

reflexions predicted for the L -Ta₂O₅ structure are 080, 0,14,0, 0,30,0 *etc.* In α -UO₃ on the other hand the reflexions with observable intensity in the electron diffraction patterns are 090, 0,13,0, 0,31,0 *etc.* However, slight alteration in the y coordinates of some of the metal atoms is sufficient to effect this change in intensities. The neutron diffraction pattern for α -UO₃ was also calculated assuming the atom positions in L -Ta₂O₅ (except for the proportion of oxygen atoms displaced in the z direction because of the presence of uranium vacancies) but with occupation parameters modified to allow for the missing uranium atoms and in accordance with one distortion plane per unit cell. The correlation was rather poor $R(I)=0.17$ but relaxation of uranium atoms in the [100] direction to correspond more closely to an ideal hexagonal arrangement reduced the R index to 0.09. A full refinement of such a large cell is impracticable from powder data but the indications from both the neutron and the electron diffraction experiments are that in α -UO₃ the position of the metal atoms approximate more closely to hexagonal symmetry than in L -Ta₂O₅.

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The Crystal Structure of Hanksite, $\text{KNa}_{22}[\text{Cl}(\text{CO}_3)_2(\text{SO}_4)_9]$ and its Relation to the K_2SO_4 I Structure Type

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The crystal structure of hanksite, $\text{KNa}_{22}[\text{Cl}(\text{CO}_3)_2(\text{SO}_4)_9]$, has been determined by three-dimensional X-ray analysis and refined by least-squares methods, using anisotropic thermal parameters; final $R=0.034$. The crystals are hexagonal ($P6_3/m$): $a=10.490$, $c=21.240$ Å, $Z=2$. The structure exhibits an ordered distribution of both SO_4 tetrahedra and CO_3 groups. The results of heating experiments are presented and similarities to a hexagonal phase of the solid solution series Ca_2SiO_4 - $\text{Ca}_3(\text{PO}_4)_2$ with respect to the K_2SO_4 I structure type are discussed.

Introduction

The mineral hanksite, $\text{KNa}_{22}[\text{Cl}(\text{CO}_3)_2(\text{SO}_4)_9]$, belongs to the sulphates containing CO_3 groups. Ramsdall (1939) found hexagonal symmetry with the unit-cell dimensions $a=10.46$ Å, $c=21.18$ Å. $P6_3$ and $P6_3/m$ are proposed as possible space groups. A structure determination has, however, not been attempted.

Furthermore Ramsdell (1939) found that the diffraction pattern of the high-temperature hexagonal Na_2SO_4 - Na_2CO_3 series resembles the hanksite pattern. Additional reflexions indicate that the unit cell of hanksite has a c axis three times and an a axis twice the size of those of the Na_2SO_4 - Na_2CO_3 series, or of Na_2SO_4 I. Eysel (1971) believes that hanksite is a variety of the hexagonal K_2SO_4 I structure type (high-

temperature form, space group $P6_3mc$) with non-identical unit cell. A unit cell similar to that of hanksite with corresponding cell dimensions has been detected (Saalfeld, 1971) in the solid solution series $\text{Ca}_2\text{SiO}_4\text{-Ca}_3(\text{PO}_4)_2$. In order to get further information on the crystallographic relations of these compounds the structure determination of hanksite was carried out. Kato (1972) has recently published preliminary results of this investigation.

Experimental

A crystal sphere ($\varnothing = 0.2$ mm), ground from a hanksite sample from Searles Lake, San Bernardino County, California, was used for the determination of the lattice constants and the intensity measurements. The following unit-cell parameters were obtained by a least-squares adjustment of high angle $\text{Cu K}\alpha$ reflexions: $a = 10.490 \pm 0.001$, $c = 21.240 \pm 0.001$ Å. There are two formula weights per unit cell. The intensity measurements of 1535 reflexions were carried out on an automated Siemens diffractometer with $\text{Cu K}\alpha$ radiation. Corrections for absorption ($\mu R = 1.07$) and extinction were applied. The $N(z)$ test (Howells, Phillips & Rogers, 1950) suggested the space group $P6_3/m$.

Heating experiments show that hanksite decomposes above 700°C forming hexagonal solid-solution crystals, Na_2SO_4 , V and NaCl . The hexagonal phase has the lattice parameters $a = 5.340$, $c = 7.110$ Å (space group $P6_3mc$) and is identical with the K_2SO_4 I type.

Structure determination and refinement of hanksite

On the basis of the chemical composition and the space group symmetry a model of the structure was proposed. The orientation of the SO_4 tetrahedra and CO_3 groups was found by the 'refinement of rigid-body groups' (Scheringer, 1965). After some cycles of least-squares refinement (Busing, Martin & Levy 1962) with anisotropic thermal parameters and isotropic extinction corrections (Zachariasen, 1967, 1968) all atoms could be located. The R index was reduced to 0.034. The scattering factors for the atoms were taken from Hanson, Herman, Lea & Skillman (1964). The atomic parameters are listed in Table 1, the anisotropic thermal parameters in Table 2 and the observed and calculated structure factors in Table 3.

Discussion

The structure of hanksite (Fig. 1) consists of isolated SO_4 tetrahedra, 12 of which are located in general position with a strong tilt with regard to the sixfold axis. The remaining six tetrahedra lie in the basal mirror planes at $z = \frac{1}{4}$ and $z = \frac{3}{4}$. The CO_3 -group positions are threefold. The atomic distances and bond angles of the anionic groups are listed in Table 4. The SO_4 tetrahedra are not regular but somewhat distorted. Baur (1964) and Larson (1965) have tabulated the

Table 1. Final positional parameters ($\times 10^5$)

The standard deviations are given in parentheses in units of the last decimal place.

	Position	x	y	z
Na(1)	12(i)	17859 (10)	36108 (9)	7435 (4)
Na(2)	12(i)	47753 (10)	-5305 (10)	16093 (3)
Na(3)	6(h)	34702 (14)	14658 (13)	$\frac{1}{2}$ *
Na(4)	6(g)	$\frac{1}{2}$ *	0	0
Na(5)	4(f)	$\frac{2}{3}$ *	$\frac{1}{3}$ *	12453 (6)
Na(6)	4(e)	0	0	17343 (6)
K	2(b)	0	0	0
C	4(f)	$\frac{1}{3}$ *	$\frac{2}{3}$ *	6968 (11)
O(1)	12(i)	38952 (18)	11372 (17)	14331 (6)
O(2)	12(i)	32254 (16)	7997 (16)	3420 (6)
O(3)	12(i)	44832 (16)	32454 (15)	8017 (6)
O(4)	12(i)	19578 (15)	15492 (16)	10588 (6)
O(5)	12(i)	19815 (18)	42962 (18)	19287 (6)
O(6)	12(i)	40396 (15)	80833 (14)	6986 (5)
O(7)	6(h)	9206 (22)	19996 (21)	$\frac{1}{2}$ *
O(8)	6(h)	35549 (23)	36790 (23)	$\frac{1}{2}$ *
S(1)	12(i)	33868 (5)	16841 (5)	9082 (2)
S(2)	6(h)	20856 (7)	35652 (8)	$\frac{1}{2}$ *
Cl	2(d)	$\frac{2}{3}$ *	$\frac{1}{3}$	$\frac{1}{4}$ *

* These values are not $\times 10^5$.

Table 2. Anisotropic thermal parameters ($\times 10^4$)

Temperature factors are of the form $\exp[-(h^2\beta_{11} + \dots + 2kl\beta_{23})]$. Standard deviations are equal to or smaller than ± 0.0003 .

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na(1)	56	40	16	22	-3	-1
Na(2)	61	67	10	38	-3	-3
Na(3)	88	57	10	35	0	0
Na(4)	50	47	8	20	0	3
Na(5)	55	55	14	28	0	0
Na(6)	54	54	9	27	0	0
K	55	55	8	27	0	0
C	39	39	4	20	0	0
O(1)	90	71	10	54	-1	5
O(2)	74	59	10	35	0	-6
O(3)	59	40	13	13	-1	4
O(4)	49	68	14	35	6	4
O(5)	77	72	15	35	-7	10
O(6)	46	31	10	15	1	1
O(7)	56	41	11	11	0	0
O(8)	60	68	12	36	0	0
S(1)	33	26	6	15	1	1
S(2)	33	30	8	16	0	0
Cl	80	80	11	40	0	0

S-O distances and bond angles of different sulphate structures. The variation interval for the S-O distances and O-S-O angles of the hanksite tetrahedra is very narrow and agrees well with values mentioned in the literature. The Cl ions are in special positions with point symmetry $\bar{6}$. The distances from a Cl ion to the next two Na(5) and three Na(3) are 2.665 and 2.918 Å respectively. The K ions are surrounded by six nearest oxygen neighbours at a distance of 2.929 Å and six other oxygens at a distance of 3.137 Å. The geometry about the Na ions is distorted octahedral with Na-O distances ranging from 2.288 to 2.687 Å. Only Na(3) has four nearest oxygen neighbours in tetrahedral arrangement with an average distance of 2.537 Å.

Table 3. Observed and calculated structure factors

F_o	F_c	F_e
H K L = 0	0 0 0	0 0 0
1 1 1	36 36 36	36 36 36
2 2 2	72 72 72	72 72 72
3 3 3	108 108 108	108 108 108
4 4 4	144 144 144	144 144 144
5 5 5	180 180 180	180 180 180
6 6 6	216 216 216	216 216 216
7 7 7	252 252 252	252 252 252
8 8 8	288 288 288	288 288 288
9 9 9	324 324 324	324 324 324
10 10 10	360 360 360	360 360 360
11 11 11	396 396 396	396 396 396
12 12 12	432 432 432	432 432 432
13 13 13	468 468 468	468 468 468
14 14 14	504 504 504	504 504 504
15 15 15	540 540 540	540 540 540
16 16 16	576 576 576	576 576 576
17 17 17	612 612 612	612 612 612
18 18 18	648 648 648	648 648 648
19 19 19	684 684 684	684 684 684
20 20 20	720 720 720	720 720 720
21 21 21	756 756 756	756 756 756
22 22 22	792 792 792	792 792 792
23 23 23	828 828 828	828 828 828
24 24 24	864 864 864	864 864 864
25 25 25	900 900 900	900 900 900
26 26 26	936 936 936	936 936 936
27 27 27	972 972 972	972 972 972
28 28 28	1008 1008 1008	1008 1008 1008
29 29 29	1044 1044 1044	1044 1044 1044
30 30 30	1080 1080 1080	1080 1080 1080
31 31 31	1116 1116 1116	1116 1116 1116
32 32 32	1152 1152 1152	1152 1152 1152
33 33 33	1188 1188 1188	1188 1188 1188
34 34 34	1224 1224 1224	1224 1224 1224
35 35 35	1260 1260 1260	1260 1260 1260
36 36 36	1296 1296 1296	1296 1296 1296
37 37 37	1332 1332 1332	1332 1332 1332
38 38 38	1368 1368 1368	1368 1368 1368
39 39 39	1404 1404 1404	1404 1404 1404
40 40 40	1440 1440 1440	1440 1440 1440
41 41 41	1476 1476 1476	1476 1476 1476
42 42 42	1512 1512 1512	1512 1512 1512
43 43 43	1548 1548 1548	1548 1548 1548
44 44 44	1584 1584 1584	1584 1584 1584
45 45 45	1620 1620 1620	1620 1620 1620
46 46 46	1656 1656 1656	1656 1656 1656
47 47 47	1692 1692 1692	1692 1692 1692
48 48 48	1728 1728 1728	1728 1728 1728
49 49 49	1764 1764 1764	1764 1764 1764
50 50 50	1800 1800 1800	1800 1800 1800
51 51 51	1836 1836 1836	1836 1836 1836
52 52 52	1872 1872 1872	1872 1872 1872
53 53 53	1908 1908 1908	1908 1908 1908
54 54 54	1944 1944 1944	1944 1944 1944
55 55 55	1980 1980 1980	1980 1980 1980
56 56 56	2016 2016 2016	2016 2016 2016
57 57 57	2052 2052 2052	2052 2052 2052
58 58 58	2088 2088 2088	2088 2088 2088
59 59 59	2124 2124 2124	2124 2124 2124
60 60 60	2160 2160 2160	2160 2160 2160
61 61 61	2196 2196 2196	2196 2196 2196
62 62 62	2232 2232 2232	2232 2232 2232
63 63 63	2268 2268 2268	2268 2268 2268
64 64 64	2304 2304 2304	2304 2304 2304
65 65 65	2340 2340 2340	2340 2340 2340
66 66 66	2376 2376 2376	2376 2376 2376
67 67 67	2412 2412 2412	2412 2412 2412
68 68 68	2448 2448 2448	2448 2448 2448
69 69 69	2484 2484 2484	2484 2484 2484
70 70 70	2520 2520 2520	2520 2520 2520
71 71 71	2556 2556 2556	2556 2556 2556
72 72 72	2592 2592 2592	2592 2592 2592
73 73 73	2628 2628 2628	2628 2628 2628
74 74 74	2664 2664 2664	2664 2664 2664
75 75 75	2700 2700 2700	2700 2700 2700
76 76 76	2736 2736 2736	2736 2736 2736
77 77 77	2772 2772 2772	2772 2772 2772
78 78 78	2808 2808 2808	2808 2808 2808
79 79 79	2844 2844 2844	2844 2844 2844
80 80 80	2880 2880 2880	2880 2880 2880
81 81 81	2916 2916 2916	2916 2916 2916
82 82 82	2952 2952 2952	2952 2952 2952
83 83 83	2988 2988 2988	2988 2988 2988
84 84 84	3024 3024 3024	3024 3024 3024
85 85 85	3060 3060 3060	3060 3060 3060
86 86 86	3096 3096 3096	3096 3096 3096
87 87 87	3132 3132 3132	3132 3132 3132
88 88 88	3168 3168 3168	3168 3168 3168
89 89 89	3204 3204 3204	3204 3204 3204
90 90 90	3240 3240 3240	3240 3240 3240
91 91 91	3276 3276 3276	3276 3276 3276
92 92 92	3312 3312 3312	3312 3312 3312
93 93 93	3348 3348 3348	3348 3348 3348
94 94 94	3384 3384 3384	3384 3384 3384
95 95 95	3420 3420 3420	3420 3420 3420
96 96 96	3456 3456 3456	3456 3456 3456
97 97 97	3492 3492 3492	3492 3492 3492
98 98 98	3528 3528 3528	3528 3528 3528
99 99 99	3564 3564 3564	3564 3564 3564
100 100 100	3600 3600 3600	3600 3600 3600

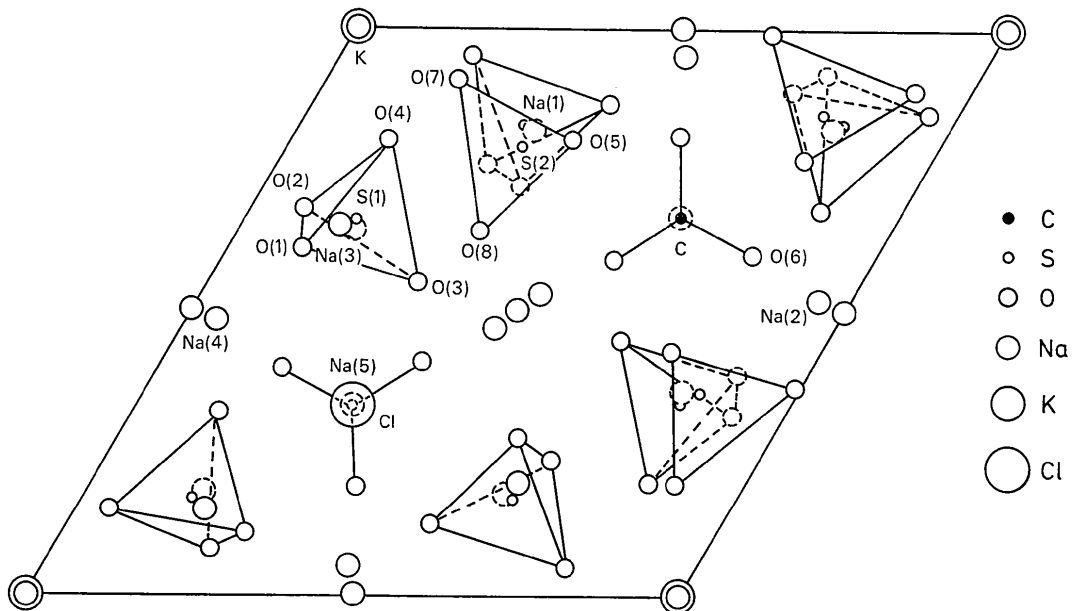


Fig. 1. Structure of hanksite (c-axis projection).

Table 4. *Interatomic distances and bond angles*

The standard deviations are equal to or smaller than ± 0.0028 Å for the bond lengths and equal to or smaller than $\pm 0.13^\circ$ for the bond angles.

(a) Tetrahedral groups

S(1)–O(1)	1.470 Å	Range of 6 O–O	2.389–2.427 Å
S(1)–O(2)	1.476	Mean of 6 O–O	2.404
S(1)–O(3)	1.474	Range of 6 O–S–O	108.4–110.7°
S(1)–O(4)	1.469	Mean of 6 O–S–O	109.5
Mean of 4	1.472		

S(2)–O(5)	1.468 Å	Range of 6 O–O	2.384–2.427 Å
S(2)–O(5')	1.468	Mean of 6 O–O	2.408
S(2)–O(7)	1.478	Range of 6 O–S–O	107.6–111.5°
S(2)–O(8)	1.485	Mean of 6 O–S–O	109.5
Mean of 4	1.475		

(b) Carbonate group

C–O(6) 1.287 Å

(c) Na–Cl distances

Na(3)–Cl	2.918 Å
Na(5)–Cl	2.665

(d) Cation–oxygen distances

K—O(4)	2.929 Å	Na(3)–O(1)	2.368 Å
K—O(2)	3.137	Na(3)–O(7)	2.994
Na(1)–O(4)	2.355	Na(3)–O(8)	2.279
Na(1)–O(5)	2.598	Na(3)–O(7')	2.506
Na(1)–O(6)	2.397	Na(4)–O(2)	2.502
Na(1)–O(6')	2.420	Na(4)–O(6)	2.288
Na(2)–O(1)	2.381	Na(5)–O(1)	2.687
Na(2)–O(6)	2.309	Na(5)–O(3)	2.435
		Na(6)–O(4)	2.362
		Na(6)–O(7)	2.440

The superstructure of low-temperature hanksite can be explained by ordered distribution of CO₃ groups, K and Cl ions and the arrangement of the tilted SO₄ tetrahedra. A similar type of ordering is found in the structure of a PO₄-containing phase of Ca₂SiO₄, where the high-temperature form is isostructural with K₂SO₄ I. The low temperature form shows a hexagonal superstructure with the space group *P*6₁. This superstructure (*a* = 10.76, *c* = 21.73 Å) which is comparable with hanksite, is caused by an ordered distribution of SiO₄ and PO₄ groups. The structure determination (Jarchow & Saalfeld, in preparation) revealed that as with hanksite the tetrahedra are tilted with respect to the six-

fold axis. Other structural relationships, however, do not exist due to the difference in chemical composition and space group symmetry.

Eysel (1971) discusses the distribution of [XO₄] tetrahedra and planar [XO₃] groups in solid-solution series of compounds crystallizing in the K₂SO₄ I type. A statistical distribution should not affect magnitude and symmetry of the unit cell. By ordering of the atomic groups, however, new periodicities can occur in connexion with supercells and change in symmetry. Hanksite serves well to illustrate this possibility. In the low-temperature form all atoms occupy definite positions and a superstructure results. At high temperatures the decomposition product consists mainly of a hexagonal phase with unit-cell and space-group symmetry comparable with K₂SO₄ I. A statistical distribution of SO₄ and CO₃ groups must be assumed. As in K₂SO₄ I the SO₄ tetrahedra can no longer be tilted with regard to the *c* axis. A detailed structure determination is in preparation.

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