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The Crystal Structure of Sodium Perxenate Hexahydrate[1]

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Crystals of $Na_4XeO_6 \cdot 6H_2O$ were studied by X-ray diffraction, and the subsequent crystal structure analysis determined its composition. This material crystallizes in the orthorhombic space group Pbca, with $a = 18.44$, $b = 10.103$, and $c = 5.873$ Å. There are four molecules per unit cell and the calculated X-ray density is 2.59 g./cc. The structure consists of two types of layers stacked alternately in the a direction and tied to each other by hydrogen bonds. One type layer contains a hexagonal array of all of the perxenate and half of the sodium ions, and the second type has all of the water in octahedra about the remaining sodium ions. The perxenate ion in this salt is octahedral with an average Xe–O bond distance of 1.84 ± 0.02 Å.

Introduction

Malm, Bane, and Holt[2] produced hydrated sodium salts of +8 xenon by hydrolyzing XeF_6 in sodium hydroxide. Siegel and Gebert[3] reported the cell dimensions of three such phases. Hamilton, Ibers, and MacKenzie[4] identified one of these phases by a crystal structure determination as $Na_4XeO_6 \cdot 8H_2O$; they found the perxenate ion to be a regular octahedron. The hexahydrate reported here is a different crystallographic species from any of the above-mentioned phases. We undertook the crystal structure analysis of this material to determine its composition and to study the chemical and geometric properties of xenon in the compounded state.

Experimental

Preparation.—Crystals of $Na_4XeO_6 \cdot 6H_2O$ were prepared[5] from the reaction of aqueous XeO_3[6,7] and sodium hydroxide. Several preparations were required for the production of enough fresh crystals to complete the X-ray analysis. A typical preparation was as follows: 0.100 ml. of 0.208 *M* XeO_3 (aqueous) and 0.06 *M* NaOH were mixed together resulting in a pale yellow solution; upon setting in a refrigerator for 1 day at 5°, very thin, fragile, colorless crystals developed. This plate-like appearance of the hexahydrate makes it easy to distinguish from the granular octahydrate which was found on occasion in some of the solutions.

Preliminary Observations.—The crystals of the hexahydrate are fairly unstable. Our first attempt to study the crystal was to remove one from the mother liquor and to glue it to a glass fiber for the X-ray work. Weissenberg patterns were taken for about 2 days before diffraction from the sample ceased. The patterns were of very poor quality, with elongated spots indicating a great deal of disorder. The crystal physically curled on its mount. A space group could not be determined from these films, but an orthorhombic cell with $a = 10.10$, $b = 5.87$, and $c = 6.23$ Å. was measured which corresponds to that described by Siegel and Gebert[3] as possibly a dihydrate; the values they report are 10.28, 5.77, and 6.25 Å.

To keep the crystals from dehydrating they were placed inside 0.5-mm. capillaries that had been wetted by the mother liquor, and the capillaries were then sealed. In spite of these precautions, the crystals decayed during the data taking period. The half-life of the phase (as measured by monitoring the 400 reflection) varied from 2 to 24 hr. Upon decomposition two phases grew into the crystal *in situ* without changing the physical shape of the crystal. These phases were also unstable, yielding diffraction patterns for a day or two before they ceased to diffract. From some poor Weissenberg patterns two phases were measured as well as possible. One phase is possibly orthorhombic with $a = 6.25$, $b = 5.16$, and $c = 5.89$ Å. The second phase appears to be twinned and seems to be monoclinic with $a = 6.25$, $b = 20.16$, $c = 5.89$ Å., and $\beta = 91.5°$.

Our experience with the octahydrate[4] shows it to be considerably more stable than the hexahydrate. The octahydrate would undergo X-radiation for days with no apparent decomposition, whereas the hexahydrate would decompose at a steady rate. The octahydrate could be handled in air for several hours with no serious dehydration, and under the same conditions the hexahydrate would be badly desiccated.

X-Ray Diffraction.—Data for this work were obtained from five different crystals, though more were used for some of the preliminary investigations. The crystals were fragile thin plates about 0.3 mm. in the planar dimensions, and very thin, probably less than 0.05 mm. The crystal thickness was impossible to measure with our microscope as it has to be viewed through the capillary wall into the drop of mother liquor surrounding it, and it just could not be seen clearly. The crystals could be rapidly oriented along the b or c axis of the cell with the use of polarized light. The a axis is normal to the crystal plate. The alignment and data taking were done on a G.E. XRD-5 and goniostat using 0.001-in. Zr-filtered Mo Kα radiation ($\lambda_{K\alpha_1}$ 0.70926 Å.) and a scintillation counter.

Ultimately 992 independent reflections were measured. The maximum 2θ value was 60°. Up to 30° of 2θ all of the available reflections were measured. As the crystals had a short lifetimes data taking in the 30 to 60° region was limited to those reflection, that would give some economy on setup time. Most of the data above 30° of 2θ were equal to or below twice the background.

The data were adjusted for decomposition and normalized among the five crystals. The 400 reflection was used as a standard and was measured frequently during the data taking. Small adjustments of the normalizing factors were made toward the end of the work after least squares had shown systematic variations among the five sets of data. The crystals varied in shapes and sizes, which accounts for some of the systematic errors; because of these complexities absorption corrections were not even attempted.

The data were corrected for the Lorentz and polarization effects. All of the calculations were made on an IBM-7094 using a goniostat-setting program by A. C. Larson, a Fourier and data processing program by A. Zalkin, and a modified least-squares

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[1] Work done under the auspices of the U. S. Atomic Energy Commission.

[2] J. G. Malm, B. D. Holt, and R. W. Bane, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 167.

[3] S. Siegel and E. Gebert, *ibid.*, p. 193.

[4] W. C. Hamilton, J. A. Ibers, and D. R. MacKenzie, *Science*, **141**, 532 (1963); *Inorg. Chem.*, **3**, 1412 (1964).

[5] A. Zalkin, J. D. Forrester, D. H. Templeton, S. M. Williamson, and C. W. Koch, *Science*, **142**, 501 (1963).

[6] D. F. Smith, *J. Am. Chem. Soc.*, **85**, 816 (1963).

[7] D. H. Templeton, A. Zalkin, J. D. Forrester, and S. M. Williamson, *ibid.*, **85**, 817 (1963).

TABLE I

FINAL POSITIONAL PARAMETERS AND TEMPERATURE FACTORS, AND THEIR STANDARD DEVIATIONS IN $Na_4XeO_6 \cdot 6H_2O$

Atom	x	y	z	B, Å.^{2}	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$
Xe	0.0	0.0	0.0	(0.85)[a]	0.0	0.0	0.0	(0.05)[a]
Na(1)	0.009	0.164	0.492	1.4	0.001	0.001	0.003	0.2
Na(2)	0.252	0.155	0.539	1.6	0.001	0.001	0.002	0.2
O(1)	0.060	0.004	0.253	1.2	0.001	0.003	0.003	0.2
O(2)	0.064	0.115	0.854	1.7	0.001	0.002	0.004	0.4
O(3)	0.951	0.136	0.127	1.0	0.001	0.002	0.003	0.4
O(W1)[b]	0.169	0.200	0.242	1.6	0.001	0.002	0.004	0.3
O(W2)	0.340	0.183	0.835	1.5	0.001	0.002	0.004	0.3
O(W3)	0.192	0.518	0.242	2.2	0.001	0.002	0.004	0.4

[a] Isotropic value equivalent to average of anisotropic values. [b] O(Wn) means the oxygen of water molecule n.

TABLE II

INTERATOMIC DISTANCES AND STANDARD DEVIATIONS LESS THAN 3.0 Å. IN $Na_4XeO_6 \cdot 6H_2O$

Atoms	D, Å.	$\sigma(D)$	Atoms	D, Å.	$\sigma(D)$	Atoms	D, Å.	$\sigma(D)$
Xe–2O(1)	1.86	0.02[a]	O(1)–Xe	1.86[a]	0.02	O(3)–Xe	1.80[a]	0.02
Xe–2O(2)	1.87	0.02[a]	O(1)–Na(1)	2.35	0.03	O(3)–Na(1)	2.41	0.03
Xe–2O(3)	1.80	0.02[a]	O(1)–Na(1)	2.60	0.03	O(3)–Na(1)	2.42	0.03
			O(1)–O(2)	2.60	0.03	O(3)–O(1)	2.52	0.03
Na(1)–O(1)	2.35	0.03	O(1)–O(2)	2.66	0.03	O(3)–O(1)	2.65	0.03
Na(1)–O(1)	2.60	0.03	O(1)–O(3)	2.52	0.03	O(3)–O(2)	2.55	0.03
Na(1)–O(2)	2.41	0.03	O(1)–O(3)	2.65	0.03	O(3)–O(2)	2.63	0.03
Na(1)–O(2)	2.58	0.03	O(1)–O(W1)	2.81[b]	0.03	O(3)–O(W2)	2.76[b]	0.03
Na(1)–O(3)	2.41	0.03	O(1)–O(W2)	2.69[b]	0.03			
Na(1)–O(3)	2.42	0.02				O(W1)–Na(2)	2.37	0.02
			O(2)–Xe	1.87[a]	0.02	O(W1)–Na(2)	2.44	0.02
Na(2)–O(W1)	2.37	0.02	O(2)–Na(1)	2.41	0.03	O(W1)–O(1)	2.81[b]	0.03
Na(2)–O(W1)	2.44	0.02	O(2)–Na(1)	2.58	0.03	O(W1)–O(2)	2.77[b]	0.03
Na(2)–O(W2)	2.39	0.02	O(2)–O(1)	2.60	0.03			
Na(2)–O(W2)	2.59	0.02	O(2)–O(1)	2.66	0.03	O(W2)–Na(2)	2.39	0.02
Na(2)–O(W3)	2.39	0.02	O(2)–O(3)	2.55	0.03	O(W2)–Na(2)	2.59	0.02
Na(2)–O(W3)	2.45	0.02	O(2)–O(3)	2.63	0.03	O(W2)–O(1)	2.69[b]	0.03
			O(2)–O(W1)	2.77[b]	0.03	O(W2)–O(3)	2.76[b]	0.03
			O(2)–O(W3)	2.79[b]	0.03	O(W2)–O(W3)	2.97[b]	0.03
						O(W3)–Na(2)	2.39	0.02
						O(W3)–Na(2)	2.45	0.02
						O(W3)–O(2)	2.79[b]	0.03
						O(W3)–O(W2)	2.97[b]	0.03

[a] Perxenate Xe–O bonds. [b] Hydrogen bonds.

TABLE III

HYDROGEN BOND DISTANCES AND ANGLES[a]

Atom	D, Å.	Atom	D. Å.	Atom	Angle, deg.
O(1)	·····2.81——	O(W1)	——2.77·····	O(2)	88
O(1)	·····2.69——	O(W2)	——2.76·····	O(3)	88
O(2)	·····2.79——	O(W3)	——2.97·····	O(W2)	107

[a] Estimated standard deviation of the distances are ±0.03 Å., and of the angles ±1°.

TABLE IV

GEOMETRY OF THE PERXENATE ION IN $Na_4XeO_6 \cdot 6H_2O$

Bond	Distance, Å.	Bond Angle	Angle, deg.
Xe–O(1)	1.86 ± 0.02	O(1)–Xe–O(2)	89 ± 1°
Xe–O(2)	1.87 ± 0.02	O(1)–Xe–O(3)	87 ± 1°
Xe–O(3)	1.80 ± 0.02	O(2)–Xe–O(3)	88 ± 1°

program by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood (all unpublished). The function minimized in the least-squares computations was $\Sigma\, w(|F_o| - |F_c|)^2/\Sigma w F_o^2$, where w is the weighting factor and F_o and F_c are the observed and calculated structure factors; 491 reflections were given unit weight; 501 reflections with 2θ greater than 40° and whose intensities were measured to be equal to or less than background (3 counts/sec.) were given zero weight. The zero weighted data have no effect on the results, but were included to assure us that those reflections that were observed very weak are also calculated very weak.

Atomic scattering factors were taken for Na^+, neutral Xe, and neutral oxygen (Ibers[8]) unmodified for dispersion (Templeton[9]) which for the heaviest atom Xe is only -0.5 electron.

Unit Cell and Space Group.—The crystals are orthorhombic with unit cell dimensions: $a = 18.44 \pm 0.01$, $b = 10.103 \pm 0.007$, and $c = 5.875 \pm 0.005$ Å. With four molecules per unit cell, the density calculated from the above dimensions is 2.59 g./cc.; the crystals were observed to sink in ethylene bromide (density 2.17 g./cc.). The space group is Pbca (D_{2h}^{15}), the only one which requires the systematic extinctions: $0kl$, $k \neq 2n$; $h0l$, $l \neq 2n$; and $hk0$, $h \neq 2n$.

Determination of Structure.—The arrangement of the Xe atoms was inferred from the pseudo-face-centering indicated by the data. Since there were only four Xe atoms in the unit cell they were placed at the origin and at the face centers. Three Fourier projections perpendicular to the three major axes were calculated using only the face-centered terms, the signs of all these terms being positive. These early calculations were done in space group $P2_12_12_1$ as a few weak spurious reflections had been observed which indicated no glide plane extinctions. These reflections were later found to be absent on a freshly prepared crystal. These projections showed a grouping of small peaks about the Xe which were interpreted as an octahedron of oxygen, a couple of larger peaks that were interpreted as sodium atoms, and a scattering of small peaks which were interpreted as being

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(8) J. A. Ibers in "International Table for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1962, Vol. III, pp. 202–211.

(9) D. H. Templeton, *ibid.*, p. 215.

TABLE V: TABLE OF OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $Na_4XeO_6 \cdot 6H_2O$[a]

CRYSTAL 1

H	K	L	FOB	FCA
0	2	0	167	164
0	2	1	0	6
0	2	4	135	136
0	2	5	22	-7*
0	2	7	27	29*
0	2	8	69	72
0	4	0	96	95
0	4	1	0	-9
0	4	2	31	26
0	4	5	0	2*
0	4	7	23	-17*
0	6	0	317	320
0	6	3	26	29
0	6	4	178	171
0	6	5	0	-32*
0	6	6	89	87
0	6	7	24	3*
0	8	0	135	138
0	8	1	0	-10*
0	8	2	92	92
0	8	3	0	10*
0	8	4	86	81
0	8	5	0	16*
0	10	0	87	96
0	10	1	0	-24*
0	10	3	0	5*
0	10	5	0	-2*
0	12	0	101	100
0	12	1	0	-0*
0	12	3	0	13*
0	12	4	91	94
0	14	0	55	73
0	14	1	0	-2*
1	0	2	40	27
1	0	4	45	-49
1	0	6	34	-35
1	0	8	0	2*
1	1	1	220	202
1	1	2	32	-22
1	1	3	104	98
1	1	4	0	13*
1	1	5	83	84
1	1	6	0	10*
1	1	7	90	84
1	1	8	0	5*
1	2	2	0	-11
1	2	4	42	22
1	2	5	0	1*
1	2	6	0	8*
1	2	7	0	-3*
1	2	8	0	-0*
1	3	1	214	212
1	3	2	0	14
1	3	3	228	212
1	3	4	0	-11*
1	3	5	161	145
1	3	6	0	3*
1	3	7	96	88
1	3	8	0	4*
1	4	1	0	-29
1	4	2	0	-10*
1	4	3	41	-44
1	4	4	0	30*
1	4	5	0	1*
1	4	6	46	17
1	4	7	0	2*
2	0	0	223	243
2	0	4	103	110
2	0	6	107	120
2	0	8	75	92
2	2	0	224	226
2	2	2	141	133
2	2	4	133	126
2	2	6	82	81
2	2	8	58	64
2	4	4	143	140
2	6	0	136	140
2	6	2	151	143
2	6	4	136	123
2	6	6	81	89
2	8	0	137	149
2	8	2	78	77
2	8	4	78	74
2	8	6	70	68
3	0	6	28	6
3	3	3	251	225
3	3	6	0	-0*
3	6	3	0	7*
3	6	6	35	15
3	9	3	119	118
3	9	6	0	3*
3	12	3	29	15*
4	0	0	275	309
4	0	8	83	76
4	4	0	73	77
4	4	4	101	90
4	8	0	122	130
4	8	4	85	82
4	12	0	99	103
4	12	4	72	85
5	5	5	83	83
5	10	5	0	-10*
6	0	6	107	105
6	6	0	164	159
6	6	6	110	99
6	12	0	80	79
8	8	0	63	59
10	10	0	76	81
12	12	0	80	81

CRYSTAL 2

H	K	L	FOB	FCA
1	8	1	17	36*
1	5	1	105	94
1	6	1	33	-28
1	7	1	131	124
1	9	1	146	147
1	6	2	16	-5*
1	7	2	0	-16*
1	8	2	0	-3*
1	9	2	19	-5*
1	5	2	23	17
1	6	3	0	-0*
1	8	3	19	19*
1	5	3	127	145
1	7	3	84	77
1	9	3	104	103
1	5	4	0	-8*
1	7	4	20	16*
1	9	4	22	-5*
1	6	4	40	-26
1	6	5	20	-8*
1	8	5	0	4*
1	5	5	98	91
1	7	5	70	67
1	9	5	96	91
1	5	6	22	-12*
1	6	6	22	-17*
1	7	6	23	6*
1	8	6	24	-4*
1	9	6	25	9*
1	6	7	24	2*
1	5	7	70	57
1	7	7	75	71
1	10	1	0	-3*
1	12	1	23	-19*
1	14	1	25	10*
1	11	1	67	69
1	13	1	51	61
1	13	2	0	8*
1	10	2	0	12*
1	11	2	0	5*
1	12	2	0	-6*
1	10	3	21	-11*
1	12	3	0	3*
1	11	3	80	87
1	13	3	47	61
1	10	5	0	-2*
1	11	5	59	66
2	1	0	0	-4
2	1	1	0	4
2	3	1	48	32
2	1	2	0	16
2	3	2	0	-14
2	1	3	29	25
2	3	3	44	-27
2	3	4	0	20*
2	1	4	45	-33
2	1	5	31	-16
2	1	6	25	13*
2	3	6	0	-14*
2	0	7	0	-0*
2	1	7	28	-1*
2	2	7	28	-18*
2	3	7	28	7*
2	1	8	31	-6*
2	3	8	0	5*
2	10	0	100	99
2	14	0	73	66
2	10	2	96	97
2	12	2	90	77
2	10	4	95	81
2	12	4	90	90
4	2	0	180	172
4	6	0	206	213
4	6	2	185	202
4	0	2	273	310
4	2	4	112	106
4	6	4	137	145
4	2	6	70	81
4	4	6	78	76
4	6	6	86	92
4	0	6	110	112
4	2	8	64	64
6	9	0	0	23*
6	3	0	0	13
6	3	6	26	-5*
6	9	6	0	-2*
8	4	0	74	73
8	0	4	148	152
8	12	0	120	98
10	5	0	0	7*
10	5	5	26	-0*
12	6	0	162	158
12	0	6	106	93
14	7	0	25	-11*
16	8	0	109	108
18	9	0	0	-1*

CRYSTAL 3

H	K	L	FOB	FCA
2	5	0	0	-11*
2	7	0	21	24
2	9	0	12	14*
2	11	0	20	-10*
2	13	0	0	4*
4	1	0	0	-14
4	5	0	0	-7*
4	7	0	11	-19*
4	9	0	13	-7*
4	10	0	38	48
4	11	0	20	-7*
4	13	0	28	-28*
4	14	0	61	72
6	1	0	0	-10
6	2	0	91	94
6	5	0	19	5
6	7	0	20	-0*
6	8	0	55	46
6	10	0	107	109
6	11	0	0	1*
6	13	0	0	-11*
8	1	0	0	-3
8	2	0	57	62
8	3	0	0	15*
8	5	0	0	-9*
8	7	0	29	-12
8	9	0	23	4*
8	10	0	47	35
8	11	0	0	2*
8	13	0	29	-3*
10	1	0	0	9*
10	2	0	162	165
10	3	0	0	6*
10	4	0	173	177
10	6	0	98	92
10	7	0	17	-27*
10	8	0	84	77
10	9	0	0	-3*
10	11	0	0	17*
10	12	0	79	78
10	13	0	0	-12*
12	1	0	15	-35*
12	2	0	61	55
12	3	0	31	22
12	4	0	95	87
12	5	0	0	40*
12	7	0	0	-22*
12	8	0	61	52
12	9	0	0	7*
12	10	0	77	72
12	11	0	0	24*
14	1	0	0	-20*
14	2	0	134	131
14	3	0	0	-2*
14	4	0	110	112
14	5	0	0	10*
14	6	0	91	88
14	8	0	94	89
14	9	0	0	-13*
14	10	0	85	83
14	11	0	23	2*
16	1	0	0	-32*
16	2	0	122	126
16	3	0	18	-17*
16	4	0	61	76
16	5	0	0	42*
16	6	0	129	124
16	7	0	0	-5*
16	9	0	22	-16*
16	10	0	65	57
16	11	0	24	17*
18	1	0	0	-38*
18	2	0	83	76
18	4	0	81	82
18	5	0	0	26*
18	6	0	91	86
18	8	0	65	66
18	10	0	70	77
20	1	0	20	-27*
20	2	0	81	78
20	3	0	0	-13*
20	4	0	55	53
20	5	0	30	14
20	6	0	100	97
20	7	0	23	-5*
20	8	0	77	73
20	9	0	0	-12*
22	1	0	21	-2*
22	3	0	22	-4*
22	4	0	65	67
22	5	0	0	8*
22	6	0	52	51
22	7	0	0	-1*
24	1	0	0	-16*
24	2	0	40	33
24	3	0	28	6*
24	4	0	47	41
24	5	0	0	7*

CRYSTAL 4

H	K	L	FOB	FCA
2	4	1	33	28
2	4	3	47	38
2	5	1	80	-77
2	5	2	23	1*
2	5	3	31	13*
2	5	4	20	16*
2	6	1	28	23*
2	6	3	32	2*
2	7	1	18	26*
2	7	2	26	-11*
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2	11	1	33	-22*
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3	5	2	23	-5*
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3	6	2	39	22
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12	7	3	32	-24*
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13	3	2	0	18*
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13	4	2	0	33*
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13	6	2	21	-5*
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13	7	2	0	-15*
13	7	3	81	79
13	8	1	32	25*
13	8	2	23	-21*
13	8	3	42	29*
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13	9	2	35	15*
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14	0	6	81	85
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15	6	1	0	13*
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15	6	3	24	1*
15	7	1	83	73
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16	0	4	109	115
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16	2	4	88	88
16	2	6	54	51
16	3	1	0	0*
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16	6	4	98	104
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16	8	4	66	63
16	10	2	54	43
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17	3	1	94	91
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18	0	4	69	69
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18	2	4	74	70
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18	4	4	80	86
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20	0	4	63	69
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20	8	2	55	52
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22	0	4	54	53
22	2	2	67	67
22	2	4	61	55
22	4	2	78	70
22	6	2	54	60
24	0	2	80	76
24	2	2	76	71
24	4	2	55	55

CRYSTAL 5

H	K	L	FOB	FCA
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0	0	4	219	209
0	0	6	97	107
0	0	8	89	103
0	2	2	86	83
0	2	3	37	42
0	2	6	60	63
0	4	3	26	-19
0	4	4	175	164
0	4	6	34	46
0	6	1	35	-38
0	6	2	162	150
0	8	6	63	59
0	10	2	15	29
0	10	4	78	83
0	12	0	90	100
0	12	2	92	96
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1	10	4	0	10*
1	11	4	0	-6*
1	12	4	0	-7*
2	0	2	207	207
2	2	1	14	-13
2	2	3	55	-62
2	2	5	22	-21
2	3	0	19	6
2	3	5	0	9*
2	4	0	115	117
2	4	2	163	164
2	4	6	67	73
2	12	0	75	85
4	0	4	196	182
4	2	2	96	88
4	3	0	51	-45
4	3	1	206	-180
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4	4	2	85	85
4	7	5	0	-34*
5	1	4	0	18*
5	3	4	0	0*
6	0	0	243	218
6	3	1	26	-37
6	3	3	0	-13*
6	4	0	212	198
6	6	3	13	31*
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6	9	3	0	11*
7	0	4	0	22*
7	1	4	17	21*
7	9	1	107	118
8	0	0	91	97
8	0	2	316	329
8	4	4	23	24
8	6	0	144	148
8	6	2	215	207
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10	0	2	170	158
10	3	2	0	9*
12	0	0	221	225
12	0	2	176	164
12	2	4	55	69
12	6	6	82	82
14	0	0	110	106
14	1	6	17	7*
14	4	2	106	107
14	8	2	51	63
16	0	0	179	181
18	0	0	125	125
18	3	0	0	-8*
18	7	0	0	-7*
20	0	0	132	122
22	0	0	45	50
22	2	0	75	74
24	0	0	70	73

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[a] Reflections given zero weight are marked with an asterisk.

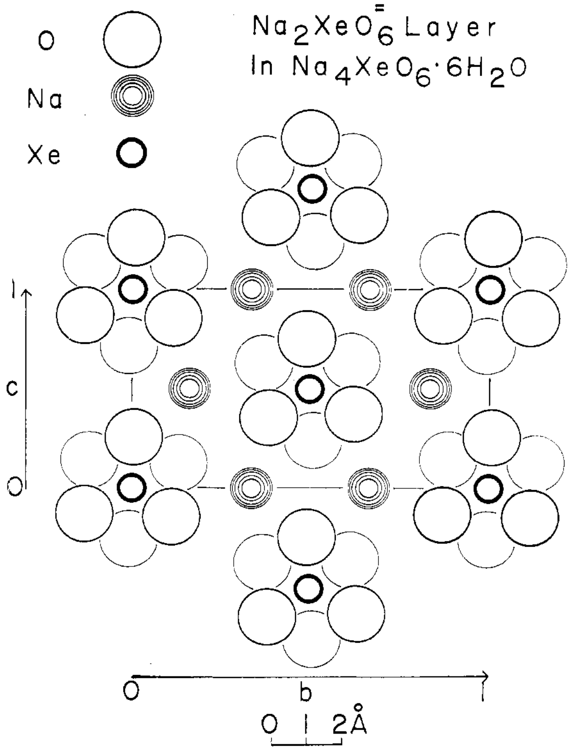

Fig. 1.—The layer containing the perxenate ions and half of the sodium ions.

water of hydration about the sodium. On the basis of these calculations we were able to propose the composition as $Na_4XeO_6 \cdot 6H_2O$. This trial structure was geometrically and chemically very satisfactory, and except for the detailed numbers was substantially the same structure at the end of the analysis.

The least-squares refinement of the structure was started while the data were being taken, and progress was slow. When all of the data were available, a three-dimensional Patterson function was calculated which was in excellent agreement with the trial structure. The structure being refined consisted of one Xe, four sodium, and twelve oxygen atoms all in general positions in space group $P2_12_12_1$. All of the atoms were treated isotropically with a temperature factor of the form $\exp(-B \sin^2 \theta/\lambda^2)$, where B is the thermal parameter in Å.^{2}, θ is the Bragg diffraction angle, and λ is the X-ray wave length in Å. At the end of the twelfth series of refinements the structure had refined to an unreliability factor, $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$, of 0.12.

A study of the structure indicated that it could be described rather accurately in space group Pbca. A new crystal was obtained from a fresh sample and immediately checked for space group extinctions, and indeed the extinctions corresponded exactly to Pbca. The nonextinguished reflections agree very well with the previous measurements.

In Pbca the Xe is in a special fourfold position at the origin, which is also a center of symmetry. The sodium and oxygen atoms occupy general eightfold positions. The intensities were corrected for several blunders such as the mistyping of data cards and the missetting of the goniostat. After a series of refinement the five scale factors were readjusted. At the end of the fifteenth series of refinement the R factor was 0.092. Although this is a respectable R factor, we were haunted by some disturbing features of the results. In particular, one of the water molecules (W5) was less than 2.1 Å. away from a sodium (Na3), whereas all the other water molecule distances were greater than 2.3 Å. Also a few of the weaker reflections were in bad agreement, a fact that was confirmed by carefully remeasuring these data. Temperature factors of similar oxygen atoms were quite different.

Several series of refinements were tried with minor adjustments in the structure. First the z parameter of the errant water molecule was moved to a location that gave it better interatomic distances, but it refined back to its old location. Then the z parameters of sodium and the other two water oxygens were reset, and this refined to a less desirable structure with an R factor of 0.11. Xe was given an anisotropic temperature factor of the form $\exp \sum_{i=1}^{3}\sum_{j=1}^{3} -B_{ij}a_i^*a_j^*h_ih_j/4$, where B_{ij} are the thermal parameters in Å.^{2}, a^* is the reciprocal axis length, and h is the Miller index. This made no basic change in the structure, although it lowered the R factor to 0.082.

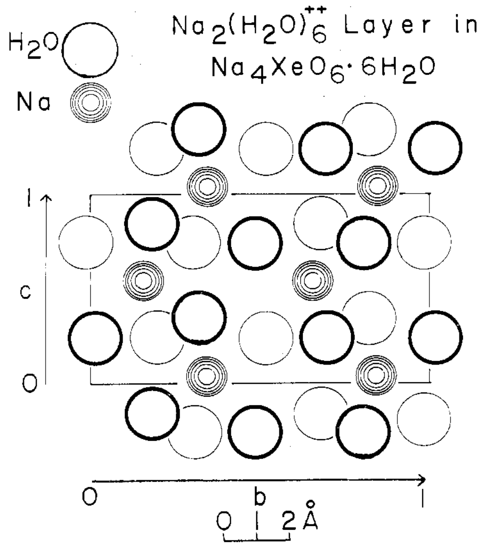

Fig. 2.—The layer containing the water oxygens and half of the sodium ions.

Success was achieved when the y parameter of the troublesome water molecule (W5) was reset to a value greater than 0.5, whereas previously it had refined to a value of less than 0.5. This last change made a dramatic difference. The bad distance improved considerably, the temperature factors of the oxygen atoms became more uniform, and the discrepancies between the observed and calculated values of certain weak reflections disappeared.

Xenon was treated anisotropically in the final refinements. Since the standard deviations of the B_{12}, B_{13}, and B_{23} parameters were larger than the parameters themselves, these parameters were set to zero and not refined. The values for B_{11}, B_{22}, and B_{33} are 1.10 ± 0.06, 0.73 ± 0.05, and 0.71 ± 0.05 Å.^{2}, respectively. The average of these values is reported in Table I. The final R factor is 0.073.

Results and Discussion

Description of Structure.—The xenon atoms are located at the origin and face centers of the cell in a fourfold position. Each of the two sodiums, three perxenate oxygens, and three water oxygens occupy the general eightfold position: $\pm(x, y, z;\ ^1/_2 + x,\ ^1/_2 - y,\ -z;\ -x,\ ^1/_2 + y,\ ^1/_2 - z;\ ^1/_2 - x,\ -y,\ ^1/_2 + z)$. The final atomic parameters and temperature factors and their standard deviations are shown in Table I. All of the interatomic distances less than 3.0 Å. are listed in Table II.

The structure consists of the stacking of two types of layers in the a direction held together with a rich network of hydrogen bonds. The first type of layer has the composition Na_2XeO_6 and consists of octahedral perxenate ions and the Na(1) type sodium ions as shown in Fig. 1. In this layer the sodium ions sit in the center of distorted octahedra of oxygens from the

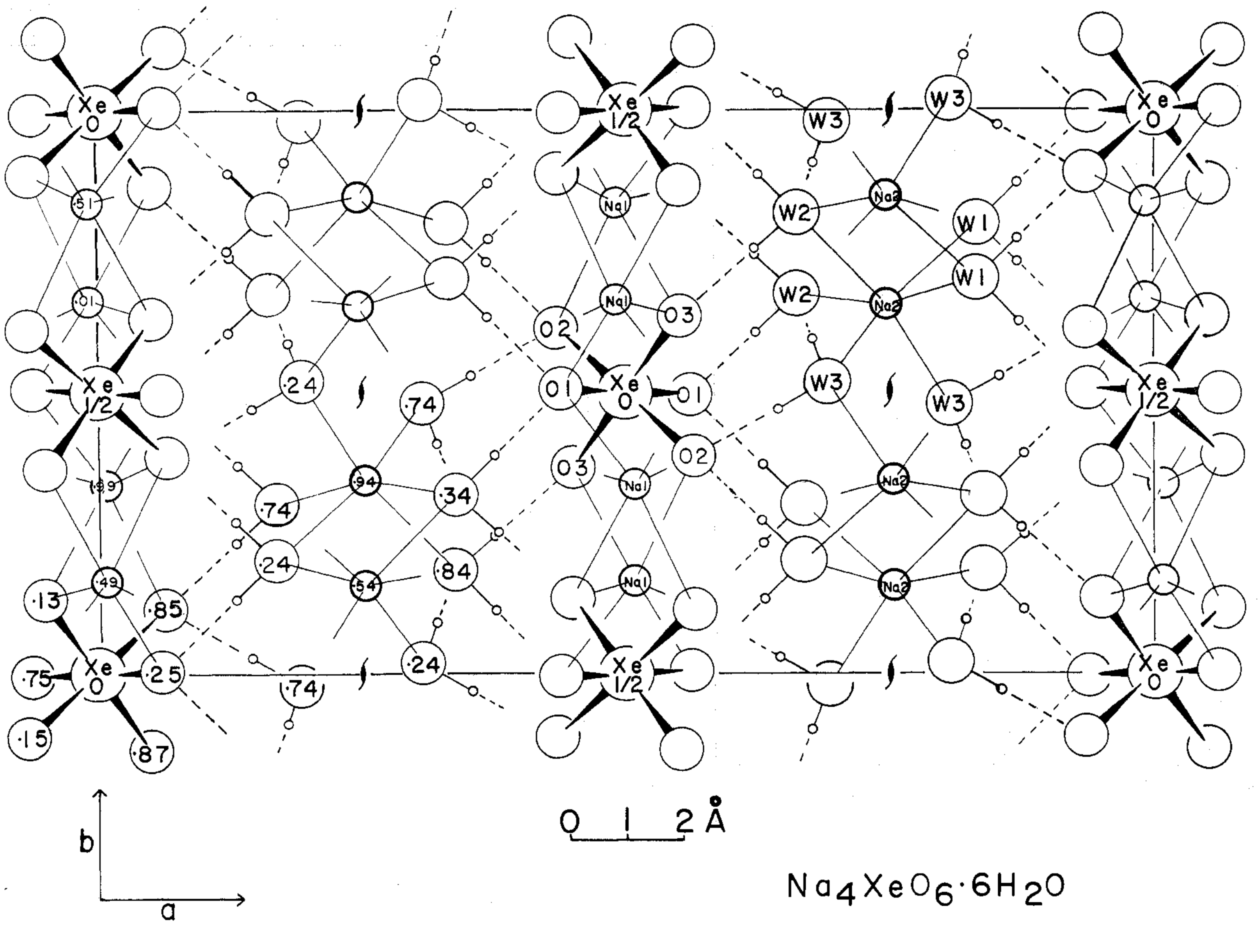

Fig. 3.—Projection of the structure in the *ab* plane. The hydrogen bonding is represented by the dotted lines.

neighboring perxenate ions. The packing is very nearly hexagonal. The second type layer has the composition $Na_2(H_2O)_6$ and consists of Na(2) type sodium atoms located in the centers of distorted octahedra of water molecules as shown in Fig. 2. The end-on stacking of these layers in the *a* direction is shown in Fig. 3.

Hydrogen Bonding.—Direct evidence of the hydrogen positions was unobtainable from our data; however, the assignment of six hydrogen bonds was possible from the interatomic distances and angles. Five of the six bonds are between the layers as described above, and one hydrogen bond is in the same layer to another water oxygen. A summary of the hydrogen bonds is shown in Table III.

Perxenate Ion.—The geometry of the XeO_6^{-4} octahedra in the hexahydrate is summarized in Table IV.

The bond distances were not corrected for thermal vibrational effects. The effect is 0.005 Å. or less on the above three distances, and is negligible. The average value of the Xe–O bond distance is 1.84 ± 0.02 Å. This is to be compared with 1.87 ± 0.02 Å. observed in the octahydrate[4] and 1.86 ± 0.01 Å. observed in the potassium salt $K_4XeO_6 \cdot 9H_2O$.[10]

The possibility that some of the hydrogen atoms are associated with the perxenate ion is neither confirmed nor ruled out by these results. Two of the three independent Xe–O distances are longer by about three standard deviations than the third, but this difference could be the result of systematic errors in the data. Our determination does not establish any deviation from ideal octahedral symmetry.

A list of observed and calculated structure factors is given in Table V.

Acknowledgment.—We thank Prof. S. M. Williamson and Dr. C. W. Koch for their close cooperation which made this work possible.

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(10) A. Zalkin, J. D. Forrester, D. H. Templeton, S. M. Williamson, and C. W. Koch, unpublished work.