

structures should then allow some definite conclusions to be drawn.

The bond distances and valency angles in the *p*-bromobenzenesulphonyl group (Table 3) are all normal. The intermolecular separations (Table 5) all correspond to van der Waals interactions.

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The Crystal Structure of Alunite*

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A single-crystal diffraction analysis of alunite, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, yields an internally consistent set of bond lengths and angles which include significant revisions of previously determined values. The sulfate group includes one unique oxygen more strongly bonded to sulfur than are the other three.

Introduction

An analysis of the alunite structure, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, has been reported previously by Hendricks (1937). The structure is rhombohedral, but with α quite close to 60° , which provides aspects related to a face centered cube. In his analysis, Hendricks assigned alunite to the space group $R\bar{3}m$ on the basis of a pyroelectric test, although the reported structural coordinates display a center of symmetry. Pabst (1947) carried out the computations for assumed models for alunite and two other isostructural compositions which were necessary for the correct assignment of rhombohedral or hexagonal indices which properly accounted for the observed intensities of the several powder patterns.

The dimensions of the alunite hexagonal cell found by Pabst agreed closely with those reported by Hendricks, and the structural model which best accounted for the observed intensities was in space group $R\bar{3}m$. The Hendricks bond lengths deviated somewhat from comparable subsequently determined

values in other hydrous aluminum-bearing compositions (Kamb, 1960; Radoslovich, 1960; Newnham, 1961), although not to such degree but that the Hendricks parameters afforded adequate basis for Pabst's index assignments. This refinement of parameters based on single-crystal data was undertaken to examine these deviations.

Experimental

Least-square refinements of measurements from a powder photograph yield hexagonal unit-cell dimensions $a = 6.970 \pm 0.001$, $c = 17.27 \pm 0.01$ Å. These agree essentially with the previous determinations. Two single-crystal flakes were used for the collection of intensity data. A triangular shaped fragment whose edges measured 0.3 mm and which was 0.025 mm thick was used for the precession camera, and a hexagonal fragment with sides of 0.1 mm and 0.025 mm thick was used for the Weissenberg camera. The $hk0$, $hk2$, $hk3$, $hk10$, and $hk11$ reflections were collected with the Weissenberg camera with the multiple film technique and $\text{Cu } K\alpha$ radiation. The hhl and $h0l$ reflections were obtained from precession photographs taken with molybdenum $K\alpha$ radiation; a total of 123

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reflections were recorded which constitute approximately 34% of the copper sphere. The intensities were estimated visually by comparing them with an intensity scale which was prepared from timed exposures of the diffracted beam from the (220) plane of an alunite crystal. No corrections for absorption were made.

Structure determination

The space group $R\bar{3}m$ was chosen by Hendricks on the basis of the pyroelectric properties displayed by alunite, but his final atomic parameters were clearly related to a center of symmetry. Pabst (1947) and Wilson (1947) both noted that the pyroelectric behavior reported by Hendricks remains unexplained on the basis of the postulated structure. Statistical tests (Howell, Phillips & Rogers, 1950) were applied to the data and provided a hypercentric distribution, which is possibly suggestive, but not conclusive, of the true space group. It is to be noted that the detailed structure analysis of diopside by Heide & Boll-Dornberger (1955) also resulted in a centrosymmetric structure, in apparent contradiction to the sometimes observed pyroelectric properties of diopside crystals.

The acentric space groups $R32$ and $R3m$, as well as the centrosymmetric space group $R\bar{3}m$, are consistent with the diffraction data. The refinement of

Table 2. *Tabulated, observed and calculated structure factors*

h	k	l	F _{obs}	F _{calc}	h	k	l	F _{obs}	F _{calc}	h	k	l	F _{obs}	F _{calc}
6	0	0	87.2	86.5	6	0	3	54.2	57.0	6	0	-12	84.6	79.7
1	1	0	102.9	108.3	6	0	6	78.2	90.0	6	0	-15	63.3	-61.4
4	1	0	65.5	68.5	6	0	15	72.9	-71.1	7	0	-2	32.0	-34.7
7	1	0	49.7	64.0	7	0	7	61.1	72.6	8	0	-4	46.2	48.1
2	2	0	196.5	210.1	7	0	10	41.6	45.5	8	0	-7	58.2	50.4
3	3	0	126.2	145.6	7	0	13	71.2	68.0	3	1	2	61.3	-54.9
4	4	0	80.7	87.3	8	0	5	68.2	-68.3	1	2	2	71.2	60.3
2	5	0	37.1	37.5	8	0	8	65.0	43.2	4	2	2	22.5	18.3
0	0	3	23.3	-13.3	1	0	-2	97.7	-103.1	2	3	2	75.6	-74.8
0	0	6	117.9	143.7	1	0	-5	47.5	-46.4	5	3	7	44.0	-40.8
0	0	9	166.0	-164.8	1	0	-8	30.1	24.0	3	4	2	29.0	-28.1
0	0	18	42.1	36.0	1	0	-11	31.6	31.7	1	5	2	48.5	-41.2
1	0	1	59.5	53.0	1	0	-14	39.9	40.6	2	6	2	69.5	66.5
1	0	4	14.6	12.0	1	0	-17	37.1	34.0	4	1	3	115.1	106.2
1	0	7	190.7	185.3	1	0	-20	37.0	22.8	7	1	3	38.3	47.7
1	0	10	33.4	29.0	2	0	-1	123.7	-118.3	5	2	3	75.4	69.8
1	0	13	86.6	93.4	2	0	-4	55.8	56.8	2	1	10	47.7	39.1
1	0	19	34.4	39.2	2	0	-7	40.8	-30.7	5	1	10	81.0	86.3
2	0	2	14.8	20.9	2	0	-10	242.8	231.4	3	2	10	20.2	20.6
2	0	5	52.4	46.2	2	0	-16	118.0	118.5	1	3	10	81.1	90.1
2	0	8	54.5	57.1	2	0	-19	60.9	-59.5	4	3	10	31.9	34.2
2	0	11	44.5	-36.2	3	0	-3	200.9	228.7	2	4	10	96.4	94.5
2	0	14	33.3	31.0	3	0	-6	33.6	29.2	1	6	10	27.9	37.4
2	0	17	33.1	-27.5	3	0	-9	92.4	95.6	3	1	11	22.2	22.7
2	0	20	110.2	109.8	3	0	-12	94.3	-95.3	4	2	11	36.4	-34.7
2	0	23	26.7	20.7	3	0	-15	41.5	-32.2	3	4	11	21.6	21.9
3	0	3	49.8	43.2	3	0	-18	36.1	-24.8	1	5	11	21.0	23.5
3	0	6	26.4	21.8	4	0	-2	90.8	89.0	1	1	3	144.3	163.7
3	0	9	28.0	23.1	4	0	-5	58.9	-64.1	1	1	6	20.9	23.1
3	0	12	48.4	56.3	4	0	-8	29.2	20.7	1	1	9	29.2	31.7
3	0	18	31.5	-31.4	4	0	-11	53.0	-54.3	1	1	12	32.5	-33.2
4	0	1	52.7	-55.7	4	0	-14	56.9	53.0	2	2	6	106.3	116.8
4	0	4	100.3	98.9	4	0	-20	87.0	84.2	2	2	9	58.7	-61.7
4	0	7	45.5	-47.1	5	0	-4	32.1	39.5	2	2	12	28.3	33.3
4	0	10	130.8	125.0	5	0	-10	27.5	27.4	2	2	15	45.0	-52.9
4	0	13	31.7	21.4	5	0	-13	105.9	93.5	3	3	3	72.5	73.3
4	0	16	93.3	102.9	5	0	-16	35.4	29.4	3	3	6	26.6	12.9
5	0	2	41.2	40.6	5	0	-19	78.1	62.9	3	3	12	37.9	-43.9
5	0	5	32.4	-28.6	6	0	-3	30.4	-26.0	3	3	15	33.1	35.7
5	0	8	41.2	-43.0	6	0	-6	83.7	76.6	4	4	6	57.6	66.9
5	0	17	91.6	88.4	6	0	-9	37.9	-31.8	4	4	12	30.7	27.3

Table 1. *Atomic positional parameters in alunite*

		Hendricks* parameters	Final least- square parameters	Standard deviation
K	x	0	0	—
	y	0	0	—
	z	0	0	—
	B	—	0.49	0.17
S	x	0	0	—
	y	0	0	—
	z	0.305	0.3030	0.0004
	B	—	0.15	0.14
Al	x	0.167	0.1667	—
	y	-0.167	-0.1667	—
	z	-0.167	-0.1667	—
	B	—	0.29	0.15
O(1)	x	0	0	—
	y	0	0	—
	z	0.393	0.3844	0.0013
	B	—	2.05	0.58
O(2)	x	0.215	0.2180	0.0009
	y	-0.215	-0.2180	0.0009
	z	-0.058	-0.0588	0.0005
	B	—	0.15	0.18
OH	x	0.150	0.1247	0.0011
	y	-0.150	-0.1247	0.0011
	z	0.126	0.1416	0.0005
	B	—	0.49	0.19

* These data were obtained from his Fig. 1, the projection of the alunite structure on (001). In his tabulated parameters the entries $x = \frac{1}{2}$ and $x = -\frac{1}{2}$ for O(1) appear to have been omitted.

the structure was successfully carried out in $R\bar{3}m$, and this is considered to be the most probable space group for this structure.

The atomic parameters reported by Hendricks were used to calculate the signs for the (010) electron density projection, which showed that the positions of potassium, sulfur, and aluminum were correct but large deviations from the assumed values of the z parameters for O and OH were observed. The initial discrepancy coefficient R for the 123 structure factors calculated with the original coordinates was 37%, which reduced to 24% when the z parameters, recovered from the electron density projection, were used.

The coordinates obtained from the projection were used as the starting values in a three-dimensional full-matrix, least-square refinement with isotropic temperature factors. The final discrepancy coefficient R for the 123 reflections is 0.092 and the coordinates and standard deviations are listed in Table 1. The tabulated data form which these are derived are reproduced in Table 2.

Discussion of structure

Bond lengths and bond angles together with their standard deviations are shown in Table 3. Fig. 1 shows the positions of sulfur tetrahedra and of

Table 3. Bond distances and angles in alunite

(a) Distances. (Standard deviations in parentheses)

		Hendricks	Final
Tetrahedra			
1	S-O(1)	1.52 Å	1.406 Å (0.024) Å
3	S-O(2)	1.51	1.477 (0.014)
3	O(1)-O(2)	2.49	2.354 (0.024)
3	O(2)-O(2')	2.47	2.412 (0.016)
Octahedra			
2	Al-O(2)	1.98	1.963 (0.009)
4	Al-OH	2.05	1.864 (0.015)
4	O(2')-OH	3.08	2.717 (0.019)
4	O(2'')-OH	2.59	2.697 (0.019)
2	OH-OH'	2.64	2.664 (0.021)
2	OH'-OH''	3.13	2.608 (0.021)
K surroundings			
3	K-O(2)	2.79	2.821 (0.013)
3	O(2)-O(2')	4.49	4.558 (0.018)
6	K-OH	2.84	2.871 (0.015)
3	OH-OH'	3.13	2.608 (0.021)
	Al ··· S	3.13	3.097 (0.006)
	Al ··· K	3.52	3.512 (0.006)
Hydrogen bond			
	O-H ··· O	2.52	2.96

(b) Angles. (Standard deviations in parentheses)

3	O(2)-S-O(2')	109°	109.49° (0.49°)
3	O(2)-S-O(1)	109	109.45 (0.92)
4	O(2)-Al-OH	100	90.43 (0.46)
4	O(2')-Al-OH	80	89.57 (0.46)
2	OH-Al-OH'	80	91.22 (0.46)
2	OH'-Al-OH''	100	88.78 (0.46)
	S-O(2)-Al	126	127.84 (0.43)

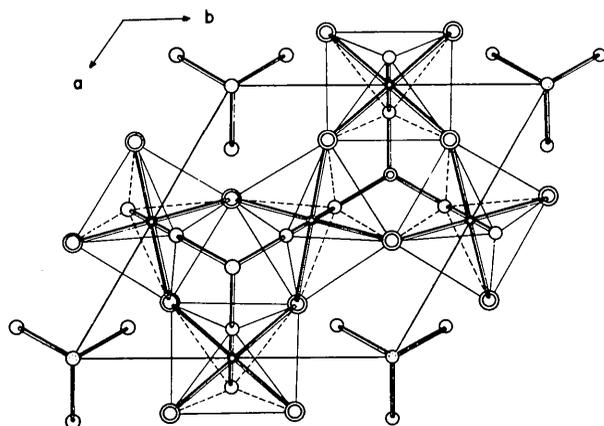


Fig. 1. *c*-Axis projection illustrating the articulation of coordination polyhedra in alunite.

S	at	0.3637	and	0.6363
Al	at	$\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$		
O(1)	at	0.2827	and	0.7177
O(2)	at	0.3922	and	0.6078
OH	at	0.5251	and	0.4749

aluminum octahedra in the unit cell. Only polyhedral contacts between $z=\frac{1}{3}$ and $z=\frac{2}{3}$ are shown, except that the positions of tetrahedra near the origin are indicated as isolated entries. The full framework structure is made up of this array and its crystallographic equivalents translated $\frac{1}{3}$ to the left and down and $\frac{1}{3}$ to the right and up. The potassium positions, 000, $\frac{2}{3}\frac{1}{3}\frac{1}{3}$ and $\frac{1}{3}\frac{2}{3}\frac{2}{3}$ are not marked.

Aluminum is coordinated in an only slightly distorted octahedron formed by four OH groups and two oxygen atoms from two separate SO₄ groups. The distance between aluminum and oxygen is 1.963 Å which is close to the 2.0 Å reported by Hendricks. The Al-OH bond length is 1.864, which is significantly shorter than the 2.04 Å distance of Hendricks. In Newnham's dickite structure the average Al-OH bond is 1.87 Å and the average Al-O is 1.96 Å. The OH-OH edge distances of the octahedron are 2.608 and 2.664 Å; O-OH edge distances are 2.697 and 2.717 Å, respectively. Each aluminum atom is in a symmetry center with paired internal angles O-Al-OH 89.57° and 90.43° and OH-Al-OH 88.78° and 91.22°. The configuration of a single octahedron is illustrated in Fig. 2. The octahedra share only corners, four OH groups with each other and two oxygen ions with tetrahedra.

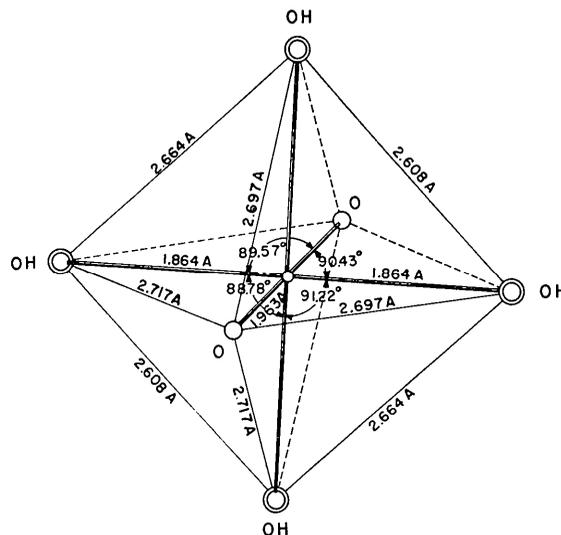


Fig. 2. Bond lengths and bond angles in aluminum octahedron.

The sulfur atoms lie on the trigonal axis and are surrounded by three oxygen atoms which form the base of the tetrahedron and one apical oxygen which also lies on the threefold axis. The distance between sulfur and the basal oxygen atoms is 1.477 Å, while the bond length between the sulfur atom and the apical oxygen is 1.406 Å. The considerable degree of covalent character distinguishes this oxygen atom as the 'doubly' bonded one. It has no other close cation neighbors and has by far the greatest isotropic temperature amplitude. It is but little different from

the close S–O contacts in sulfuric acid. The other three tetrahedral oxygen atoms have electrostatic bond strengths of $\frac{4}{3}$ to sulfur, $\frac{1}{2}$ to Al and $\frac{1}{6}$ to K. All S–O bonds are shorter than in Hendricks's or Pabst's models.

The environment of potassium is presumably to be considered as octahedral. Six oxygen neighbors from 6 sulfate groups afford a flattened octahedron about each potassium at a bond length of 2.821 Å, while the six OH neighbors of aluminum octahedra in the elongated octahedral arrangement about each potassium are 2.871 Å distant. The 2.821 Å length is comparable to the shorter K–O contacts in Radoslovich's muscovite structure.

The stylized electrostatic bond summations of even fractions conform exactly with Pauling's rules. Inspection of the several bond lengths within each polyhedron indicates that bond strengths actually depart from even fractions but maintain proper sums. In sulfate tetrahedra the 'single' strengths are slightly more than $\frac{4}{3}$ and the 'double' less than 2. In aluminum octahedra, bonds to OH are slightly more than $\frac{1}{2}$ and those to O slightly less than $\frac{1}{2}$. Potassium strengths to O are less than $\frac{1}{6}$ and there is some association with the OH polyhedron, affording a small residual association between protons and the unique sulfate oxygen.

The unique sulfate oxygen has three OH neighbors distant 2.96 Å in directions inclined 32° to the basal plane. These three associations are presumed to be hydrogen bonds. Along them the protons would have positions of the form $x\bar{x}z$ with $x \simeq 0.20$ and $z \simeq 0.11$, so that, with the sulfur, they provide a vague tetrahedral aspect to that oxygen. The calculated amplitude most sensitive to possible allowance for a hydrogen contribution is that for the 003, for which calculated amplitudes would be some 8 or 10 electron units greater, clearly in agreement with the observed data. The number of other observations at small values of $\sin \theta/\lambda$ is inadequate to improve the tentative hydrogen positions cited.

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The Crystal Structure of *o*-Nitroperoxybenzoic Acid

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The crystal structure of *o*-nitroperoxybenzoic acid, C₇H₅NO₅, has been determined by a three-dimensional structure analysis. The peroxy-carboxyl group is shown to have the skewed conformation and the dihedral angle is 146°. Evidence is given suggesting that the intermolecular hydrogen bond largely determines the value of the dihedral angle in the hydrogen bonded peroxides in the solid state. The influence upon the angle exerted by exchange repulsion forces between the lone pair electrons of the peroxide oxygen atoms appears to be small in comparison. The bond lengths in the peroxy-carboxyl group are C=O 1.21₄, C–O 1.33₇, O–O 1.47₈ Å, and O–H 1.1₂ Å. The valency angles are O=C–O 124.7, C–O–O 108.9, and O–O–H 112°. A 5° torsional angle about the C–O bond displaces the carboxyl oxygen atom 0.09 Å (20σ) from the C–O–O plane, so that the carboxyl oxygen atom and the hydrogen atom are on opposite sides of the plane.

Five of the atoms in the benzene ring are coplanar, and the C atom attached to the NO₂ group is displaced 0.025 Å (5σ) from this plane. The N atom is displaced 0.154 Å (30σ) in the same direction. The C atom of the OCOOH group is displaced 0.074 Å (15σ) on the opposite side of the plane. The plane of the ring atoms makes a 58° angle with the OCO plane and a 28° angle with the ONO plane. There are indications of steric strain between the substituent groups. Glide related molecules are hydrogen bonded into an infinite chain.

Introduction

Swern & Silbert (1963) have given a resume of the information that has been acquired within the past

decade on the structure of several important classes of organic peroxides. They point out that single-crystal studies are needed to establish the structures of the peroxy acids, diacyl peroxides, and tertiary-butyl