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THE CRYSTAL STRUCTURE OF RANSOMITE

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ABSTRACT

The crystal structure of ransomite, $CuFe_2(SO_4)_4 \cdot 6H_2O$, is monoclinic, $P2_1/c$, and has been refined to $R=0.12$. Iron coordination octahedra with an average Fe—O distance of 1.98 Å are concentrated in bands one octahedron wide and two deep which extend in the *a* axial direction. Individual iron octatehedra of the bands are linked by sulfate tetrahedra and translational equivalent bands are connected through these tetrahedra by distorted copper coordination octahedra to form sheets parallel to (010). The sheets are joined by hydrogen bonds to account for the perfect {010} cleavage. Two groups of Cu—O bonds of the distorted copper coordination octahedron average 1.99 Å and 2.44 Å. A short S—O bond of 1.41 ± 0.01 Å is noted in one of the sulfur coordination tetrahedra.

The complexity of metal sulfate hydrate structures is suggested to be a function of the percentage of oxygen atoms of the sulfate tetrahedra that are involved in coordination of the metal cations of the structure.

INTRODUCTION

Recent classifications of sulfate and hydrated sulfate minerals (Bokij and Gorogotskaya, 1969; and Wood, 1969) have paralleled the studies of several sulfate crystal structures. Sulfate hydrates containing both divalent and trivalent metal cations, however, have received little attention compared to minerals containing a single metal cation species. Investigation of these more complex structures is critical to the refinement of the sulfate classification scheme.

Ransomite, $CuFe_2(SO_4)_4 \cdot 6H_2O$, occurs only in the United Verde mine at Jerome, Arizona where it formed as the result of a mine fire. The mineral, as described by Lausen (1928), is an easily soluble sulfate which forms pale-blue crusts and tufts of small radiating crystals in cavities in the crushed rocks. Although previously reported as orthorhombic with seven water molecules, X-ray and structure studies show it to be monoclinic, $P2_1/c$, and to contain six water molecules. Cell data for ransomite is presented in Table 1.

EXPERIMENTAL DATA

Intensity data for ransomite were collected by Weissenberg camera from a cleavage fragment of the mineral which measured approximately 0.06 mm by 0.10 mm by 1.00 mm and which was rotated around the elongated axis. Ni-filtered Cu radiation was used and an absorption correction was made by applying cylindrical transmission factors (Lonsdale and Kasper, 1959), modified graphically for the roughly elliptical cross section of the crystal, to 1186 observed reflections.

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TABLE 1. STRUCTURE CELL DATA FOR RANSOMITE

a	4.811(2)
b	16.217(4)
c	10.403(2)
β	93°01′(02′)
Z	2 [$CuFe_2(SO_4)_4 \cdot 6H_2O$]
V	810.5 Å^3
Space group	$P2_1/c$

STRUCTURE DETERMINATION

The two symmetry related copper atoms in the cell were assigned to positions on centers of symmetry at the origin of the cell. The remaining independent iron and two sulfur atoms were then located routinely from the three dimensional Patterson map. The oxygen atoms of the sulfate groups and of the six water molecules were obtained from difference Fourier synthesis.

A full-matrix least-squares refinement (Busing, Martin, and Levy, 1962) with isotropic temperature factors was begun at an R value of 0.40 and was terminated after three cycles with an R value of 0.14. Three strong low-theta reflections (031, 131, and $12\bar{2}$) showing extinction effects were eliminated and two additional refinement cycles then lowered R to a final value of 0.12. The positional and thermal parameters for ransomite

TABLE 2. POSITIONAL AND THERMAL PARAMETERS FOR RANSOMITE

	x	y	z	B
Cu	0.0	0.0	0.0	1.33(8)
Fe	.7377(6)	.6272(1)	.0223(2)	0.81(6)
S(1)	.7906(9)	.2869(2)	.1399(3)	0.82(7)
S(2)	.2502(8)	.5298(2)	.1704(3)	0.60(7)
O(1)	.0309(26)	.2144(6)	.5549(10)	1.57(19)
O(2)	.5880(26)	.1470(6)	.5927(9)	1.62(17)
O(3)	.6687(30)	.2922(7)	.6322(7)	2.33(22)
O(4)	.8927(28)	.1906(7)	.7713(11)	2.05(21)
O(5)	.1427(25)	.4554(6)	.0999(9)	1.24(16)
O(6)	.0705(26)	.5999(6)	.1405(9)	1.25(17)
O(7)	.5340(25)	.5474(5)	.1267(9)	1.17(16)
O(8)	.2717(26)	.5128(6)	.3098(10)	1.58(18)
$O_w(1)$	.7150(26)	.0661(6)	.9072(9)	1.28(17)
$O_w(2)$	.3508(26)	.2814(6)	.8570(9)	1.18(17)
$O_w(3)$	.1937(31)	.1065(7)	.0483(12)	2.40(22)

Standard errors in the last decimal places are in brackets. Oxygens of the water molecules are represented as O_w.

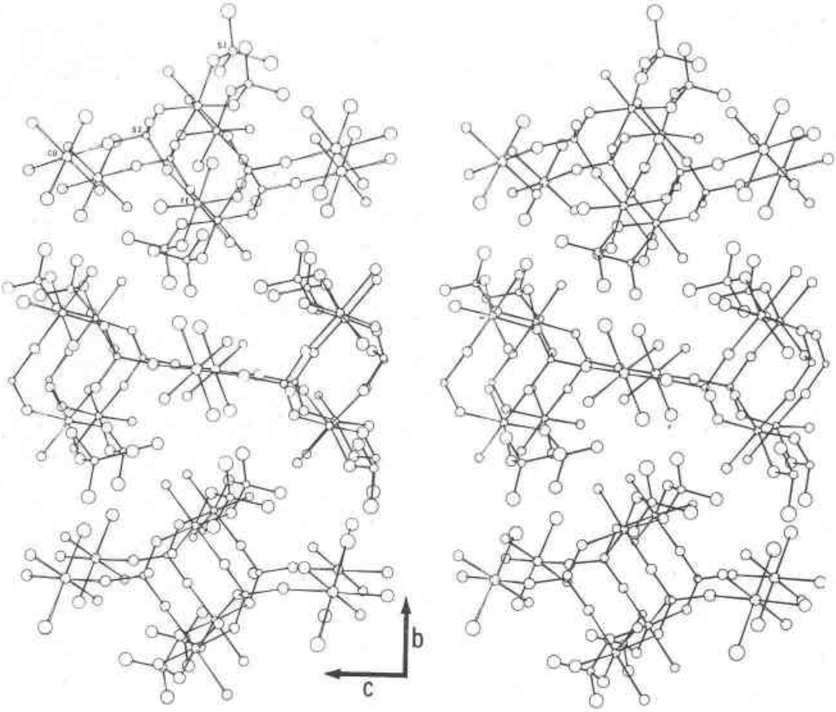

FIG. 1. Stereoscopic view of the structure of ransomite approximately normal to (100).

are given in Table 2, and observed and calculated structure factors are listed in Table 4.[1]

DESCRIPTION OF THE STRUCTURE

The structure of ransomite contains chains and bands of interconnecting octahedral and tetrahedral coordination polyhedra arranged to form sheets. A stereoscopic view of the structure in Figure 1 shows that the iron octahedra are concentrated in bands of infinite length one octahedron wide and two deep extending in the *a* axial direction. Individual iron octahedra within a band are connected by S(1) and S(2) tetrahedra on the outer edges of the band. The structure contains one such band at about $y=0$ and $z=\frac{1}{2}$ and another at about $y=\frac{1}{2}$ and $z=0$. Translation

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[1] To obtain a copy of Table 4 order NAPS Document No. 0947 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New York, New York 10022, remitting $2.00 for microfiche or $5.00 for photocopies, in advance payable to CCMIC-NAPS.

equivalent bands are interconnected in the [10$\bar{1}$] direction by chains consisting of one copper octahedron attached on each of opposite vertices to one of the S(2) tetrahedra of the iron octahedral bands. The result is a sheet-like unit containing iron octahedral bands united by S(2)—Cu—S(2) polyhedral chains. The sheets are parallel to (010) and are distributed in the cell at $y=0$ and at $y=\frac{1}{2}$.

Both the copper and iron atoms in ransomite are octahedrally coordinated by oxygen atoms. Copper at a center of symmetry is coordinated by four water oxygens in square planer configuration at an average distance of 1.99 Å and by two sulfate oxygens at opposite vertices at a distance of 2.44 Å due to the Jahn-Teller distortion. The iron coordination octahedron consists of five sulfate oxygens and one water oxygen with an average Fe^{3+}—O distance of 1.98 Å.

An interesting feature of the S(1) tetrahedron is the large temperature factor and the short sulfur-oxygen distance of O(3). The 1.41 ± 0.01 Å separation probably reflects an intensification of the covalent component of this bond. The two shortest sulfur-oxygen distances in the tetrahedron are directed toward oxygens not participating in extratetrahedral coordination while the two longer distances involve oxygen atoms that are included in the iron coordination octahedron.

Positions of the hydrogen atoms were not located during the structure determination. Subsequently, however, a hydrogen bonding scheme based on reasonable O_w—O distances has been hypothesized. A list of the distances and angles between participating sulfate and water oxygens is given with selected bond information for ransomite in Table 3. The hydrogen bonds between $O_w(2)$ of the iron octahedron and O(3) and O(4) of the S(1) tetrahedron serve to join the structural sheet at $y=0$ to the sheet at $y=\frac{1}{2}$. A similar role is played by the single hypothesized bond between $O_w(3)$ and O(3). Both O(3) and O(4) are unshared oxygens of the S(1) tetrahedron. Intrasheet hydrogen bonding is supplied by the O(8)—$O_w(1)$—O(4) hydrogen bonds. The perfect {010} cleavage of ransomite is nicely accounted for by this structural arrangement.

DISCUSSION OF THE STRUCTURE

Because the structure of ransomite as well as the structures of many of the transition metal sulfate hydrates contain appreciable amounts of water there are usually more ligands available for octahedral coordination than are required by the metal cations. And since water oxygens are usually preferentially employed in coordination of the metal cations as compared to sulfate oxygens, the sulfate tetrahedra of such structures are frequently not tetradentate. Minerals whose structures are governed by these principles are unlikely to contain sharing of corners, edges, or

Table 3. Selected Bond Angles and Distances in Ransomite

1	2	3	Angle 1—2—3	Distance 1—2	Distance 2—3
O(1)	S(1)	O(3)	106.6° (.7)	1.492(13)	1.410(11)
		O(2)	108.9 (.6)		1.514(10)
		O(4)	108.8 (.7)		1.474(11)
O(2)		O(3)	111.5 (.7)		
		O(4)	107.7 (.6)		
O(3)		O(4)	113.3 (.7)		
O(6)	S(2)	O(5)	109.9 (.6)	1.452(10)	1.490(9)
		O(7)	109.2 (.6)		1.489(12)
		O(8)	111.6 (.6)		1.474(10)
O(5)		O(7)	107.8 (.6)		
		O(8)	109.7 (.6)		
O(7)		O(8)	108.5 (.6)		
O(8)	Cu	$O_w(3)$	90.8 (.5)	2.437(11)	2.013(12)
		$O_w(1)$	87.8 (.4)		1.956(11)
		$O_w(3)$	89.2 (.5)		
O(8)		$O_w(1)$	92.2 (.4)		
$O_w(1)$		$O_w(3)$	92.5 (.5)		
		$O_w(3)$	87.5 (.5)		
$O_w(2)$	Fe	O(7)	90.7 (.4)	2.002(9)	1.982(10)
		O(1)	82.6 (.4)		1.994(11)
O(1)		O(5)	92.0 (.4)		1.956(9)
O(5)		O(7)	94.5 (.4)		
O(2)		O(7)	92.2 (.4)	1.947(11)	
		$O_w(2)$	94.2 (.4)		
		O(1)	94.8 (.4)		
		O(5)	88.2 (.4)		
O(6)	Fe	O(7)	85.5° (.4)	2.017(11)	
		$O_w(2)$	88.2 (.4)		
		O(1)	87.7 (.4)		
		O(5)	89.6 (.4)		
Angles and distances between hydrogen bonded oxygens:					
O(4)	$O_w(1)$	O(8)	116.3° (.5)	2.63(1)	2.64(1)
O(3)	$O_w(2)$	O(4)	102.7 (.5)	2.86(1)	2.75(1)
$O_w(3)$	O(3)			2.91(2)	

Note: Standard errors for the last decimal places are in brackets.

faces between coordination octahedra. They are also unlikely to exhibit a continuous three dimensional structural framework.

The structure of ransomite as well as the structures of a number of transition metal sulfate hydrates contain either individual octahedra, or groupings of the type,—*tetrahedron—octahedron—tetrahedron*—, the particular arrangement being controlled primarily by the percentage of extratetrahedrally bonded oxygen atoms in the sulfate coordination tetrahedra. In many cases this imposes severe limitations on the structural configuration of the mineral. A hypothetical example is one in which a single extratetrahedrally coordinating oxygen atom of the sulfate tetrahedra requires that the structure maintain a *tetrahedron—octahedron*, or a *tetrahedron—octahedron—tetrahedron* finite chain type arrangement. The more complexly linked structure of ransomite is a consequence of the increased percentage of sulfate oxygens employed in cation coordination.

It is interesting to note that the essential information for this type of analysis can often be obtained from the formula of a mineral by first assigning water oxygen ligands to the octahedral coordination locations and then noting the ratio of the sulfate ligands necessary to complete octahedral coordination to those not so employed.

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