) & C(1) - O(1) & x/3 & 1.283(6) \\
\text{O}(2A) - O(2B) & 0.86(2) & C(2) - O(2A)^* & x/3 & 1.25(1) \\
\text{O}(4) - O(4)^* & 0.88(3) & C(2) - O(2B)^* & x/3 & 1.25(1) \\
\text{Na} - O(5) & 2.414(2) \end{align*}\]

* the starred bonds to each cation are mutually exclusive

\[\begin{align*}
\text{Cu} & \quad \text{Na} & \quad \text{C}(1) & \quad \text{C}(2) & \quad \text{K} & \quad \Sigma & \quad \text{H}(1) & \quad \text{H}(2) & \quad \text{H}(3) & \quad \Sigma \\
\hline
O(1) & 0.25 & 1.33^a & & & 1.83 & 0.20^a & 2.03 \\
O(2) & 0.25 & 1.33^a & & & 1.83 & 0.20^a & 2.03 \\
O(2A)^* & 0.58^a & 1.40^a & 0.06^a & 2.02 & 2.02 \\
O(2B)^* & 0.58^a & 1.40^a & 0.06^a & 2.04 & 2.04 \\
O(3) & 0.50^a & & & 1.50 & 0.75 & 2.25 \\
O(4) & 0.54^a & 0.54^a & 0.20^a & 1.28 & 0.90 & 2.18 \\
O(5) & 0.19^a & & & 0.11^a & 0.41 & 0.83^a & 2.01 \\
C(1) & 0.20^a & & & 0.80 & 0.10^a & 1.10 \\
C(2) & & & & 0.25^a & & 1.00 \\
\hline
\Sigma & 2.11 & 1.15 & 3.99 & 4.20 & 1.01 & 1.00 & 2.00 \\
\end{align*}\]

Bond-valence curves are from Brown & Altermatt (1985).

* the starred entries are mutually exclusive for each cation.

\[\begin{align*}
\text{D-H} & \quad \text{A (Å)} & \quad \text{D-A (Å)} & \quad \text{D-H (Å)} & \quad \text{H (Å)} & \quad \text{D-H (Å)} & \quad \text{H (Å)} & \quad \text{D-H (Å)} & \quad \text{H (Å)} & \quad \text{D-H (Å)} \\
\hline
\text{O}(3)-\text{H}(1). & \text{Cl}(2) & 2.752(8) & 1.20 & 1.53 & 180 & - \\
\text{O}(4)-\text{H}(2). & \text{Cl}(1) & 3.51(1) & 1.02 & 2.51 & 151 & 21 \\
\text{O}(5)-\text{H}(3). & \text{O}(1) & x2 & 2.940(6) & 0.93 & 2.04 & 159 & 27 & 136.6 \\
\end{align*}\]
[Cu$^{2+}$ O$_3$ (OH)$_2$]$^{6-}$, has a $<\text{Cu–O,OH}>$ distance of 2.024 Å.

There is one Na site occupied by Na and coordinated by a regular octahedral arrangement of six (H$_2$O) groups, with Na–O(5) = 2.414(2) Å. There is one K site with 62% occupancy by K and surrounded by thirteen sites, nine of which are half-occupied (Table 4). The anion sites O(2A), O(2B) and O(4) have 50% occupancy to give O$_3$(OH)$_{1.5}$, and the O(5) × 3 and C(1) sites are completely occupied to give an average coordination number of [8.5] and a $<\text{K–O}>$ distance of 3.001 Å for the polyhedron [K O$_3$(OH)$_{1.5}$ (H$_2$O)$_3$Cl]$^{7.5-}$. There are two C sites, C(1) and C(2), with point symmetry 3, that are occupied by C atoms with $<\text{C–O}>$ distances of 1.283 and 1.245 Å, respectively. The arrangements of O atoms around the C sites are different: the C(1) site is

**FIG. 1.** Fragments of the crystal structure of K$_5$Na$_2$Cu$_{2+24}$ (CO$_3$)$_{16}$Cl$_3$ (OH)$_{20}$ (H$_2$O)$_{12}$ and murataite, (Y,Na)$_6$ (Zn,Fe)$_5$ Ti$^{4+}$_{12}O$_{29}$ (O,F)$_{10}$ F$_4$. (a) A trimeric [Cu$^{2+}$ O$_6$ (OH)$_4$]$^{10-}$ cluster of [5]-coordinated (Cu$^{2+}$)$_5$ polyhedra shown from one side. (b) A trimeric [Ti$^{4+}$ O$_{12}$]$^{12-}$ cluster of (Ti$^{4+}$O$_6$) octahedra shown from one side. (c) A trimeric [Cu$^{2+}$ O$_{6}$ (OH)$_{12}$]$^{10-}$ cluster of [5]-coordinated (Cu$^{2+}$)$_5$ polyhedra shown from the other side. (d) A trimeric [Ti$^{4+}$ O$_{12}$]$^{12-}$ cluster of (Ti$^{4+}$O$_6$) octahedra shown from the other side. (e) A sixteen-membered [Cu$^{2+}$$_{12}$ (CO$_3$)$_{12}$O$_{12}$ (OH)$_{12}$]$^{8+}$ cluster of twelve (Cu$^{2+}$)$_5$ polyhedra and four (CO$_3$) groups. (f) A thirteen-membered [Ti$^{4+}$$_{12}$ Zn O$_{40}$]$^{30-}$ cluster of twelve (Ti$^{4+}$O$_6$) octahedra and one (ZnO$_4$) tetrahedron. The (Cu$^{2+}$)$_5$ and (Ti$^{4+}$O$_6$) octahedra are yellow, (CO$_3$) groups and (ZnO$_4$) tetrahedron are violet. Figures a, c, and e were drawn with averaged positional parameters for O(4) (0, 0, 0.75) and with only the O(2A) anion [i.e., omitting the O(2B) anion].
surrounded by three O(1) anions in a triangular arrangement; the Cl(2) site is surrounded by three O(2A) atoms and three O(2B) atoms, each of which is half-occupied, giving two triangular arrangements, C(2)O(2A) and C(2)O(2B), that are rotated 60° relative to each other.

**Structure topology**

In the structure of K$_5$Na$_2$Cu$_{2+24}$ (CO$_3$)$_{12}$Cl$_3$ (OH)$_{20}$ (H$_2$O)$_{12}$. [Cu$^{2+}$O$_2$(OH)$_2$] polyhedra link through common edges to form the trimeric [Cu$^{2+}$O$_6$(OH)$_6$]$^{10-}$ cluster. This cluster has one vertex common to all three polyhedra (Figs. 1a, c), and this common vertex is occupied by the OH group at O(3). Four of these trimeric clusters are connected through common vertices to form a twelve-membered cluster of point symmetry 23. This cluster is decorated by four (disordered) (CO$_3$) groups. The resulting cluster, [Cu$^{2+}_{12}$ (CO$_3$)$_4$ O$_{12}$(OH)$_8$]$^{8+}$ (Fig. 1e) can be regarded as the fundamental building block (FBB) of the structure. The sixteen-membered clusters are linked into a framework by an ordered (CO$_3$)$_3$ groups (Fig. 2a). Each (CO$_3$) group shares common vertices with three [Cu$^{2+}_{12}$ (CO$_3$)$_3$ O$_{12}$(OH)$_3$]$^{18+}$ clusters.

Within the framework, there are two types of channels within which K and Na atoms are distributed in accord with their size: $^{[8,5]K}$ = 1.53, $^{[6]Na}$ = 1.02 Å (Shannon 1976). Larger channels extend along [110]$_{\bar{L}}$, and incorporate K and Cl(I) atoms (Fig. 2a) in linear arrays along the channel. Smaller channels extend along [001]$_{\bar{L}}$ and contain alternating Na and Cl(2) atoms (Fig. 2b). There are two types of cages that incorporate Cl atoms. Intersection of two [110]$_{\bar{L}}$ channels gives rise to a cage that contains Cl(I) atoms tetrahedrally surrounded by four K atoms. As each cage has its own pattern of hydrogen bonding, we will discuss them in the next section.

**Hydrogen bonding**

Intersection of three [001]$_{\bar{L}}$ channels gives rise to a cage containing the Cl(2) site that is half-occupied by Cl (Fig. 3a). Each Cl(2) site is coordinated by four H(1) atoms of the (OH) group at O(3) site, and accepts hydrogen bonds from the H(1) atoms (Tables 5, 6). The multiplicity of the H(3) site is twice that of the O(5) site, and two H(3) atoms of the (H$_2$O) group are related by a two-fold rotation axis. Extensive hydrogen bonding is critical to the stability of the structure, and it is probably damage to the hydrogen bonds that causes decrepitation of the crystals in the beam of the electron microprobe.

**Comparison of K$_5$Na$_2$Cu$_{2+24}$ (CO$_3$)$_{16}$ Cl$_3$ (OH)$_{20}$ (H$_2$O)$_{12}$ with murataite, (Y,Na)$_6$(Zn,Fe)$_5$ Ti$_{12}$ O$_{29}$(O,F)$_{10}$ F$_4$**

There is a very close relation between the FBB in our compound and the FBB in murataite, ideally (Y,Na)$_6$(Zn,Fe)$_5$ Ti$_{12}$ O$_{29}$(O,F)$_{10}$ F$_4$. Murataite is cubic, F$^4$3m, a = 14.886(2) Å, Z = 4 (Ercit & Hawthorne 1995). The crystal structure of murataite contains thirteen-membered [Ti$^{4+}_{12}$ Zn O$_{10}$]$^{36+}$ clusters topologically similar to the sixteen-membered [Cu$^{2+}_{12}$ (CO$_3$)$_3$ O$_{12}$(OH)$_3$]$^{18+}$ cluster in our compound. Figure 1 shows a triplet of [5]-coordinated (Cu$^{2+}$O$_3$) polyhedra in our compound (a, c) and a triplet of (Ti$^{4+}$O$_6$) octahedra in murataite (b, d).

For both types of triplet, there is one common vertex, i.e., common to all three polyhedra. Where four triplets link together in the structure of the anthropogenic compound, these common vertices occur on the outside of the cluster. Where four triplets link together in the crystal structure of murataite, they occur on the inside of the cluster. In the anthropogenic compound, each [5]-coordinated (Cu$^{2+}$O$_3$) polyhedron shares one vertex with an adjacent triplet. In murataite, each (Ti$^{4+}$O$_6$) octahedron shares two vertices with two different triplets (Fig. 1f).

Thus, the central cage of a cluster of [5]-coordinated (Cu$^{2+}$O$_3$) polyhedra is empty, and the sides occlude (CO$_3$) triangles. In murataite, a (ZnO$_3$) tetrahedron occupies the central cage of the cluster. This (ZnO$_3$) tetrahedron shares corners with all three octahedra of each triplet. There are other possibilities for clusters of triplets of such polyhedra, but they will be described in a separate paper.
Fig. 2. Projection of the crystal structure of $K_5Na_2Cu^{2+}_{24}(CO_3)_{16}Cl_3(OH)_{20}(H_2O)_{12}$ (a) onto (110), and (b) onto (001). The $(Cu^{2+})$ polyhedra are yellow, $(Na)$ octahedra are orange, $(CO_3)$ groups are violet, Cl and K atoms are shown as large green and magenta circles. The figure is drawn with average positional parameters for O(4) and with O(2A) only.
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FIG. 3. Details of the hydrogen bonding in the crystal structure of K5 Na2 Cu12+24 (CO3)16 Cl1 (OH)20 (H2O)12. (a) The Cl(2) atom tetrahedrally coordinated by H(1) atoms of OH groups {O(3)}. (b) The Cl(1) atom bonded to six half-occupied H(2) atoms that are part of the (OH) group at O(4). (c) Hydrogen bonds between the H(3) atoms of the (H2O) groups coordinating Na and the O(1) anion that is part of the {Cl(1)O1} group. Legend as in Figure 2. The H atoms are shown as small red circles. The figure was drawn with average positional parameters for O(4) and with O(2A) [i.e., omitting O(2B)].