Structure of ungemachite, $K_3Na_8Fe^{3+}(SO_4)_6(NO_3)_2 \cdot 6H_2O$, a mixed sulfate-nitrate mineral

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Abstract

The crystal structure of ungemachite, $K_3Na_8Fe^{3+}(SO_4)_6(NO_3)_2 \cdot 6H_2O$, trigonal-rhombohedral, $a = 10.898(1)$, $c = 24.989(6)$ Å, $V = 2570.2(9)$ Å³, space group R$\bar{3}$, $Z = 3$, was solved by trial-and-error and difference Fourier methods, and refined to an R index of 3.9% using 1421 observed ($\geq 4\sigma F$) reflections. The refined structure contains hitherto unrecognized nitrate groups, making it only the second mixed sulfate-nitrate mineral known.

The *fundamental building block* of the structure is an $[Fe^{3+}(SO_4)_6]$ heteropolyhedral finite cluster that is centered on the threefold axes of the unit cell. These clusters link via trigonal prismatic–coordinated Na to (NO_3) groups on adjacent threefold axes, forming a sheet parallel to {001}; further intrasheet linkage is provided by ten-coordinate K. Each (FeO_6) octahedron shares two faces with $[NaO_3(H_2O)_3]$ octahedra to form a linear octahedral trimer parallel to [001]. The only intersheet linkage is provided by hydrogen bonds from these (H_2O) groups to adjacent sulfate groups from neighboring layers. This weak intersheet bonding accounts for the perfect {001} cleavage in ungemachite.

Introduction

Ungemachite is a complex hydrated sulfate mineral discovered by Bandy (1938) in his classic work on the mineralogy of the northern Chile sulfate deposits. The detailed mineralogy was described by Peacock and Bandy (1938) who recognized two polymorphs, rhombohedral ungemachite and monoclinic clino-ungemachite, the latter being extremely rare. Ungemachite occurs in massive iron sulfate "veins" that have formed by oxidation of the primary pyrite in the Chuquicamata deposit in northern Chile. These veins are principally massive jarosite and metasideronatrite, with ungemachite occurring as granular vein fillings and vug linings, associated with metavoltine, fibroferrite, and sodium alum. Our interest in the structure of ungemachite stems from a long-term study of the relationship between crystal structure and paragenesis in these secondary sulfate deposits.

Experimental details

The crystals used in this work are from Chuquicamata, Chile, and are from the original material collected by Bandy (1938); they were obtained from the Harvard University Mineralogical Museum, catalog number 98283, through the courtesy of Dr. Carl Francis.

X-ray precession photographs confirmed the rhombohedral symmetry and cell dimensions assigned by Peacock and Bandy (1938). A crystal was mounted on a Nicolet R3m automated four-circle diffractometer, and the cell dimensions were refined from the setting angles of 25 automatically aligned intense reflections. The (hexagonally constrained) cell dimensions are listed in Table 1, together with other information pertinent to data collection and refinement. Intensity data were collected according to the experimental procedure of Hawthorne and Groat (1985).

A total of 1928 reflections were collected out to a maximum 2θ of 60°. An empirical absorption correction was applied (ψ-scan method), reducing R (symmetric) for the azimuthal data from 1.3% to 1.0%. Lorentz, polarization, and background corrections were done, and the data were reduced to structure factors; of the 1692 unique reflections, 1421 were classed as observed ($\geq 4\sigma F$).
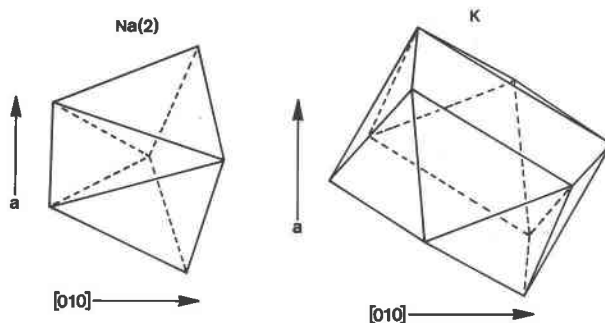
Solution and refinement

Scattering curves for neutral atoms together with anomalous dispersion coefficients were taken from Cromer and Mann (1968) and Cromer and Libermann (1970). R indices are of the form given in Table 1 and are expressed as percentages.

Peacock and Bandy (1938) assigned the point symmetry $\bar{3}$ to ungemachite. The distribution of E values indicated the presence of a center of symmetry, and the space group R$\bar{3}$ was assumed. The solution of the structure was an interesting problem, as the complex formula placed considerable restrictions on the equipoints occupied by the various atoms. There are 3 Fe atoms in the cell, and hence Fe can be placed at the $3a$ position (0,0,0). There are 9 K atoms, and these can occupy the $9e(\frac{1}{2},0,0)$, $9d(\frac{1}{2},0,\frac{1}{2})$ or $6c(0,0,z) + 3b(0,0,\frac{1}{2})$ positions. There are 24 Na atoms in the cell, and as the rank of the general equipoint is 18, the $6c(0,0,z)$ position must be occupied by Na. Consequently, there are a limited number of possibilities for the placement of these atoms; the z coordinate of position $6c$ is the only variable, and this may be determined by trial-and-error. In fact, the first solution tried gave an R index of 60% (not normally significant) and a strong peak on the difference Fourier map. Inclusion of this position as S gave an R index of 45% and showed additional atom

Table 1. Miscellaneous information on ungemachite

	Crystal size (mm)	0.29x0.15x0.11
a = 10.898(1)	Rad/Mono	MoKα/Graphite
c = 24.989(6)	Total Unique $|F_0|$	1692
V = 2570.2(9)	No. of $|F_0|>4\sigma$	1421
	R (observed)	3.9%
Space Group R$\bar{3}$	R_W (observed)	4.1%

Unit cell contents: $3[Fe^{3+}K_3Na_8(SO_4)_6(NO_3)_2 \cdot 6H_2O]$

$R = \Sigma(|F_0|-|F_c|)/\Sigma|F_0|$

$R_W = [\Sigma w(|F_0|-|F_c|)^2/\Sigma wF_0^2]^{\frac{1}{2}}, w=1$

Table 3. Selected bond distances (Å) in ungemachite

Fe-O(1)b	1.994(2) x6	Na(1)-O(1)b	2.492(3) x3
S-O(1)	1.512(2)	Na(1)-O(5)	2.329(4) x3
S-O(2)	1.457(2)	<Na(1)-O>	2.411
S-O(3)	1.465(3)		
S-O(4)	1.461(3)	Na(2)-O(2)g	2.336(3)
<S-O>	1.474	Na(2)-O(3)h	2.437(2)
		Na(2)-O(4)i	2.392(3)
N-O(6)	1.249(2) x3	Na(2)-O(5)j	2.359(3)
		Na(2)-O(6)	2.552(4)
K-O(2)a,b	2.953(3) x2	Na(2)-O(6)k	2.550(3)
K-O(2)c,d	2.918(2) x2	<Na(2)-O>	2.438
K-O(3)a,b	2.859(3) x2		
K-O(4)c,d	2.997(3) x2	O(5)-H(5)A	0.85(3)
K-O(6)e,f	3.041(3) x2	O(5)-H(5)B	0.81(3)
<K-O>	2.954	O(5)-O(4)	2.788(3)
		H(5)A-O(4)	1.95(4)
		O(5)-O(3)	2.768(3)
		H(5)B-O(3)	1.97(4)

a: 1/3+x,2/3+y-1,2/3+z-1; b: 2/3-x,1/3-y,1/3-z; c: 1/3-y,
2/3+x-y,2/3+z-1; d: 2/3+y,1/3-x+y,1/3-z; e: x,y-1,z; f:
1-x,1-y,-z; g: 1/3+x,2/3+y,2/3+z-1; h: 2/3+x-y,1/3+x,1/3-z;
i: 2/3+y,1/3-x+y,1/3-z; j: y-x+1,x̄,z; k: y-x,x̄,z; l: 2/3+y
-1,1/3+y-x,1/3-z; m: ȳ,x-y,z; n: 2/3+x-y-1,1/3+x-1,1/3-z.

positions on the difference Fourier map. Continuation of this process resulted in convergence at an R index of 8.5% for individual isotropic temperature factors. It was apparent at this stage that the formula previously assigned to ungemachite was not correct. Occupying the $6c$ position was an atom coordinated by a triangle of oxygen atoms, with a bond length of approximately 1.25 Å. A bond-valence calculation, using the parameters of Brown (1981), identified the H_2O groups in the structure and indicated this unknown atom to be pentavalent; also for the cell content to be neutral, this additional atom had to be pentavalent, and the mean bond length indicated the cation to be N^{5+}. Insertion of this scatterer, together with conversion of all temperature factors to an anisotropic form, resulted in convergence at an R index of 4.1%. A difference Fourier map calculated at this stage showed two peaks, each approximately 1 Å away from O(6), the H_2O group. Insertion of these two hydrogen atoms and least-squares refinement of all variables converged to an R index of 3.9%.

We noted that the structure has pseudomirror symmetry and tried refinement in the space group R$\bar{3}$m; an isotropic thermal model would not refine below an R index of 17.7% in R$\bar{3}$m, and this model was not pursued further.

Final parameters are given in Table 2, interatomic distances and angles in Tables 3 and 4, and an empirical bond-valence calculation (Brown, 1981) in Table 5. Observed and calculated structure factors are listed in Table 6.[1]

STRUCTURE DESCRIPTION

There is one unique N atom position that has planar triangular coordination and occupies the $6c$ position with point symmetry 3; consequently all three N–O distances are symmetrically equivalent and the observed N–O distance of 1.249(2) Å is typical of values observed in well-refined structures. Note the short O–O distances that are characteristic of triangular (NO_3) groups. There is one unique sulfur atom that occupies the general position $18f$ and is tetrahedrally coordinated by oxygen atoms; the observed geometry of the (SO_4) group falls within the normal range observed in orthosulfate structures. There is one unique Fe^{3+} cation occupying the $3a$ position; the point symmetry of this position is $\bar{3}$, and the cation is

[1] To obtain a copy of Table 6, order Document AM-86-307 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006. Please remit $5.00 in advance for the microfiche.

Table 2. Atomic parameters for ungemachite

	x	y	z	U_{11}	U_{22}	U_{33}	U_{11}	U_{13}	U_{23}	$U_{equiv.}$
Fe	0	0	0	92(3)	92(3)	84(4)	46(1)	0	0	89(2)
S	0.34609(7)	0.17748(7)	0.27813(3)	97(3)	134(3)	130(3)	56(2)	-18(2)	-9(2)	121(2)
N	1/3	2/3	0.0951(2)	215(14)	215(14)	245(24)	108(7)	0	0	225(12)
K	1/2	0	0	198(4)	295(5)	263(5)	153(4)	2(4)	-27(4)	239(4)
Na(1)	0	0	0.1285(1)	255(7)	255(7)	168(10)	127(4)	0	0	226(6)
Na(2)	0.6440(1)	0.8170(1)	0.09069(5)	248(7)	216(6)	238(6)	119(5)	-35(5)	-16(5)	232(5)
O(1)	0.5046(2)	0.2737(3)	0.28304(8)	91(9)	283(12)	163(10)	49(8)	-34(7)	3(8)	199(8)
O(2)	0.2824(4)	0.1394(3)	0.33119(9)	182(10)	266(12)	164(10)	89(9)	54(8)	42(9)	214(9)
O(3)	0.2953(3)	0.2600(3)	0.24891(9)	212(11)	212(11)	253(12)	135(9)	-49(9)	19(9)	213(9)
O(4)	0.3212(3)	0.0515(3)	0.2485(1)	301(13)	202(11)	277(12)	152(10)	-89(10)	-118(9)	248(10)
O(5)	0.1200(3)	-0.1006(3)	0.1700(1)	241(12)	245(12)	158(10)	71(10)	-12(9)	23(9)	237(9)
O(6)	0.4016(3)	0.7990(3)	0.0951(1)	285(13)	165(12)	552(18)	73(10)	-8(12)	-4(11)	352(11)
H(5)A	0.774(4)	-0.181(4)	0.192(1)	-	-	-	-	-	-	100*
H(5)B	0.772(4)	-0.066(4)	0.190(1)	-	-	-	-	-	-	100*

Table 4.   Selected polyhedral edge-lengths (Å) and angles (°) in
ungemachite

O(1)b-O(1)l	2.680(4) ×6	O(1)b-Fe-O(1)l	84.5(1) ×6
O(1)b-O(1)c	2.952(4) ×6	O(1)b-Fe-O(1)c	95.5(1) ×6
<O-O>Fe	2.816	<O-Fe-O>	90.0
O(1)-O(2)	2.431(3)	O(1)-S-O(2)	109.9(1)
O(1)-O(3)	2.369(4)	O(1)-S-O(3)	105.4(1)
O(1)-O(4)	2.400(3)	O(1)-S-O(4)	107.7(2)
O(2)-O(3)	2.406(4)	O(2)-S-O(3)	110.8(2)
O(2)-O(4)	2.402(4)	O(2)-S-O(4)	110.8(2)
O(3)-O(4)	2.425(4)	O(3)-S-O(4)	112.0(2)
<O-O>S	2.406	<O-S-O>	109.4
O(6)-O(6)k	2.164(3) ×3	O(6)-N-O(6)k	120.0(1) ×3
O(1)b-O(1)n	2.680(4) ×3	O(1)b-Na(1)-O(1)n	65.1(1) ×3
O(1)b-O(5)	3.378(5) ×3	O(1)b-Na(1)-O(5)	88.9(1) ×3
O(1)b-O(5)m	3.695(5) ×3	O(1)b-Na(1)-O(5)m	100.0(1) ×3
O(5)-O(5)m	3.610(4) ×3	O(5)-Na(1)-O(5)m	101.6(1) ×3
<O-O>Na(1)	3.341	<O-Na(1)-O>	88.9
O(2)g-O(3)h	3.334(4)	O(2)g-Na(2)-O(3)h	88.6(1)
O(2)g-O(4)i	3.273(5)	O(2)g-Na(2)-O(4)i	87.6(1)
O(2)g-O(6)	3.344(5)	O(2)g-Na(2)-O(6)	86.2(1)
O(2)g-O(6)k	3.361(4)	O(2)g-Na(2)-O(6)k	86.8(1)
O(3)h-O(5)j	3.230(4)	O(3)h-Na(2)-O(5)j	84.9(1)
O(3)h-O(6)k	3.177(4)	O(3)h-Na(2)-O(6)k	79.1(1)
O(4)i-O(5)j	3.219(4)	O(4)i-Na(2)-O(5)j	85.1(1)
O(4)i-O(6)	3.216(4)	O(4)i-Na(2)-O(6)	81.1(1)
O(5)j-O(6)	4.195(5)	O(5)j-Na(2)-O(6)	117.3(1)
O(5)j-O(6)k	4.180(5)	O(5)j-Na(2)-O(6)k	116.7(1)
O(6)-O(6)k	2.164(3)	O(6)-Na(2)-O(6)k	50.1(1)
<O-O>Na(2)	3.336	<O-Na(2)-O>	87.6

octahedrally coordinated by six oxygens. All six Fe–O bonds are equivalent, and the bond lengths and angles of the (FeO$_6$) octahedron fall well within the ranges of values normally shown in Fe^{3+} minerals. There are two unique Na atoms, occupying the 6c and 18f positions, respectively. Na(1) is octahedrally coordinated by three oxygen atoms and three (H$_2$O) groups, all (H$_2$O) groups being *cis* to each other. Na(2) is coordinated by five oxygens and one (H$_2$O) group, in a distorted trigonal prismatic arrangement (Fig. 1). There is one unique K atom occupying the 9e position and coordinated by ten oxygen atoms in the arrangement shown in Figure 1.

The *fundamental building block* (fbb) of the structure is the [(Fe^{3+}(SO$_4$)$_6$] heteropolyhedral cluster that is shaded in Figures 2–4. These clusters are centered on the $\bar{3}$-fold axes of the cell, being situated at $z = 0$ on the axes through the lattice points (Fig. 2) and at $z = \frac{1}{3}$ and $\frac{2}{3}$ at the $(\frac{2}{3}, \frac{1}{3}, z)$ and $(\frac{1}{3}, \frac{2}{3}, z)$ threefold axes, respectively. Each (FeO$_6$) octahedron shares two (*trans*) faces with (Na(1)O$_3$(H$_2$O)$_3$) octahedra to form a face-sharing linear trimer parallel to

Fig. 1.   Selected coordination polyhedra in ungemachite: left— the Na(2)ϕ_6 distorted trigonal prism; right—the Kϕ_{10} polyhedron.

the c axis (Fig. 3). Each of the three (H$_2$O) groups of the Na(1) octahedron hydrogen-bonds to oxygens of neighboring sulfate groups attached to the fbb at $z = \pm\frac{1}{3}$. Each Na(2) atom bonds to the neighboring [Fe^{3+}(SO$_4$)$_6$] heteropolyhedral cluster and also has two bonds with a nitrate group that lies on the adjacent $\bar{3}$-fold axis. Because of the local point symmetry, each nitrate group bonds to a triangular arrangement of Na(2) atoms, and these bonds cross-link the finite heteropolyhedral clusters into a continuous sheet parallel to {001}, as shown in Figure 2. Additional linkage is provided by the ten-coordinate K atoms that link clusters centered on adjacent lattice points. Figure 3 shows this sheet seen "edge on"; this view shows the difference in level of the nitrate groups on either side of the K atom.

The only linkage between these sheets is the hydrogen-bonding between O(5), the (H$_2$O) group, and the O(3) and O(4) oxygens bonded to the neighboring sulfate groups in the adjacent sheet (Fig. 4). This weak bonding between sheets accounts for the perfect {001} cleavage shown by ungemachite.

A bond-valence analysis, calculated from the curves of Brown (1981), is given in Table 5. This supports the cation coordination numbers and hydrogen-bond arrangement reported here. The hydrogen-bond valences were arbi-

Table 5.   Empirical bond-valence (v.u.) table for ungemachite

	S	N	K	Na(1)	Na(2)	Fe	H(5)A	H(5)B	Σ
O(1)	1.352			0.158$^{×3}_↓$	0.524$^{×6}_↓$				2.034
O(2)	1.584		0.094$^{×2}_↑$ 0.104$^{×2}_↓$		0.209				1.991
O(3)	1.548		0.126$^{×2}_↓$		0.174			0.20	2.048
O(4)	1.566		0.082$^{×2}_↓$		0.189	0.20			2.037
O(5)				0.212$^{×3}_↓$	0.201		0.80	0.80	2.013
O(6)		1.718$^{×3}_↓$	0.072$^{×2}_↓$		0.143 0.144				2.077
Σ	6.050	5.154	0.956	1.110	1.060	3.140	1.00	1.00	
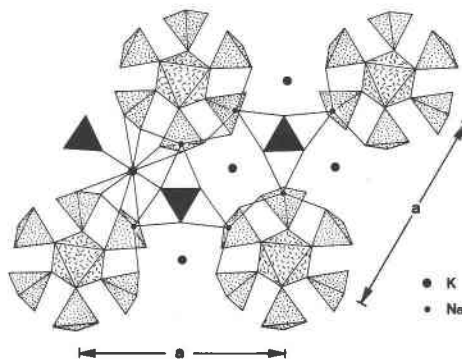
Fig. 2.   The structure of ungemachite viewed down [001]. (FeO$_6$) octahedra are dashed, (SO$_4$) tetrahedra are dotted, (NO$_3$) triangles are black. Note the prominent [Fe^{3+}(SO$_4$)$_6$] finite clusters that constitute the fundamental building block of the structure.

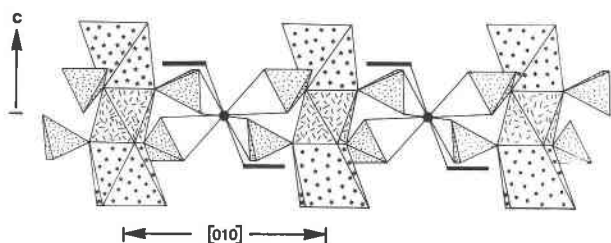Fig. 3. The structure of ungemachite viewed down [010]; legend as in Fig. 2. (Na(1)ϕ_6) octahedra are starred, and the (NO$_3$) triangles, seen edge-on, are thickened for emphasis. Note that the structure forms a continuous sheet at $z = 0$.

trarily assigned as 0.80 and 0.20 v.u. (valence units) to the donor and acceptor anions, and this produces satisfactory bond-valence sums for all anions. The ob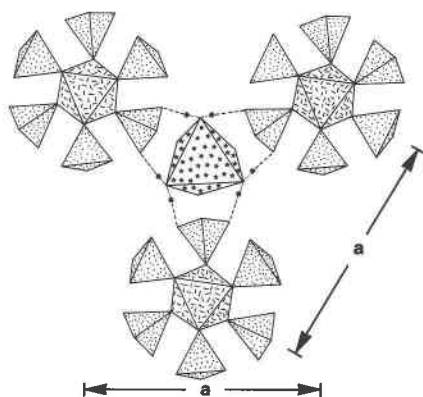served geometry (Table 3) falls within the range normally encountered in X-ray studies, and the fact that hydrogen-bonding is the only linkage between layers attests to the important role played by bonded (H$_2$O) groups in this structure.

Fig. 4. The hydrogen-bonding arrangement in ungemachite; (H$_2$O) groups bonded to Na(1) cations hydrogen-bond to sulfate oxygens in the adjacent sheet. This provides the only intersheet linkage in this structure.

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