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Refinement of the crystal structure of jurbanite, $Al(SO_4)(OH) \cdot 5H_2O$

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Abstract. The crystal structure of jurbanite, $Al(SO_4)(OH) \cdot 5H_2O$, was refined from 1470 independent reflections measured on a computer-controlled single-crystal diffractometer. The positional and anisotropic thermal parameters (isotropic for hydrogen atoms) were refined by full-matrix least-squares calculations to a final $R = 0.047$, for 581 reflections with $I > 3\sigma(I)$. Hydrogen atoms were located on a ΔF map. Lattice parameters are $a = 8.3965(6)$, $b = 12.479(2)$, $c = 8.1549(9)$ Å and $\beta = 101.917(6)°$; space group $P2_1/n$; $Z = 4$. In the structure pairs of $Al(OH)_2(H_2O)_4$ octahedra and isolated SO_4 groups are connected by a hydrogen bonding system. The atomic arrangement is discussed in relation to other hydrated aluminum sulfates, such as aluminite $Al_2(SO_4)(OH)_4 \cdot 7H_2O$, and rostite $Al(SO_4)F \cdot 5H_2O$. It is pointed out that jurbanite and rostite, so far considered as dimorphs, have really a different chemical composition, with $(OH)^-$ in jurbanite and F^- in rostite.

Introduction

The crystal structure of the synthetic compound $[Al_2(OH)_2(H_2O)_8](SO_4)_2 \cdot 2H_2O$ was determined by Johansson (1962) from diffraction data measured on Weissenberg photographs. Later the new mineral jurbanite, $Al(SO_4)(OH) \cdot 5H_2O$, was discovered (Anthony and McLean, 1976) at the San Manuel mine, Arizona, and was found to be identical with the above mentioned compound. This seems to be the only reported natural occurrence of jurbanite, in post-mine stalactitic pipe material. Associated minerals are pickeringite, epsomite, and hexahydrite.

During an investigation on the alteration minerals at the Cetine mine, an antimony deposit in Tuscany (Italy), a few uncommon, minute crystals were collected from the lower levels of the mine, where many sulfate minerals occur. An X-ray diffraction study revealed them to be jurbanite. It occurs in white aggregates of clear crystals, which grow on argillaceous rocks and is associated with gypsum and pickeringite, as well as metavoltine, sideronatrite, uklonskovite and rostite. A mineralogical and chemical study of jurbanite, together with its "dimorph" rostite, has been presented in a recent paper (Sabelli, 1984).

The present study confirms the known structural model, provides interatomic distances and angles of higher precision, as well as the H atom positions, which allows the hydrogen-bonding system to be fully described.

Experimental

A small, prismatic, colorless crystal, with dimensions of approximately 0.15 × 0.06 × 0.05 mm was used for intensity data collection, on a PW 1100 four-circle diffractometer (Centro di Cristallografia Strutturale del CNR, Pavia, Italy). The cell dimensions, obtained by least-squares refinement with 21 reflections, are: $a = 8.3965(6)$, $b = 12.479(2)$, $c = 8.1549(9)$ Å, $\beta = 101.917(6)°$. Calculated density is 1.828 gcm^{-3} on the basis of the cell volume of 836.08 A^3 and of 4 formula units. The observed value is 1.786(6) gcm^{-3} (Anthony and McLean, 1976).

Intensity data were collected for one hemisphere ($l > 0$) in reciprocal space with graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.7107$), in the range $2° < \vartheta < 25°$. Peaks were monitored by $\omega - 2\,\vartheta$ scans with a constant width of 1.0° and scan speed of 0.05°/s. The experimental stability was checked by regular testing of three strong reflections (210, 130, 002); the maximum standard deviation is 0.059. Out of the 2939 measured intensities a total of 1470 independent reflections were obtained by averaging the equivalent ones. Of these data only 581 observations were judged to be actually measured according to the criterion $I > 3\,\sigma\,(I)$, with σ derived from counting statistics. Intensities were corrected for Lorentz-polarization effects, while absorption correction ($\mu = 14.7\ \mathrm{cm}^{-1}$) was considered negligible because of the small size of the crystal. The space group $P2_1/n$ (Johansson, 1962) has been confirmed with the extinction rule that $h0l$ and $0k0$ reflections occur when $h + l$ and k respectively are even.

Atomic scattering factors for atoms were taken from the International Tables for X-ray Crystallography (1974). Computations were carried out on the Honeywell DPS-7 computer of the Computer Center of Florence University, using a local version of ORFLS (Busing et al., 1962) and BONDLA (XRAY System, 1972).

Refinement and discussion of the structure

The previous structure determination by Johansson (1962) on synthetic material was the starting step for the location of atoms other than hydrogen

Table 1. Fractional atomic parameters for jurbanite. Thermal parameters as $B_{eq} = 4/3\ \Sigma_i \Sigma_j \beta_{ij}\, \mathbf{a}_i\, \mathbf{a}_j$ (Å^2) (isotropic B fixed at 4 Å^2 for hydrogen atoms)

Atom	x	y	z	B_{eq}
S	0.1358(2)	0.8151(1)	0.7866(2)	1.38
Al	0.1158(2)	0.5106(1)	0.1536(2)	1.26
O(1) OH	0.0325(4)	0.4075(2)	−0.0042(5)	1.33
O(2) Ow	0.2569(4)	0.4175(3)	0.3003(5)	2.32
O(3) Ow	0.1932(4)	0.6288(3)	0.2916(5)	2.28
O(4) Ow	−0.0346(3)	0.4814(2)	0.2929(4)	1.57
O(5) Ow	0.2890(4)	0.5316(2)	0.0367(4)	1.40
O(6)	0.1899(4)	0.7123(2)	0.7249(5)	2.28
O(7)	0.0789(4)	0.8842(3)	0.6395(5)	2.54
O(8)	0.2773(4)	0.8675(3)	0.8968(5)	2.07
O(9)	0.0069(4)	0.8000(3)	0.8784(5)	1.91
O(10) Ow	0.0223(4)	0.8027(3)	0.3143(5)	2.54
H(1)	0.001(8)	0.345(5)	0.013(12)	
H(21)	0.238(5)	0.400(3)	0.410(7)	
H(22)	0.354(5)	0.383(3)	0.290(6)	
H(31)	0.136(6)	0.688(4)	0.310(7)	
H(32)	0.299(5)	0.643(3)	0.354(6)	
H(41)	−0.100(7)	0.520(5)	0.355(7)	
H(42)	−0.090(9)	0.410(5)	0.285(10)	
H(51)	0.395(6)	0.557(4)	0.080(7)	
H(52)	0.320(7)	0.478(4)	−0.040(7)	
H(101)	−0.097(6)	0.800(5)	0.290(7)	
H(102)	0.045(8)	0.818(5)	0.424(7)	

atoms (x and z are exchanged because a and c are transposed with respect to Johansson's lattice orientation). Least-squares refinement with isotropic temperature factors converged to an R value, $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, of 0.085. Two cycles with anisotropic thermal parameters caused the R value to decrease to 0.062. A difference electron density map at this stage showed several peaks in the positions where the H atoms were expected. The introduction and the refinement of their positional parameters (with temperature factors fixed at 4.0 Å^2) lowered R to the final value of 0.047 and R_w to 0.040 for the observed reflections ($R = 0.14$ for all data). Final positional parameters are given in Table 1. Bond distances and angles are listed in Table 2. A list of observed and calculated structure factors, together with the anisotropic thermal parameters and the O−O interatomic distances, has been deposited[1].

The a-axis projection of the structure is shown in Figure 1. The $Al(OH)_2(H_2O)_4$ octahedra are joined in pairs by sharing an edge on the

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[1] Additional material to this paper can be ordered referring to the no. CSD 51570, name of the author and citation of the paper at the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG

Table 2. Bond distances (Å) and bond angles (°) for jurbanite

Al – O(1)	1.852(4)	S – O(6)	1.483(3)
Al – O(1^{ii})	1.858(3)	S – O(7)	1.475(4)
Al – O(2)	1.897(4)	S – O(8)	1.485(4)
Al – O(3)	1.887(4)	S – O(9)	1.450(4)
Al – O(4)	1.901(4)	Mean	1.473
Al – O(5)	1.914(4)		
Mean	1.885	O(6) – S – O(7)	107.5(2)
		O(6) – S – O(8)	108.9(2)
O(1) – Al – O(1^{ii})	79.7(1)	O(6) – S – O(9)	112.1(2)
O(1) – Al – O(2)	96.3(2)	O(7) – S – O(8)	108.6(2)
O(1) – Al – O(3)	172.5(2)	O(7) – S – O(9)	110.2(2)
O(1) – Al – O(4)	94.6(2)	O(8) – S – O(9)	109.5(2)
O(1) – Al – O(5)	88.0(2)		
O(1^{ii}) – Al – O(2)	175.5(1)		
O(1^{ii}) – Al – O(3)	93.6(2)	Symmetrie code:	
O(1^{ii}) – Al – O(4)	93.4(2)	none:	x, y, z
O(1^{ii}) – Al – O(5)	94.2(2)	i)	$-x, 1-y, 1-z$
O(2) – Al – O(3)	90.5(2)	ii)	$-x, 1-y, -z$
O(2) – Al – O(4)	84.9(2)	iii)	$\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$
O(2) – Al – O(5)	87.6(2)	iv)	$\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$
O(3) – Al – O(4)	89.0(2)	v)	$\frac{1}{2}+x, \frac{3}{2}-y, z-\frac{1}{2}$
O(3) – Al – O(5)	89.2(2)	vi)	$x-\frac{1}{2}, \frac{3}{2}-y, z-\frac{1}{2}$
O(4) – Al – O(5)	172.3(2)		

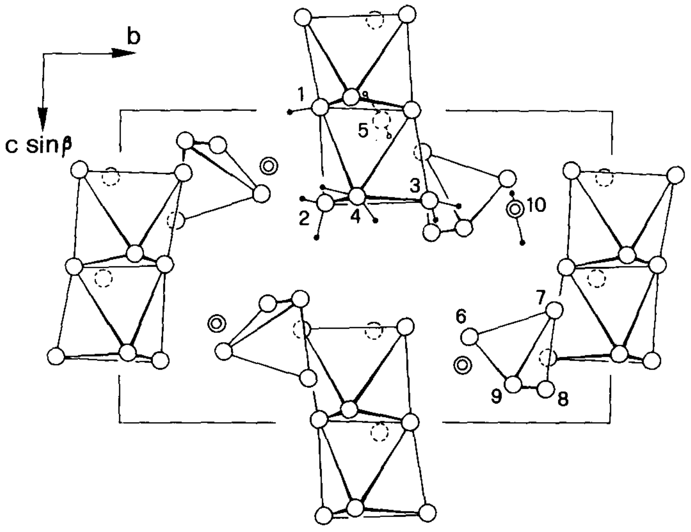

Fig. 1. Projection of the structure of jurbanite parallel to [100]. Open circles represent O atoms, double circles O atoms of free water molecules, and solid circles H atoms

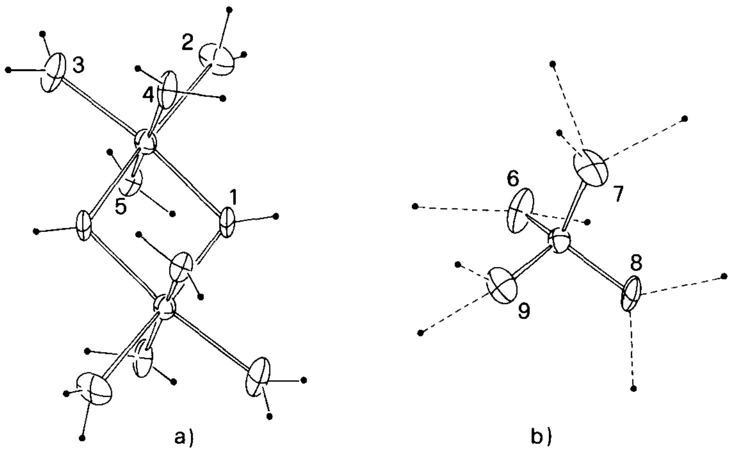

Fig. 2. Thermal behaviour of the atoms of polyhedra (ellipsoids are scaled at the 50% probability level): a) a pair of Al octahedra; b) environment of the SO_4 group

inversion center. Among the aluminum sulfate minerals containing isolated SO_4 groups, the dimeric unit $Al_2(OH)_2(H_2O)_8$ (Fig. 2a) represents an intermediate term between the insular $Al(H_2O)_6$, which is found, for instance, in alunogen $[Al(H_2O)_6]_2(SO_4)_3 \cdot 4.4H_2O$ (Menchetti and Sabelli, 1974), and the linearly polymerized complex group $Al_4(OH)_8(H_2O)_6$ found in aluminite $[Al_2(OH)_4(H_2O)_3](SO_4) \cdot 4H_2O$ (Sabelli and Trosti-Ferroni, 1978). The increase of polymerization, however, does not seem always correlated with a decrease of free water molecules in the structures; in jurbanite $[Al_2(OH)_2(H_2O)_8]\ (SO_4)_2 \cdot 2H_2O$, indeed, there is only one free water molecule, while the structure of aluminite contains two free water molecules for each Al atom.

The mean Al – O distance of 1.885 Å, when compared with 1.91 Å from the radii values given by Shannon and Prewitt, is slightly shorter than the value expected for an Al – O octahedron. This is due to the shortening of Al – OH distance with respect to the Al – H_2O distances. The shared edge O(1) – O(1), with a length of 2.377(4) Å, is significantly shorter than the O – O mean distance of the whole octahedron, which is 2.665 Å, and the bond angle involved O(1) – Al – O(1), of 79.7(1)°, is considerably smaller than 90°. These deviations from the ideal values, and the resulting distortion of the octahedra, are comparable with those found in aluminite, in which the mean value of shared edges is 2.382 Å and the bond angles O – Al – O involved range from 74.7(2) to 79.2(2)°. On the other hand, the respective values of repulsive Al – Al distances, 2.849(2) Å in jurbanite and 2.988(8) Å in aluminite, are markedly different. This is mainyl due to different Al – OH distances, which are on the average 1.856 Å in jurbanite and 1.891 Å in aluminite.

Table 3. Distances (Å) and angles (°) involving hydrogen atoms

Donor atom (D)	Acceptor atom (A)	Distances			Angles		
		D...A	D−H	H...A	DHA	HDH	ADA
O(1)−H(1)	...O(9^{i})	2.830(5)	0.84(6)	2.02(7)	160(6)	–	–
O(2)−H(21)	...O(8^{iii})	2.620(6)	0.97(6)	1.66(6)	175(4)	107(4)	115.0(2)
O(2)−H(22)	...O(10^{iv})	2.661(6)	0.94(4)	1.78(5)	154(4)		
O(3)−H(31)	...O(10)	2.629(5)	0.91(5)	1.72(5)	172(5)	103(4)	103.0(2)
O(3)−H(32)	...O(9^{v})	2.731(5)	0.94(4)	1.86(4)	153(4)		
O(4)−H(41)	...O(8^{vi})	2.706(4)	0.95(6)	1.81(6)	155(5)	100(6)	109.3(1)
O(4)−H(42)	...O(6^{i})	2.736(4)	1.00(7)	1.74(7)	178(7)		
O(5)−H(51)	...O(7^{v})	2.625(5)	0.94(5)	1.69(5)	173(5)	97(5)	89.3(2)
O(5)−H(52)	...O(7^{iv})	2.709(5)	0.99(6)	1.74(6)	166(5)		
O(10)−H(101)	...O(6^{vi})	2.741(5)	0.98(5)	1.76(5)	173(5)	102(5)	104.0(2)
O(10)−H(102)	...O(7)	2.788(6)	0.90(6)	1.91(6)	166(6)		

Table 4. Electrostatic balance

Atom	Al	S	H_{don}	H_{acc}	Sums
O(1)	1.09		0.82		1.91
O(2)	0.48		1.53		2.01
O(3)	0.49		1.55		2.04
O(4)	0.48		1.58		2.06
O(5)	0.46		1.54		2.00
O(6)		1.46		0.40	1.86
O(7)		1.49		0.65	2.14
O(8)		1.45		0.46	1.91
O(9)		1.60		0.39	1.99
O(10)			1.61	0.47	2.08
Sums	3.00	6.00	11.00		20.00

The short Al−OH value in jurbanite could also be caused by a partial substitution of OH by F in this mineral (indeed, typical Al−F distances, which are significantly shorter than Al−OH averages, range from 1.80 to 1.86 Å). This assumption is apparently supported by the presence of fluorine in the structure of rostite (also known as khademite), which is known to be the orthorhombic dimorph of jurbanite. In the structure of rostite (Bachet et al., 1981) F completely substitutes OH and the Al−F distance is 1.734(3) Å. However, the chemical analysis of jurbanite do not show traces of fluorine (Sabelli, 1984), and there are no structural reasons, such as the lowering of the thermal factor of the site or electrostatic imbalance of chargs involved, for assuming the presence of F instead of OH in the structure. From these considerations it also follows that jurbanite,

$Al(SO_4)(OH) \cdot 5H_2O$, need not be considered a dimorph of rostite, $Al(SO_4)F \cdot 5H_2O$, in the strict sense of the word.

No unusual feature is shown by the SO_4 tetrahedron, in which the mean S–O bond length is 1.473 Å. This value is identical to the S–O distance in well-refined structures of hydrated sulfates (Baur, 1964). The SO_4 tetrahedron is "entrapped" in a closed net of nine H-bonds (Fig. 2b). The H-bond due to OH is the weakest in the structure (Tab. 3).

The H-bonding system is of a particular relevance to the cohesion of the structure of jurbanite. On the whole, there are four ligand water molecules, one free water molecule, and one hydroxyl, which supply the eleven H-bonds of the asymmetric unit. The donor-acceptor average distance is 2.707 Å, while the individual values range from 2.620 to 2.830 Å. All H-bonds involving the four ligand water oxygens are strong bonds according to Brown's (1976) criterion, which fixes 2.73 Å as the limit value between strong and weak H-bonds.

An electrostatic valence balance (Tab. 4) was computed according to Brown and Shannon (1973); the curve by the same authors quoted in Donnay and Donnay (1973) was employed for H-bonds. The balance is on the whole satisfactory, except for O(6) and O(7), both belonging to the SO_4 group, which appear to be underbonded and overbonded respectively.

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