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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–hydro-hydroxyl–carbonate–chloride, $K_5\ Na_2\ Cu^{2+}_{24}\ (CO_3)_{16}\ Cl_3\ (OH)_{20}\ (H_2O)_{12}$, 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 *F*23, *a* 15.463(1) Å, *V* 3697.5(1.6) $Å^3$, *Z* = 2, was solved by direct methods and refined to an *R*1 index of 4.3% based on 409 observed (> 4σ*F*) reflections measured with Mo*K*α X-radiation. Electron-microprobe analysis gave the following empirical formula: $K_{6.97}\ Na_{1.22}\ (Cu^{2+}_{22.46}\ Ni_{0.12}\ As_{0.15})_{\Sigma 22.73}\ C_{16.57}\ O_{48}\ (OH)_{20}\ (H_2O)_{12}\ Cl_{1.97}$ based on 83 (Cl + O) *apfu*. There is one *Cu* site surrounded by three O atoms and two (OH) groups, with <Cu–O,(OH)> = 2.025 Å. There are two alkali sites, the *Na* site in regular octahedral coordination by six (H_2O) groups, with <Na–H_2O> = 2.414 Å, and the *K* site coordinated by three oxygen atoms, 1.5 (OH) groups, three (H_2O) groups and one Cl atom, with <K–ϕ> = 2.998 Å. There are two *C* sites, each coordinated by three oxygen atoms, with <C–O> = 1.283 and 1.245 Å, respectively. There are two types of *Cl* sites: *Cl*(1) is a ligand for K, and *Cl*(2) receives four hydrogen bonds from OH groups in a tetrahedral arrangement. Three $\{Cu^{2+}\ O_3\,(OH)_2\}$ polyhedra link through common edges to form a trimeric $[Cu^{2+}_3\ O_6\,(OH)_4]^{10-}$ 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 (CO_3) group, resulting in a $[Cu^{2+}_{12}\ C_4\ O_{24}\ (OH)_8]^{8+}$ cluster. These large clusters link through (CO_3) 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 (H_2O) groups and O atoms.

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

SOMMAIRE

Un carbonate–chlorure de Cu–K–Na hydro-hydroxylé, $K_5\ Na_2\ Cu^{2+}_{24}\ (CO_3)_{16}\ Cl_3\ (OH)_{20}\ (H_2O)_{12}$, 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 mauchérite 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 *F*23, *a* 15.463(1) Å, *V* 3697.5(1.6) $Å^3$, *Z* = 2, a été résolue par méthodes directes et affinée jusqu’à un résidu *R*1 de 4.3% en utilisant 409 réflexions observées (>4σ*F*), mesurées avec rayonnement Mo*K*α. Une analyse à la microsonde électronique a donné la formule empirique suivante: $K_{6.97}\ Na_{1.22}\ (Cu^{2+}_{22.46}\ Ni_{0.12}\ As_{0.15})_{\Sigma 22.73}\ C_{16.57}\ O_{48}\ (OH)_{20}\ (H_2O)_{12}\ Cl_{1.97}$ sur une base de 83 atomes de (Cl + O) par unité formulaire. 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 (H_2O), avec <Na–H_2O> = 2.414 Å, et le site *K* est coordonné par trois atomes d’oxygène, 1.5 groupes (OH), trois groupes (H_2O) et un atome de Cl, avec <K–ϕ> = 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 $\{Cu^{2+}\ O_3\,(OH)_2\}$ sont liés par partage d’arêtes pour donner un groupe trimérique de stoechiométrie $[Cu^{2+}_3\ O_6\,(OH)_4]^{10-}$. Quatre de ces groupes sont connectés à un sommet commun pour donner ue agglomération à 12 membres ayant une symétrie ponctuelle de 23. Dans cette agglomération, chaque trois groupes trimériques sont liés à un groupe (CO_3), ce qui mène à une agglomération de stoechiométrie $[Cu^{2+}_{12}\ C_4\ O_{24}\ (OH)_8]^{8+}$. Ces agglomérations volumineuses sont liées grâce à des groupes (CO_3) pour former des cages où sont situés les sites *Na*, *K* et *Cl*(2).

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Un réseau important de liaisons hydrogène est développé entre les groupes (OH) et les atomes Cl, et entre les groupes (H_2O) et les atomes O.

(Traduit par la Rédaction)

Mots-clés: carbonate anthropogénique, structure cristalline, agglomérations de cuivre, Saxe, Allemagne.

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 arcanite, 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 $K_5\ Na_2\ Cu^{2+}_{24}\ (CO_3)_{16}\ Cl_3\ (OH)_{20}\ (H_2O)_{12}$. 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, $Cu^{2+}\ (C_4H_4O_4)\ H_2O$, 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.

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR $K_5\ Na_2\ Cu^{2+}_{24}\ (CO_3)_{16}\ Cl_3\ (OH)_{20}\ (H_2O)_{12}$

	$I_{est.}$	$d_{meas.}$ (Å)	$d_{calc.}$ (Å)	*h k l*		$I_{est.}$	$d_{meas.}$ (Å)	$d_{calc.}$ (Å)	*h k l*
	90	8.979	8.912	1 1 1		1	2.135	2.141	6 4 0
	20	7.711	7.718	2 0 0	*	25	2.065	2.063	6 4 2
	40	5.463	5.457	2 2 0	*	5	2.005	2.010	5 5 3
	70	4.677	4.654	3 1 1		3	1.870	1.872	6 4 4
	60	4.467	4.456	2 2 2		30	1.816	1.819	6 6 0
	10	3.867	3.859	4 0 0		"	"	1.819	8 2 2
*	25	3.541	3.541	3 3 1	*	15	1.770	1.771	6 6 2
*	5	3.450	3.452	4 2 0		10	1.694	1.694	9 1 1
*	10	3.156	3.151	4 2 2		"	"	1.694	7 5 3
*	100	2.971	2.971	3 3 3	*	5	1.687	1.684	8 4 2
*	20	2.728	2.729	4 4 0		3	1.644	1.646	6 6 4
	3	2.609	2.609	5 3 1	*	5	1.615	1.618	9 3 1
*	30	2.576	2.573	6 0 0		1	1.577	1.575	8 4 4
*	10	2.444	2.441	6 2 0	*	30	1.551	1.551	7 7 1
*	15	2.356	2.354	5 3 3	*	5	1.514	1.514	$\overline{10}$ 2 0
	3	2.327	2.327	6 2 2	*	15	1.492	1.492	9 5 1
*	55	2.231	2.228	4 4 4					
	60	2.163	2.162	7 1 1					
	"	"	2.162	5 5 1					

114.6 mm Debye-Scherrer powder camera
Cu radiation, Ni-filter ($\lambda CuK\alpha$ = 1.54178 Å)
not corrected for shrinkage
no internal standard
* = reflections used for unit-cell refinement
indexed on *a* = 15.436(4) Å
intensities estimated visually

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 Cu$K\alpha$ 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 *P*4 automated four-circle diffractometer equipped with a serial detector and Mo$K\alpha$ X-radiation. Sixteen reflections over the range $8.7 \leq 2\theta \leq 18.9°$ were centered, and the unit-cell dimension (Table 2) was refined by least-squares from the resultant setting angles. Intensity data were collected in θ–2θ scan-mode at a fixed scan-rate of 1.0° 2θ/min. A total of 1518 reflections was measured over the range $4 \leq 2\theta \leq 60.11°\ 2\theta$. Psi-scan data were measured on seven reflections out to 60°2θ at increments of 5°, and an absorption correction, modeling the crystal as a triaxial ellipsoid, reduced *R*(azimuthal) from 2.2 to 1.2%. The data were corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors; of the 514 unique reflections, 409 were considered as observed [$|F_o| \geq 4\sigma F$].

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods and refined to an *R* index of 4.3% with the Siemens SHELXL97 system of programs (Sheldrick 1997). Scattering curves for neutral atoms were taken from the International Tables for Crystallography (1992). *R* indices are of the form given in Table 2, and are expressed as percentages. Preliminary chemical data indicated that 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 (H_2O) 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*/Å^3. 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 $K_5 Na_2 Cu^{2+}_{24} (CO_3)_{16} Cl_3 (OH)_{20} (H_2O)_{12}$

a (Å)	15.4633(13)	Crystal size (mm)	0.06 x 0.08 x 0.10
V (A^3)	3697.5(1.6)	Radiation	Mo*K*α
Space group	*F*23	2θ-range for data collection (°)	4–60.11
Z	2	*R*(int) (%)	4.5
D_{calc} (g/cm^3)	3.044	Total no. of reflections	1518
Absorption coefficient (mm^{-1})	7.28	Independent reflections	514
F(000)	3288.0	$F_o > 4\sigma F$	409
		Refinement method	Least-squares on F^2; Fixed weights $\propto 1/\sigma(F^2)$
		No. of variables	69
		Goodness of fit on F^2	0.974
		Final R_1 index (%)	4.3
		R index (all data) (%)	5.6
		wR_2 (%)	11.1
		Gof	0.971

$w = 1 / [\sigma^2(F_o^2) + (0.739\ P)^2 + 0.00\ P]$, where $P = (\max(F_o^2,o) + 2F_c^2) / 3$

TABLE 3. ATOM POSITIONS AND ANISOTROPIC-DISPLACEMENT FACTORS FOR $K_5 Na_2 Cu^{2+}_{24} (CO_3)_{16} Cl_3 (OH)_{20} (H_2O)_{12}$

	Wyck.	Sym.	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Cu	48h	1	1.0	0.92670(8)	0.92681(8)	0.78540(7)	0.0427(7)	0.0426(7)	0.0207(5)	–0.0003(5)	0.0000(5)	–0.0222(6)	0.0353(4)
Na	4c	23	1.0	1/4	1/4	1/4	0.044(3)	0.044(3)	0.044(3)	0	0	0	0.044(3)
K	16e	3	0.625(7)	0.3838(3)	0.6162(3)	0.6162(3)	0.060(2)	0.060(2)	0.060(2)	–0.010(2)	0.010(2)	0.010(2)	0.060(2)
C(1)	16e	3	1.0	0.0923(5)	0.9077(5)	0.9077(5)	0.016(2)	0.016(2)	0.016(2)	0.005(3)	–0.005(3)	–0.005(3)	0.016(2)
C(2)	16e	3	1.0	0.8662(5)	0.8662(5)	0.6339(5)	0.023(3)	0.023(3)	0.023(3)	–0.002(3)	–0.002(3)	0.002(3)	0.023(3)
Cl(1)	4b	23	1.0	1/2	1/2	1/2	0.045(2)	0.045(2)	0.045(2)	0	0	0	0.045(2)
Cl(2)	4d	23	0.5*	3/4	3/4	3/4	0.038(4)	0.038(4)	0.038(4)	0	0	0	0.038(4)
O(1)	48h	1	1.0	0.8746(4)	0.0235(4)	0.8752(4)	0.028(3)	0.027(3)	0.026(3)	–0.011(2)	0.004(2)	–0.011(2)	0.027(1)
O(2A)	48h	1	0.5*	0.8526(9)	0.8141(9)	0.5739(9)	0.034(7)	0.032(7)	0.036(7)	0.003(6)	–0.007(6)	0.007(6)	0.036(3)
O(2B)	48h	1	0.5*	0.8134(9)	0.8531(9)	0.5745(9)	0.039(7)	0.028(6)	0.043(8)	–0.003(6)	–0.001(6)	0.009(6)	0.037(3)
O(3)	16e	3	1.0	0.8527(3)	0.8527(3)	0.8527(3)	0.014(2)	0.014(2)	0.014(2)	–0.003(2)	–0.003(2)	–0.003(2)	0.014(2)
O(4)	48h	1	0.5*	–0.0199(9)	0.0205(7)	0.7250(7)	0.06(1)	0.034(8)	0.023(5)	–0.007(5)	0.007(6)	–0.028(7)	0.038(4)
O(5W)	24g	2	1.0	0.0939(1)	1/4	1/4	0.049(6)	0.055(6)	0.058(6)	–0.018(6)	0	0	0.054(3)
H(1)	16e	3	1.0	0.816(1)	0.816(1)	0.816(1)	0.022(3)						
H(2)	24f	2	1.0	0	0	0.6670(9)	0.06(2)						
H(3)	48h	1	1.0	0.060	0.210	0.220	0.081(9)						

* 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, Ca: diopside; K: orthoclase; Cl: tugtupite; As: cobaltite; Ni: pararammelsbergite. Data were reduced using the ϕ(ρZ) 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 *apfu*: $K_{6.97}$ $Na_{1.22}$ $(Cu^{2+}_{22.46}$ $Ni_{0.12}$ $As_{0.15})_{\Sigma 22.73}$ $C_{16.57}$ O_{48} $Cl_{1.97}$ $(OH)_{20}$ $(H_2O)_{12}$. The ideal composition from the crystal structure is K_5 Na_2 Cu^{2+}_{24} $(CO_3)_{16}$ Cl_3 $(OH)_{20}$ $(H_2O)_{12}$. We regard this agreement as reasonable, considering that the crystals decrepitated severely in the electron beam.

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR K_5 Na_2 Cu^{2+}_{24} $(CO_3)_{16}$ Cl_3 $(OH)_{20}$ $(H_2O)_{12}$

Cu–O(1)a		2.187(6)	*K*–O(2A)*	x3/2	3.17(1)
Cu–O(1)b		2.193(6)	*K*–O(2B)*	x3/2	3.18(2)
Cu–O(2A)*	x1/2	1.92(1)	*K*–O(4)	x3/2	2.69(1)
Cu–O(2B)*	x1/2	1.91(1)	*K*–O(5)	x3	2.946(6)
Cu–O(3)		1.925(3)	*K*–*Cl*(1)		3.113(9)
Cu–O(4)c*	x1/2	1.90(1)	<*K*–O>		3.001
Cu–O(4)d*	x1/2	1.91(1)			
<*Cu*–O>		2.025	*C*(1)–O(1)	x3	1.283(6)
O(2A)–O(2B)		0.86(2)	*C*(2)–O(2A)*	x3	1.25(1)
O(4)c–O(4)d		0.88(3)	*C*(2)–O(2B)*	x3	1.25(1)
			<*C*(2)–O>		1.245
Na–O(5)	x6	2.414(2)			

a: *y*+1, *z*, *x*; b: *x*, *y*+1, *z*; c: –*x*+1, –*y*+1, *z*; d: *x*+1, *y*+1, *z*
* the starred bonds to each cation are mutually exclusive

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)a, O(1)b and O(3) (Table 4) have full occupancy (Table 3) and represent the coordinating anions $O_2(OH)$. O(2A), O(2B) and 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_z. The [5]-coordinated polyhedron,

TABLE 5. BOND-VALENCE TABLE FOR K_5 Na_2 Cu^{2+}_{24} $(CO_3)_{16}$ Cl_3 $(OH)_{20}$ $(H_2O)_{12}$

	Cu	*Na*	*C*(1)	*C*(2)	*K*	Σ	H(1)	H(2)	H(3)	Σ
O(1)	0.25 0.25		$1.33^{x3}\downarrow$			1.83			$0.20^{x2}\downarrow$	2.03
O(2A)*	$0.56^{x1/2}\downarrow$			$1.40^{x3/2}\downarrow$	$0.06^{x3/2}\downarrow$	2.02				2.02
O(2B)*	$0.58^{x1/2}\downarrow$			$1.40^{x3/2}\downarrow$	$0.06^{x3/2}\downarrow$	2.04				2.04
O(3)	$0.50^{x3}\rightarrow$					1.50	0.75			2.25
O(4)	$0.54^{x1/2}\downarrow$ $0.54^{x1/2}\downarrow$				$0.20^{x3/2}\downarrow$	1.28		0.90		2.18
O(5)		$0.19^{x6}\downarrow$			$0.11^{x3}\downarrow^{x2}\rightarrow$	0.41			$0.8^{x2}\downarrow\rightarrow$	2.01
Cl(1)					$0.20^{x4}\rightarrow$	0.80		$0.10^{x3}\rightarrow$		1.10
Cl(2)							$0.25^{x4}\rightarrow$			1.00
Σ	2.11	1.15	3.99	4.20	1.01		1.00	1.00	2.00	

Bond-valence curves are from Brown & Altermatt (1985);
* the starred entries are mutually exclusive for each cation.

TABLE 6. HYDROGEN BONDING IN K_5 Na_2 Cu^{2+}_{24} $(CO_3)_{16}$ Cl_3 $(OH)_{20}$ $(H_2O)_{12}$

D–H...A (Å)	D–A (Å)	D–H (Å)	H...A (Å)	∠D–H...A (°)	∠H(3)–O(5)w–H(3)' (°)
O(3)–H(1)...*Cl*(2)	2.752(8)	1.20	1.53	180	–
O(4)–H(2)...*Cl*(1)	3.51(1)	1.02	2.51	151.21	–
O(5)–H(3)...O(1) x2	2.940(6)	0.93	2.04	159.27	136.6

$[Cu^{2+} O_3 (OH)_2]^{6-}$, has a <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_2O) 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 *Cl*(1) sites are completely occupied to give an average coordination number of [8.5] and a <K–ϕ> distance of 3.001 Å for the polyhedron $[K\,O_3\,(OH)_{1.5}\,(H_2O)_3\,Cl]^{7.5-}$. There are two *C* sites, *C*(1) and *C*(2), with point symmetry 3, that are occupied by C atoms with <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

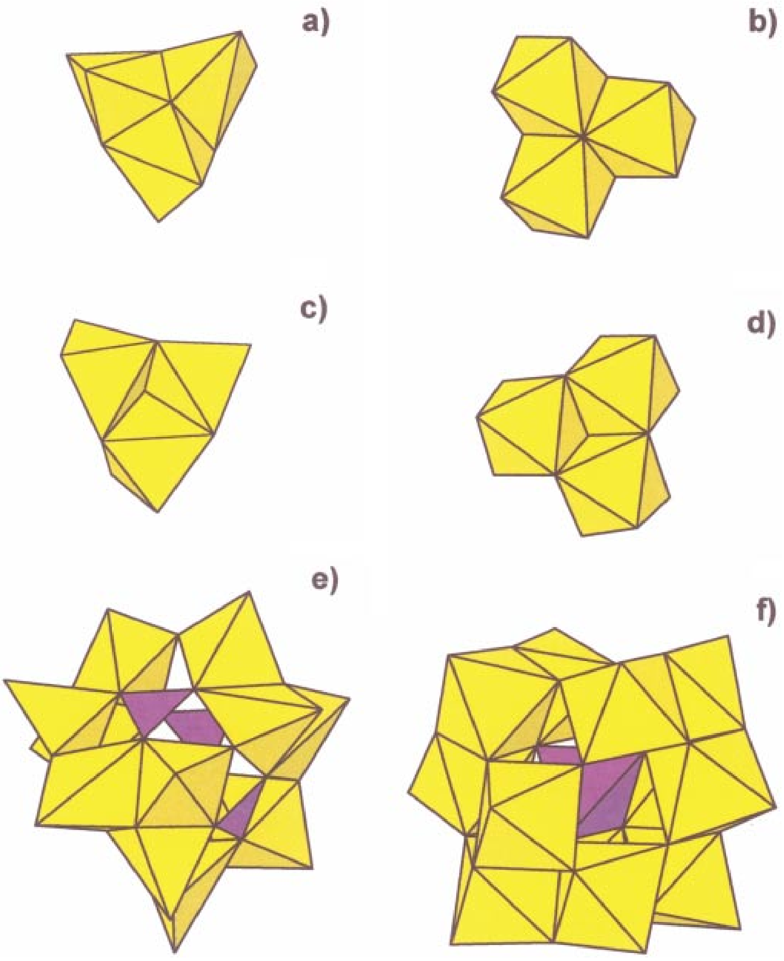

FIG. 1. Fragments of the crystal structure of $K_5\,Na_2\,Cu^{2+}_{24}\,(CO_3)_{16}\,Cl_3\,(OH)_{20}\,(H_2O)_{12}$ and murataite, $(Y,Na)_6\,(Zn,Fe)_5\,Ti^{4+}_{12}\,O_{29}\,(O,F)_{10}\,F_4$. (a) A trimeric $[Cu^{2+}_3\,O_6\,(OH)_4]^{10-}$ cluster of [5]-coordinated $(Cu^{2+}\phi_5)$ polyhedra shown from one side. (b) A trimeric $[Ti^{4+}_3O_{12}]^{12-}$ cluster of $(Ti^{4+}O_6)$ octahedra shown from one side. (c) A trimeric $[Cu^{2+}_3\,O_6\,(OH)_4]^{10-}$ cluster of [5]-coordinated $(Cu^{2+}_{12}\phi_5)$ polyhedra shown from the other side. (d) A trimeric $[Ti^{4+}_3O_{12}]^{12-}$ cluster of $(Ti^{4+}O_6)$ octahedra shown from the other side. (e) A sixteen-membered $[Cu^{2+}_{12}\,(CO_3)_4\,O_{12}\,(OH)_8]^{8+}$ cluster of twelve $(Cu^{2+}\phi_5)$ 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 $(Cu^{2+}\phi_5)$ 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 *C*(2) site is surrounded by three O(2A) atoms and three O(2B) atoms, each of which is half-occupied, giving two triangular arrangements, $C(2)O(2A)_3$ and $C(2)O(2B)_3$, that are rotated 60° relative to each other.

Structure topology

In the structure of $K_5\,Na_2\,Cu^{2+}_{24}\,(CO_3)_{12}\,Cl_3\,(OH)_{20}\,(H_2O)_{12}$, $[Cu^{2+}\,O_3\,(OH)_2]$ polyhedra link through common edges to form the trimeric $[Cu^{2+}_3\,O_6\,(OH)_4]^{10-}$ 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 ordered (CO_3) groups (Fig. 2a). Each (CO_3) group shares common vertices with three $[Cu^{2+}_{12}\,(CO_3)_4\,O_{12}\,(OH)_8]^{8+}$ 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↻], and incorporate K and *Cl*(1) atoms (Fig. 2a) in linear arrays along the channel. Smaller channels extend along [001↻] and contain alternating Na and *Cl*(2) atoms (Fig. 2b). There are two types of cages that incorporate Cl atoms. Intersection of two [110] channels gives rise to a cage that contains *Cl*(1) 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↻] 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 the O(3) site, and accepts hydrogen bonds from the H(1) atoms (Tables 5, 6). As all three atoms, Cl(2), H(1) and O(3), are situated on a 3-fold axis, this hydrogen bond is ideally linear, *i.e.*, D–H…A = 180°. There may be disorder of the H(1) atom off the 3-fold axis, but we cannot see such disorder in the refined structure. The *Cl*(1) atom is surrounded by a tetrahedral arrangement of four K atoms and also by twelve O(4) sites with 50% occupancy or by six hydrogen atoms H(2) (Fig. 3b). Table 5 shows an excess of bond valence at the Cl(1) atom, 1.4 *vu* instead of 1.0 *vu*, probably resulting from disorder of the donor O(4) atom.

The $(Na\{H_2O\}_6)$ octahedra are also situated in the intersection of three [001↻] channels. There is hydrogen bonding between the H(3) atoms of the (H_2O) group at O(5) and two O(1) atoms of the $\{C(1)O_3\}$ group (Fig. 3c, 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_2O) 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 $K_5\,Na_2\,Cu^{2+}_{24}\,(CO_3)_{16}\,Cl_3\,(OH)_{20}\,(H_2O)_{12}$ 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 $(Y,Na)_6\,(Zn,Fe)_5\,Ti^{4+}_{12}\,O_{29}\,(O,F)_{10}\,F_4$. Murataite is cubic, $F43m$, a 14.886(2) Å, $Z = 4$ (Ercit & Hawthorne 1995). The crystal structure of murataite contains thirteen-membered $[Ti^{4+}_{12}\,Zn\,O_{40}]^{30-}$ clusters topologically similar to the sixteen-membered $[Cu^{2+}_{12}\,(CO_3)_4\,O_{12}\,(OH)_8]^{8+}$ cluster in our compound. Figure 1 shows a triplet of [5]-coordinated $(Cu^{2+}O_5)$ 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 $(Cu^{2+}\phi_5)$ 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 $(Cu^{2+}\phi_5)$ polyhedra is empty, and the sides occlude (CO_3) triangles. In murataite, a (ZnO_4) tetrahedron occupies the central cage of the cluster. This (ZnO_4) 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.

TABLE 7. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA (*apfu*) FOR $K_5\,Na_2\,Cu^{2+}_{24}\,(CO_3)_{16}\,Cl_3\,(OH)_{20}\,(H_2O)_{12}$

	EMPA	Calc.			Ideal
CuO	50.92	56.33	Cu	23.38	24.00
NiO	0.25	–	Ni	0.12	–
As_2O_3	0.41	–	As	0.15	–
K_2O	9.36	6.95	Σ	23.65	24.00
Na_2O	1.08	1.83			
CO_2	19.28*	20.78	K	7.26	5.00
Cl	1.95	3.14			
H_2O	10.85*	11.69	Na	1.27	2.00
O=Cl	–0.44	–0.71	C	16.00	16.00
Total	93.66	100.00	Cl	2.00	3.00

*calculated from structure refinement and determined by stoichiometry

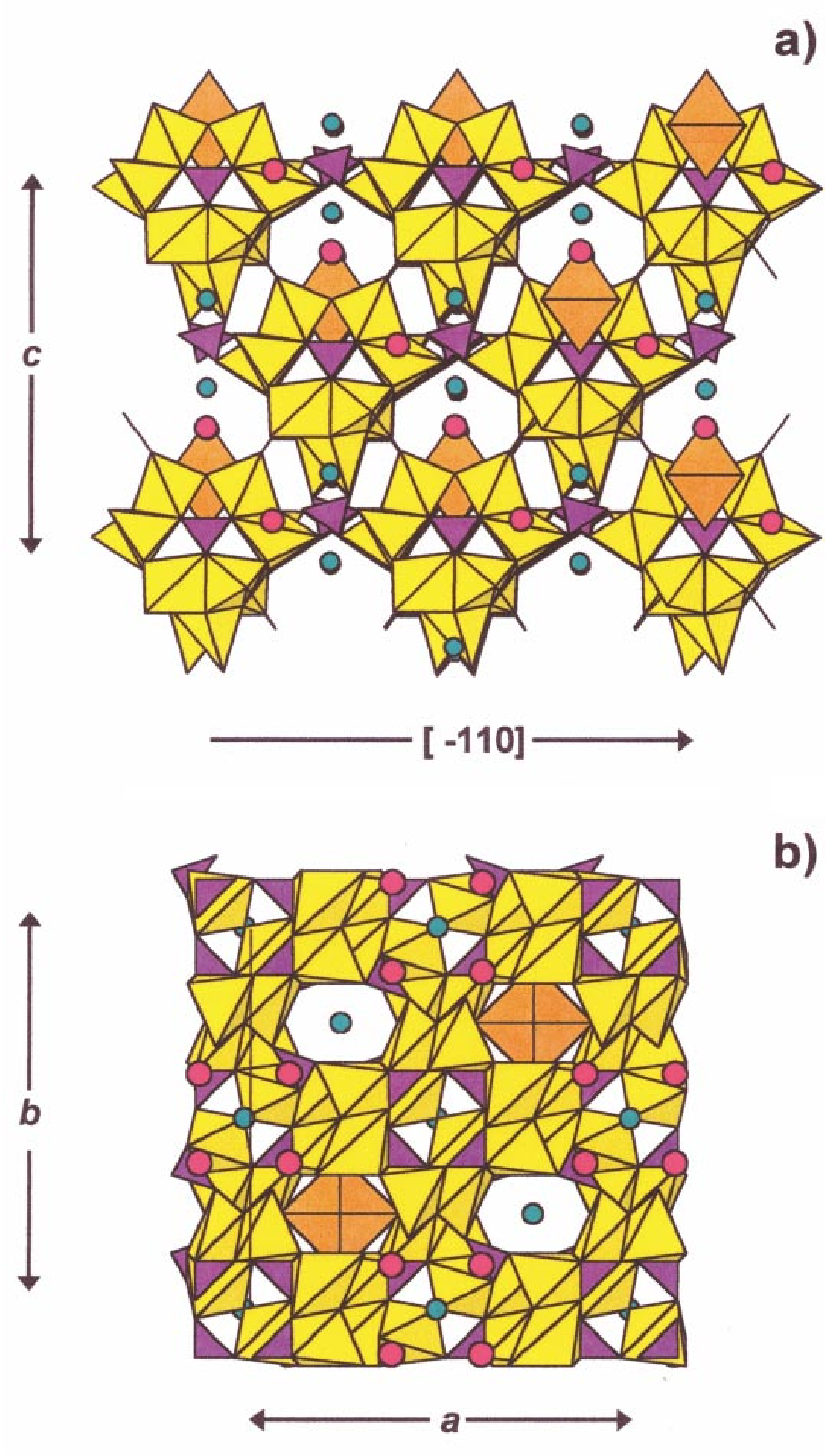

FIG. 2. Projection of the crystal structure of $K_5 Na_2 Cu^{2+}_{24} (CO_3)_{16} Cl_3 (OH)_{20} (H_2O)_{12}$ (a) onto (110), and (b) onto (001). The ($Cu^{2+}\phi_5$) polyhedra are yellow, ($Na\phi_6$) octahedra are orange, (CO_3) groups are violet, Cl and K atoms are shown as large green and magenta circles. The figure is drawn with average positional parameters for O(4) and with O(2A) only.

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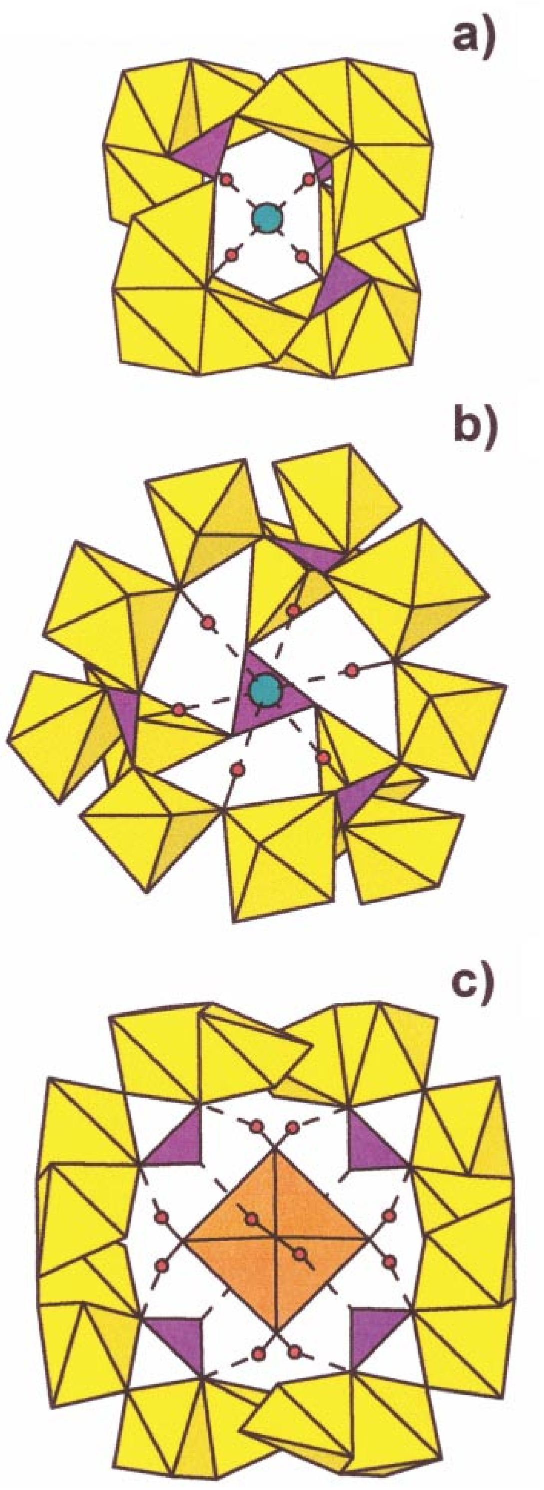

FIG. 3. Details of the hydrogen bonding in the crystal structure of $K_5\ Na_2\ Cu^{2+}_{24}\ (CO_3)_{16}\ Cl_3\ (OH)_{20}\ (H_2O)_{12}$. (a) The *Cl*(2) atom tetrahedrally coordinated by H(1) atoms of OH groups {O(3)}. (b) The *Cl*(1) atom bonded to six half-occupied H(2) atoms that are part of the (OH) group at O(4). (c) Hydrogen bonds between the H(3) atoms of the (H_2O) groups coordinating Na and the O(1) anion that is part of the {*C*(1)O_3} 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)].