Title
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Publication Date
1964-06-01

UCRL-11478

University of California

Ernest O. Lawrence Radiation Laboratory

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June 1964

Berkeley, California

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Submitted to J. Inorg. Chem.

UCRL-11478

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
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AEC Contract No. W-7405-eng-48

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CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA

The Crystal Structure of Sodium Perxenate Hexahydrate[1]

BY ALLAN ZALKIN, J. D. FORRESTER, AND DAVID H. TEMPLETON

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 an 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 $1.84 \pm .02$ Å.

Introduction

Malm, Bane and Holt[2] produced hydrated sodium salts of +8 xenon by hydrolysing 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 one 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 two 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 6.25Å.

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 two to twenty-four hours. Upon decomposition two phases grew into the crystal in situ without changing the physical shape

of the crystal. These phases were also unstable as we could only get diffraction patterns from them for a day or two of photographing before they ceased to diffract. From some poor Weissenberg patterns we measured two phases as well as we could. One phase is possibly orthorhombic with $\underline{a}$ = 6.25, $\underline{b}$ = 5.16, and $\underline{c}$ = 5.89 Å. The second phase appears to be twinned and seems to be monoclinic with $\underline{a}$ = 6.25, $\underline{b}$ = 20.16, $\underline{c}$ = 5.89Å, and $\beta = 91.5^{\circ}$.

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 had 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 $\underline{b}$ or $\underline{c}$ axis of the cell with the use of polarized light. The $\underline{a}$ 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" 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 lifetime, we limited the data taking in the 30° to 60° region to those reflections that would give some economy on set up

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 program by P. K. Gantzell, R. A. Sparks, and K. N. Trueblood (all unpublished). The function minimized in the least squares computations was $\sum \underline{w}(|\underline{F_o}|-|\underline{F_c}|)^2/\sum \underline{w}\underline{F_o}^2$, where $\underline{w}$ is the weighting factor and $\underline{F_o}$ and $\underline{F_c}$ 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/second) 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^{+1}, neutral Xe, and neutral oxygen (Ibers[8]) unmodified for dispersion (Templeton[9]) which for the heaviest atom Xe is only -0.5 electrons.

Unit Cell and Space Group.—The crystals are orthorhombic with unit cell dimensions: $a = 18.44 \pm .01$, $b = 10.103 \pm .007$, and $c = 5.875 \pm .005$ 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: $0k\ell$, $k \neq 2n$; $h0\ell$, $\ell \neq 2n$; 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, and the signs of all these terms being positive. These early calculations were done in space group $P2_12_12_1$ as we had observed a few weak spurious reflections which indicated no glide plane extinctions. We later found these reflections 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 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.

We commenced the least squares refinement of the structure while the data were being taken, and progress was slow. When all of the data were available, a 3-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. From a freshly made sample we obtained a new crystal and immediately checked for space group extinctions, and indeed found that the extinctions corresponded exactly to Pbca. The non-extinguished reflections agreed very well with the previous measurements.

In Pbca the Xe is in a special four fold position at the origin, which is also a center of symmetry. The sodium and oxygen atoms occupy general eight fold 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 re-adjusted. 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 we tried to vary the z parameter of the errant water molecule. It 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, though it lowered the R factor to 0.082 .

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 ± .06, 0.73 ± .05, and 0.71 ± .05 $Å^2$ respectively. The average of these values is reported in Table I. The final R factor is 0.073. [10]

Results and Discussion

Description of Structure.—The xenon atoms are located at the origin and face centers of the cell in a four fold position. Each of the two sodiums, three perxenate oxygens, and three water oxygens occupy the general eight fold position: ± (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.

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)	σ(x)	σ(y)	σ(z)	σ(B)
Xe	0.0	0.0	0.0	(0.85)[a]	0.0	0.0	0.0	(0.05)[a]
Na(1)	.009	.164	.492	1.4	.001	.001	.003	.2
Na(2)	.252	.155	.539	1.6	.001	.001	.002	.2
O(1)	.060	.004	.253	1.2	.001	.003	.003	.2
O(2)	.064	.115	.854	1.7	.001	.002	.004	.4
O(3)	.951	.136	.127	1.0	.001	.002	.003	.4
O(W1)[b]	.169	.200	.242	1.6	.001	.002	.004	.3
O(W2)	.340	.183	.835	1.5	.001	.002	.004	.3
O(W3)	.192	.518	.242	2.2	.001	.002	.004	.4

[a] Isotropic value equivalent to average of anisotropic values.

[b] O(Wn) means the oxygen of water molecule n.

All of the interatomic distances less than 3.0 Å are listed in Table II.

TABLE II

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

Atoms	D(Å.)	σ(D)	Atoms	D(Å.)	σ(D)	Atoms	D(Å)	σ(D)
Xe -2 O(1)	1.86	0.02[a]	O(1) - Xe	1.86[a]	0.02	O(3) - Xe	1.80[a]	0.02
-2 O(2)	1.87	.02[a]	- Na(1)	2.35	.03	- Na(1)	2.41	.03
-2 O(3)	1.80	.02[a]	- Na(1)	2.60	.03	- Na(1)	2.42	.03
			- O(2)	2.60	.03	- O(1)	2.52	.03
Na(1) - O(1)	2.35	.03	- O(2)	2.66	.03	- O(1)	2.65	.03
- O(1)	2.60	.03	- O(3)	2.52	.03	- O(2)	2.55	.03
- O(2)	2.41	.03	- O(3)	2.65	.03	- O(2)	2.63	.03
- O(2)	2.58	.03	- O(W1)	2.81[b]	.03	- O(W2)	2.76[b]	.03
- O(3)	2.41	.03	- O(W2)	2.69[b]	.03			
- O(3)	2.42	.02				O(W1)- Na(2)	2.37	.02
			O(2) - Xe	1.87[a]	.02	- Na(2)	2.44	.02
Na(2) - O(W1)	2.37	.02	- Na(1)	2.41	.03	- O(1)	2.81[b]	.03
- O(W1)	2.44	.02	- Na(1)	2.58	.03	- O(2)	2.77[b]	.03
- O(W2)	2.39	.02	- O(1)	2.60	.03			
- O(W2)	2.59	.02	- O(1)	2.66	.03	O(W2)- Na(2)	2.39	.02
- O(W3)	2.39	.02	- O(3)	2.55	.03	- Na(2)	2.59	.02
- O(W3)	2.45	.02	- O(3)	2.63	.03	- O(1)	2.69[b]	.03
			- O(W1)	2.77[b]	.03	- O(3)	2.76[b]	.03
			- O(W3)	2.79[b]	.03	- O(W3)	2.97[b]	.03
						O(W3)- Na(2)	2.39	.02
						- Na(2)	2.45	.02
						- O(2)	2.79[b]	.03
						- O(W2)	2.97[b]	.03

[a]Perxenate Xe-O bonds [b]Hydrogen bonds

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 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.

TABLE III

HYDROGEN BOND DISTANCES AND ANGLES[a]

Atom	D(Å)	Atom	D(Å)	Atom	Angle
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 ±.03 Å., and of the angles ±1°.

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

TABLE IV

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

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

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 $K_4XeO_6 \cdot 9H_2O$.[11]

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.

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

References

(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., Univ. of Chicago Press, Chicago, 1963, p. 167..

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

(10) A copy of the data is available from the authors on request.

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

Figure Captions

Fig. 1.—The layer containing the perxenate ions and half of the sodium ions. MUB 2096

Fig. 2.—The layer containing the water oxygens and half of the sodium ions. MUB 2095

Fig. 3.—Projection of the structure in the ab plane. The hydrogen bonding is represented by the dotted lines. MUB 2116

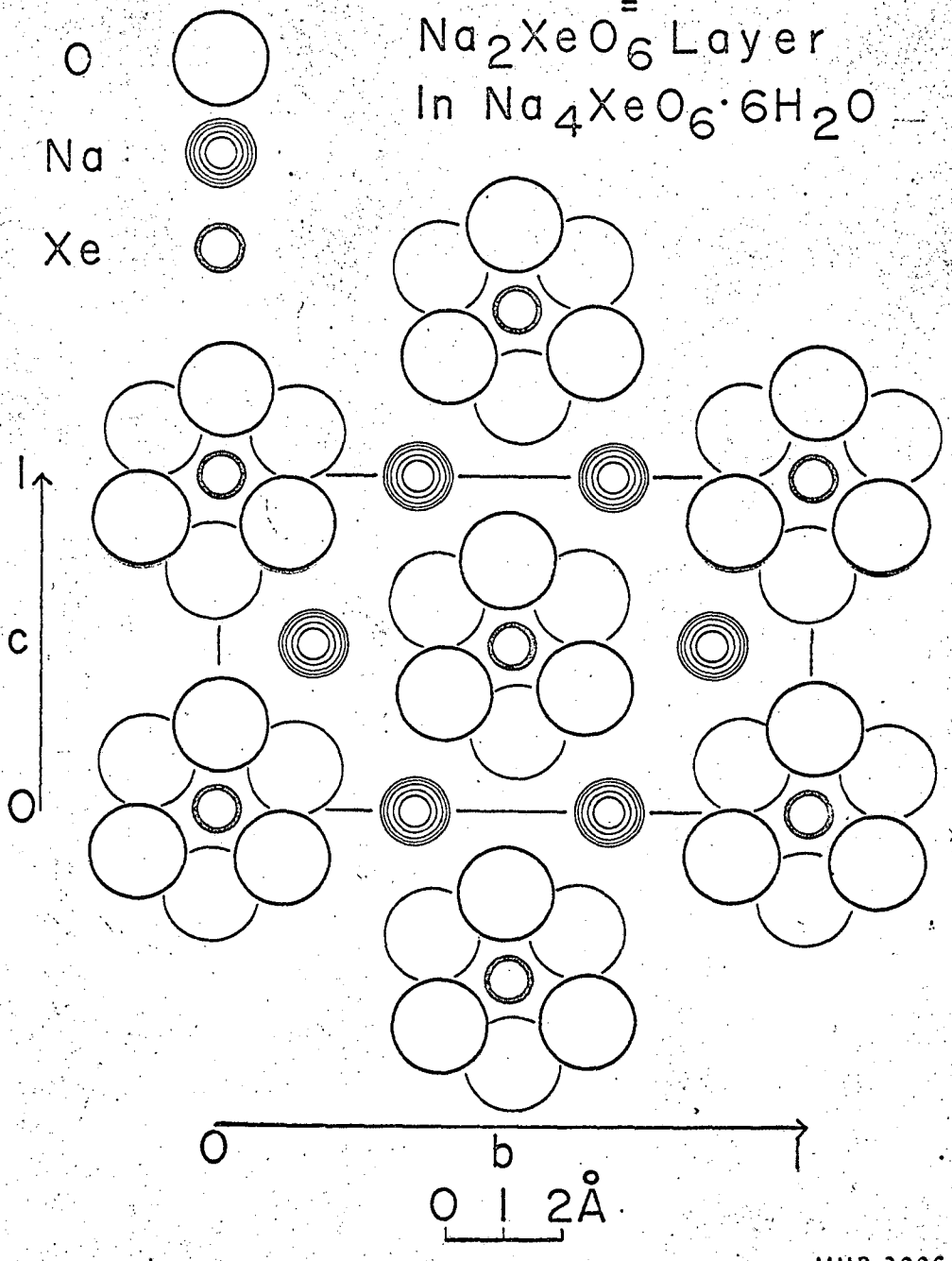
O
Na
Xe
Na_2XeO_6 Layer
In $Na_4XeO_6 \cdot 6H_2O$
1
c
0
0
b
0 1 2Å
MUB-2096

Fig. 1

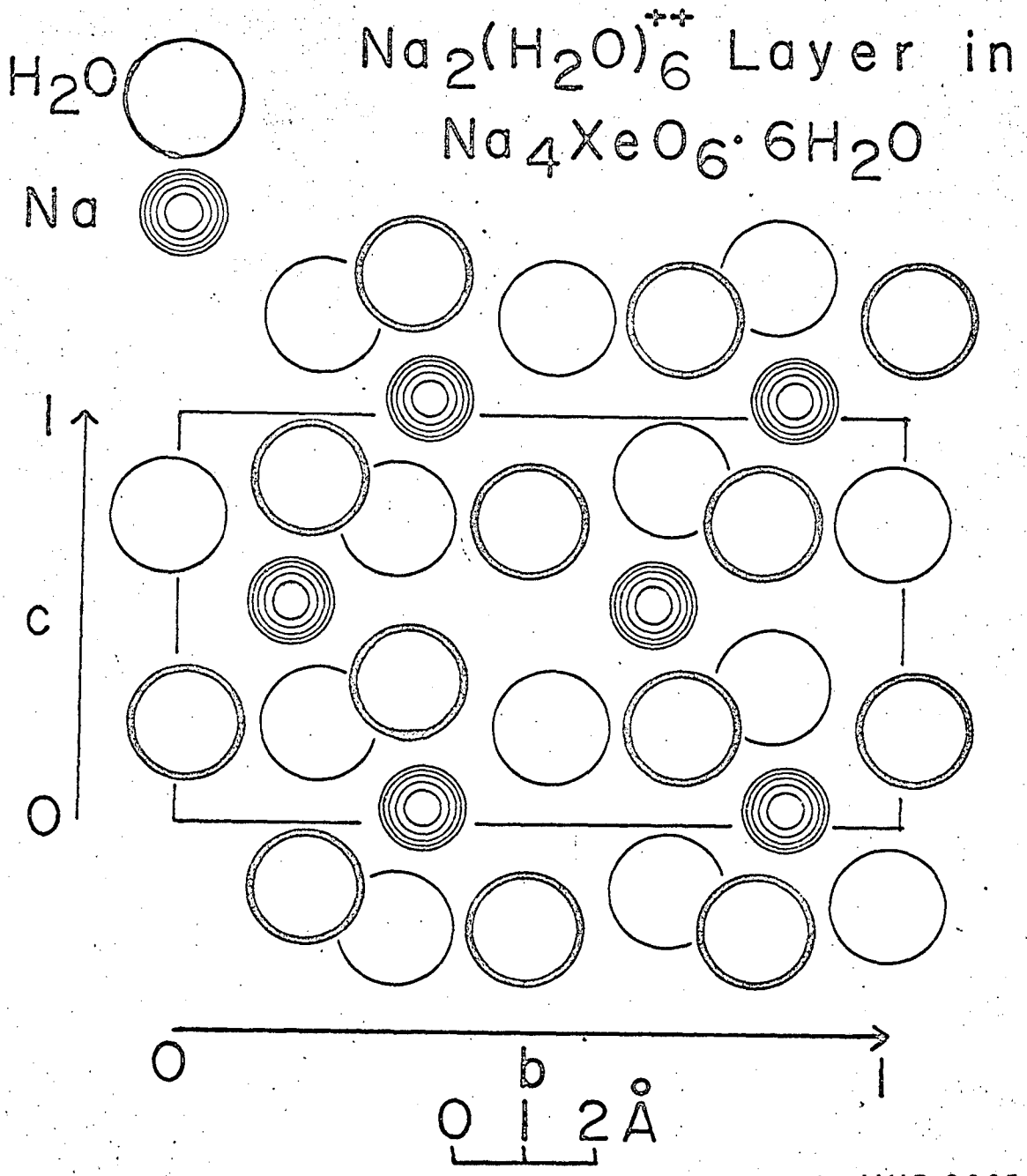
$Na_2(H_2O)_6^{++}$ Layer in
$Na_4XeO_6 \cdot 6H_2O$
H_2O
Na
1
c
0
0
b
1
0 1 2 Å
MUB-2095

Fig. 2

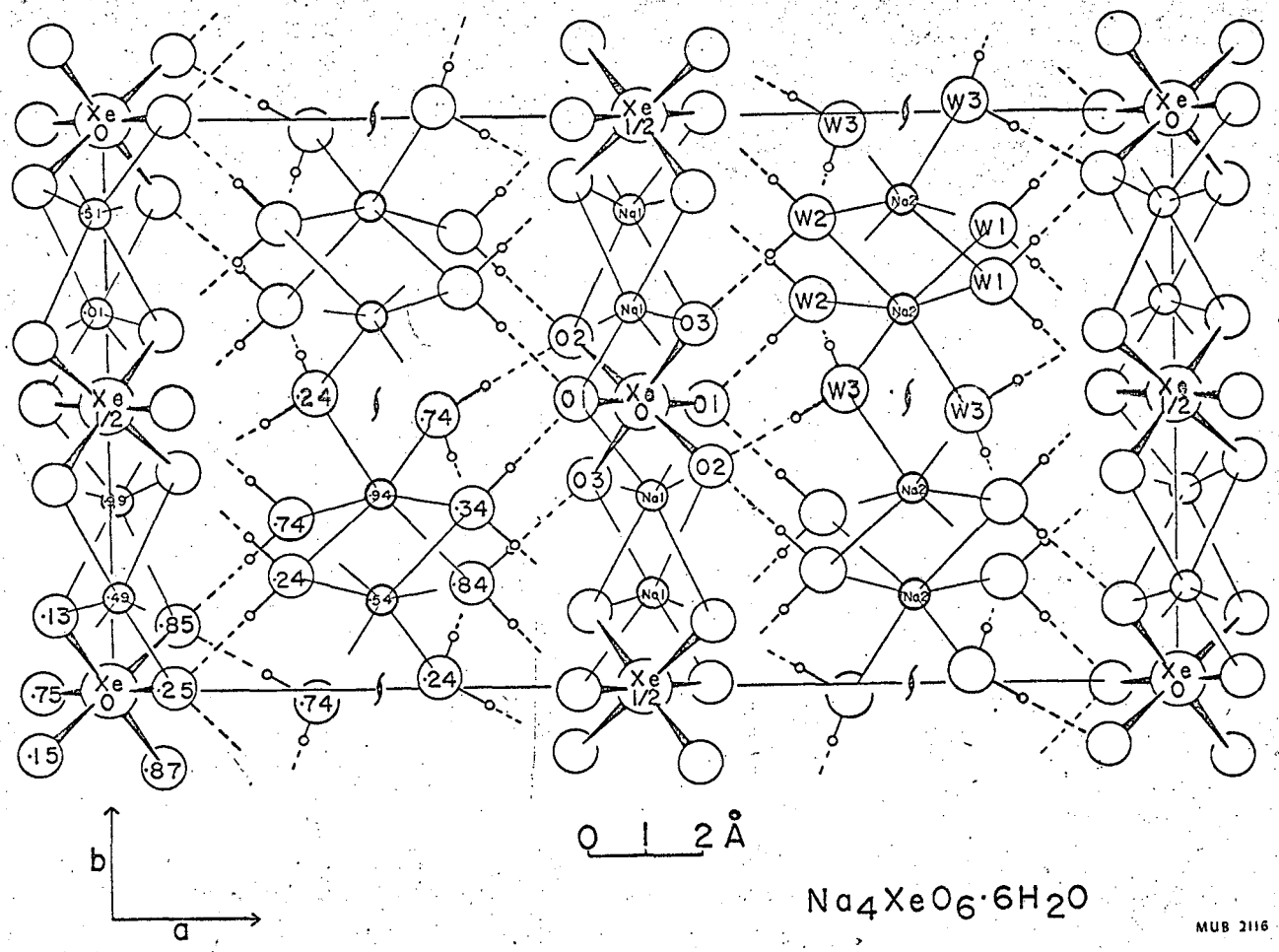
Xe 0
Xe 1/2
W3
W2
W1
Na2
Na1
O1
O2
O3
.01
.24
.74
.94
.34
.84
.54
.49
.13
.85
.75
.25
.15
.87
0 1 2 Å
b
a
$Na_4XeO_6 \cdot 6H_2O$
MUB 2116

Fig. 3

Table of observed and calculated structure factors for $Na_4XeO_6 \cdot 6H_2O$.

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*
[illegible]				

1	9	4	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	54	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
[illegible]				

CRYSTAL 2

H	K	L	FOB	FCA
[illegible]				

CRYSTAL 3

H	K	L	FOB	FCA
[illegible]				

CRYSTAL 4

H	K	L	FOB	FCA
[illegible]				

CRYSTAL 5

H	K	L	FOB	FCA
[illegible]