

The Crystal Structure of Hanksite

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Abstract

Hanksite, $\text{Na}_{22}\text{K}(\text{CO}_3)_2(\text{SO}_4)_9\text{Cl}$, from Searles Lake, California, gave the space group $P6_3/m$ and the unit cell constants $a = 10.465$ and $c = 21.191$ Å. Its structure was solved by three-dimensional Patterson synthesis and subsequent Fourier methods. The atomic coordinates and isotropic temperature factors were refined by full-matrix least-squares to $R = 6.45$ percent for 1159 reflections.

The structure is characterized by chains of Na and K octahedra running parallel to the c -axis. These chains are connected by carbon and sulfur coordination groups.

Introduction

The mineralogy and the conditions of occurrence of hanksite, $\text{Na}_{22}\text{K}(\text{CO}_3)_2(\text{SO}_4)_9\text{Cl}$, at Searles Lake, California, and the system $\text{Na}-\text{Cl}-\text{SO}_4-\text{CO}_3-\text{H}_2\text{O}$, which includes hanksite, have been extensively studied by several authors (Eugster and Smith, 1965; Hardie and Eugster, 1970; Smith, Friedman, and Matsuo, 1970). The possible crystal structure of hanksite, however, posed interesting questions due to the unusual cation ratios in its chemical composition and the identity of its morphology and space group with that of apatite.

Simultaneously and independently of this study, Kato solved the structure of hanksite on a crystal obtained from the same locality, and published a brief summary of his results (Kato, 1972).

Experimental

The unit cell dimensions of hanksite, from Searles Lake, California,² as obtained from precession photographs and refined by a least-squares method from carefully prepared powder diffraction data, are: $a = 10.465 \pm 0.021$, $c = 21.191 \pm 0.043$ Å. These unit

cell dimensions are in good agreement with those first reported by Ramsdell (1939).

Three-dimensional intensities were collected by a general inclination (Santoro and Zocchi, 1966) diffractometer using $\text{CuK}\alpha$ radiation on a crystal fragment mounted for a -axis rotation. All 1268 reflections were measured up to $\sin \theta = 0.9245$ and were corrected for absorption using the method introduced by Burnham (1966). The space group of $P6_3/m$ was concluded from the systematic absences in the $00l$ reflections, from the inequalities between hkl and $kh\ell$ intensities, and from the $N(z)$ test described by Howells *et al* (1950).

In the Patterson synthesis several prominent peaks were observed at the approximate locations of:

$UV = 0\ 1/2, 1/2\ 0, 1/2\ 1/2$ at $W = 0, 1/6$ and $2/6$ levels and $UV = 1/6\ 2/6, 2/6\ 1/6, 5/6\ 1/6, 4/6\ 2/6$ at $W = 0$ and every $1/12^{\text{th}}$ level.

On the basis of these observations sulfur atoms were located tentatively at $2/6\ 1/6\ 1/12$ and $1/6\ 2/6\ 3/12$, and sodium atoms at $2/6\ 1/6\ 3/12$ and $1/6\ 2/6\ 1/12$ and at inversion centers. The validity of this model was tested with a weighted β -general synthesis (Ramachandran and Srinivasan, 1970, pp. 80–119). The test confirmed the approximate location of sulfur and sodium atoms and revealed the sites of all the other atoms.

Five cycles of full-matrix least-squares refinement were run for 1159 reflections (that is, all but 9 strong reflections above $\frac{\sin \theta}{\lambda} = 0.25$) in order to obtain better atomic coordinates and isotropic temperature factors. The scattering curves of $\text{K}^+, \text{Na}^+, \text{Cl}^-, \text{O}^-, \text{S}$

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² The chemical composition of hanksite is assumed to be that reported by Pratt (1896) and confirmed by Ramsdell (1939), as the specimen used in this study came from the same locality and gave identical unit cell dimensions. This composition was later verified by the absence of anomalous temperature factors and peak-heights in the least squares refinement.

TABLE 1. Atomic Parameters and Isotropic Temperature Factors in Hanksite*

Atom	M	x	y	z	B
K	2	0	0	0	1.779 (48)
Na(1)	6	1/2	0	0	1.576 (51)
Na(2)	4	2/3	1/3	.37571 (16)	1.819 (60)
Na(3)	4	0	0	.32652 (16)	1.656 (57)
Na(4)	6	.34676 (32)	.14670 (32)	1/4	2.114 (55)
Na(5)	12	.17876 (22)	.36113 (23)	.42571 (10)	1.889 (43)
Na(6)	12	.52262 (21)	.05337 (22)	.66098 (9)	1.760 (41)
C1	2	2/3	1/3	1/4	2.435 (56)
C	4	2/3	1/3	.56951 (35)	1.041 (109)
S(1)	6	.20851 (17)	.35679 (16)	1/4	1.175 (35)
S(2)	12	.33869 (11)	.16831 (11)	.40910 (5)	1.007 (31)
O(1)	12	.59560 (34)	.40349 (35)	.56988 (15)	1.374 (56)
O(2)	6	.35590 (56)	.36881 (55)	1/4	1.936 (86)
O(3)	6	.09251 (54)	.20129 (55)	1/4	1.877 (85)
O(4)	12	.19799 (42)	.43019 (43)	.30711 (19)	2.457 (70)
O(5)	12	.38977 (39)	.11345 (39)	.35672 (17)	2.017 (62)
O(6)	12	.19609 (37)	.15537 (39)	.39408 (17)	1.959 (65)
O(7)	12	.44786 (39)	.32368 (38)	.41970 (17)	1.950 (63)
O(8)	12	.32292 (37)	.08012 (38)	.46573 (17)	1.871 (62)

* Figures in parentheses are standard deviations in terms of the last decimal places of determined values.

and C are those of Cromer and Man (1968). The final R value for the 1159 reflections was 6.45 percent.

The atomic coordinates and isotropic temperature factors with their standard deviations are given in Table 1.

Description of the Structure

Sodium has several coordinations in the hanksite structure, as illustrated in Figure 1. There is a chain of four sodium, Na(3), (and two potassium) octahedra, sharing faces, which runs along the 6_3 axis. There are six slightly distorted sodium [Na(1) and Na(6)] octahedra that by sharing corners form chains along the 2_1 axis. Another sodium Na(4), is coordinated to four oxygen atoms at shorter distances and to an oxygen and a chlorine at longer distances; it is sandwiched between sulfate groups. One sodium, Na(5), is coordinated to four oxygens in the horizontal and two in the vertical directions. The sixth sodium,

TABLE 2. Summary of Polyhedral Interatomic Distances

Atoms	Distances (Å)	Atoms	Distances (Å)
K-O	2.925(7)*	C-O	1.280(4)*
Na-O	2.28 to 2.98	S-O	1.46 to 1.48
Na-Cl	2.66 to 2.91	O-O	2.38 to 2.42

* Figures in parentheses are standard deviations.

TABLE 3. X-ray Diffraction Powder Pattern of Hanksite $\text{Na}_{22}\text{K}(\text{CO}_3)_2(\text{SO}_4)_6\text{Cl}$

h k l	d(obs)	d(calc)	Intensity	h k l	d(obs)	d(calc)	Intensity
0 0 2	10.60	10.60	2	4 0 3	2.158	2.157	4
1 0 0	9.039	9.062	2.5	1 1 9	2.146	2.147	3
1 0 3	5.569	5.571	4	2 1 8	2.096	2.096	13
0 0 4	5.301	5.298	5	3 2 1	2.070	2.070	3
1 1 0	5.229	5.236	10	3 2 2	2.041	2.040	10
1 1 1	5.089	5.083	1	3 2 4	1.936	1.936	3
1 0 4	4.573	4.574	4	4 0 6	1.907	1.907	22
2 0 0	4.532	4.531	6.5	1 0 11	1.884	1.884	2
1 1 3	4.205	4.206	1.5	3 2 5	1.866	1.868	1.5
1 0 5	3.843	3.840	5	4 1 4	1.852	1.853	2
2 0 3	3.812	3.814	100	3 1 8	1.823	1.824	4
0 0 6	3.531	3.532	75	5 0 0	1.813	1.813	5
2 1 0	3.425	3.426	60	5 0 1	1.805	1.806	7
2 1 1	3.383	3.383	14	2 1 10	1.802	1.802	6
1 1 5	3.292	3.290	4	4 1 5	1.793	1.792	6
2 1 2	3.259	3.260	4.5	0 0 12	1.766	1.766	7
2 1 3	3.083	3.083	1.5	4 1 6	1.726	1.726	3
3 0 0	3.024	3.021	2.5	3 3 2	1.721	1.722	3
1 1 6	2.930	2.928	31	3 3 3	1.694	1.694	3
1 0 7	2.874	2.871	15	1 1 12	1.673	1.673	1.5
2 0 6	2.787	2.785	72	5 1 10	1.628	1.628	2
2 1 5	2.665	2.665	8	3 0 11	1.624	1.624	6
1 1 7	2.618	2.621	47	5 1 1	1.623	1.623	3
2 2 0	2.618	2.618	2	3 1 10	1.620	1.620	3.5
1 0 8	2.541	2.543	2.5	5 0 6	1.613	1.613	2
3 1 0	2.513	2.514	9	5 1 2	1.609	1.609	2.5
3 1 1	2.496	2.497	11	2 1 12	1.569	1.570	1.5
2 2 3	2.452	2.455	21	4 2 6	1.541	1.542	10
3 1 2	2.446	2.446	10				
3 1 3	2.367	2.369	2				
3 0 6	2.295	2.296	3				
1 0 9	2.278	2.279	4				
3 1 4	2.271	2.271	4				
4 0 1	2.252	2.253	5				

Space group: $P6_3/m$

Unit cell: $a = 10.465 \pm 0.021 \text{ \AA}$
 $c = 21.191 \pm 0.043 \text{ \AA}$

Na(2), is on the $\bar{3}$ axis and is surrounded by six oxygens and one chlorine to form a peculiar coordination group. The carbon and sulfur atoms are in the usual triangular and tetrahedral coordination. A summary of major polyhedral interatomic distances is given in Table 2, and the calculated powder

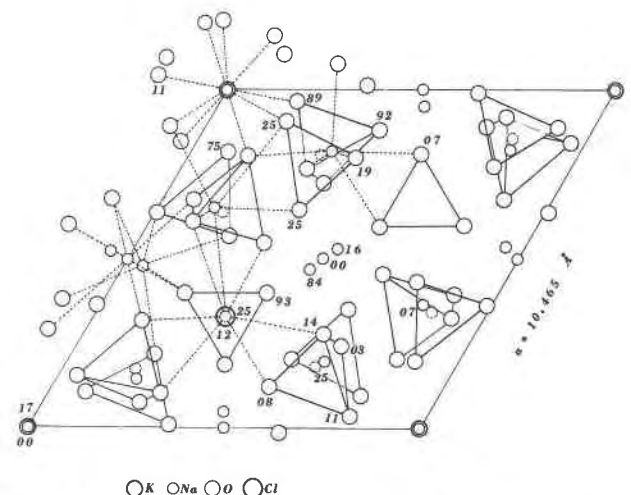


Fig. 1. c-projection of the hanksite structure. (Carbon atoms not shown.)

pattern in Table 3. A list of observed and calculated structure factors of hanksite has been deposited at the National Auxiliary Publications Service.³

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