more negative values would apply to the less shielded cores. The presumed minor importance of the 6s orbitals in the bonding would also be worthy of quantitative investigation. Such refinements would, of course, substantially increase the size of the problem, and they would be expected to result in only relatively small changes in the energies so that the essence of the present conclusions regarding the structure would remain unaltered.

The Bi_9^{5+} species is evidently the first example of a homopolyatomic cation of a metallic element that is sufficiently stable to exist in a pure state, excepting, of course, the diatomic Hg_2^{2+} and Cd_2^{2+}. It is interesting to note that this grouping may not be without analogy, however, since it is isoelectronic with Pb_9^{4-} and Sn_9^{4-}, two (of many) species of the post-transition metals for which Zintl and co-workers[19] found evidence in liquid ammonia. This relationship has also been noted by Britton.[20] On the other hand, no evidence for a bismuth analog of Pb_7^{4-}, the other lead anion suggested by Zintl's work, has been found in the $BiCl_3$–Bi system. In addition there is no evidence for any comparable, polynuclear cation of antimony in the SbX_3–Sb system,[21,22] perhaps due to its reluctance to form cations in the presence of halide. Compositions corresponding to the many species suggested by Zintl are generally not found in the binary alloy systems although a few isolated examples of other homopolyatomic ions with "closed-shell" MO's may occur in the latter.[23] Continued investigations may well disclose other examples of such ions for the post-transition elements that are commonly thought of as metallic in character.

Acknowledgments.—J. D. C. is particularly indebted to J. W. Richardson for the overlap computations and to D. S. Martin, Jr., for helpful discussions.

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[19] Summarized by H. J. Emeléus and J. S. Anderson in "Modern Aspects of Inorganic Chemistry," 3rd Ed., D. Van Nostrand Co., New York, N. Y., 1960, p. 512.

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[21] J. D. Corbett, S. von Winbush, and F. C. Albers, *J. Am. Chem. Soc.*, **79**, 3020 (1957).

[22] J. D. Corbett and F. C. Albers, *ibid.*, **82**, 533 (1960).

[23] J. D. Corbett, to be published.

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The Crystal Structure of Sodium Perxenate Octahydrate[1]

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Sodium perxenate octahydrate, $Na_4XeO_6 \cdot 8H_2O$, is orthorhombic with cell constants $a = 11.86$, $b = 10.36$, $c = 10.43$ Å., space group Pbcn, $Z = 4$. A three-dimensional X-ray diffraction investigation has resulted in a complete structure determination. The perxenate ion is approximately a regular octahedron with a mean Xe–O distance of 1.864 ± 0.012 Å. The greatest deviation of an O–Xe–O angle from the ideal 90° is $2.6 \pm 0.8°$. The two crystallographically independent sodium atoms are surrounded by very distorted octahedra composed of water molecules and perxenate oxygen atoms. A complex array of hydrogen bonds completes the structure.

Introduction

The reaction of XeF_6 with sodium hydroxide was shown by Malm, *et al.*,[2] to produce compounds which contain octavalent xenon and which, on the basis of chemical analyses, were thought to contain the perxenate ion, XeO_6^{-4}. In a previous communication[3] we sketched the evidence from an X-ray study that one of the compounds that forms is sodium perxenate octahydrate. Subsequent to that study Zalkin, *et al.*,[4] have shown that another product is sodium perxenate hexahydrate. In this paper we present in detail the results of our crystallographic study of sodium perxenate octahydrate and also discuss the geometry of the perxenate ion and the complex hydrogen bonding scheme in the octahydrate.

Experimental

The material studied here was prepared by adding about 1 ml. of 1 *M* NaOH to several mg. of XeF_6 at 77°K. The XeF_6 was almost certainly contaminated with XeF_4. A yellow color appeared in the frozen mixture and disappeared as the mixture melted. Colorless, well-developed crystals with dimensions of up to several tenths of a mm. formed within several minutes in the reaction vessel. Several of these crystals were selected for X-ray photography and were sealed in thin-walled glass capillaries to reduce dehydration or possible decomposition.

All photographs were taken with Mo $K\alpha$ X-rays from plate-like crystals with approximate dimensions $0.2 \times 0.2 \times 0.05$ mm. Data suitable for structure analysis were collected at room temperature by multiple-film Weissenberg photography. In order to minimize the time required to collect a complete data set, three crystals were photographed simultaneously on different cameras to obtain data from the reciprocal nets $0kl$, $1kl$, . . .$13kl$. All independent intensities strong enough to be observed and accessible within the scattering angle $\theta_{Mo} \leq 26°$ were estimated vis-

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[1] Research carried out 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] W. C. Hamilton, J. A. Ibers, and D. R. MacKenzie, *Science*, **141**, 532 (1963).

[4] A. Zalkin, J. D. Forrester, D. H. Templeton, S. M. Williamson, and C. W. Koch, *ibid.*, **142**, 501 (1963); A. Zalkin, J. D. Forrester, and D. H. Templeton, *Inorg. Chem.*, **3**, 1417 (1964).

ually. The 716 observed intensities were corrected for Lorentz and polarization effects, but not for absorption. The linear absorption coefficient calculated for the formula $Na_4XeO_6 \cdot 8H_2O$ is 29 cm.$^{-1}$, so that absorption errors should not seriously affect the intensity measurements. Although a number of the strong reflections seem to suffer from extinction, no corrections were made. A final set of photographs of the $0kl$ net was taken at the end of the experiment. The identity of these photographs with the initial photographs provides good evidence for the stability of the material during the photography.

The crystals investigated are orthorhombic with cell constants $a = 11.864$, $b = 10.358$, $c = 10.426$, each ± 0.005 Å.[5] The observed extinctions ($hk0$, $h + k$ odd; $h0l$, l odd; $0kl$, k odd) indicate that the space group is probably D_{2h}^{14}-Pbcn.[6] The density, as measured by flotation in mixtures of methylene dibromide and carbon tetrachloride, is 2.33 ± 0.05 g. cm.$^{-3}$. Siegel[7] ascribes to a compound of formula $Na_4XeO_6 \cdot 5H_2O$ an orthorhombic cell with constants $a = 10.36$, $b = 10.45$, $c = 11.87$ Å. It is clear on the basis of the agreement between that cell and the one found here (after redefinition of axes) that the two compounds are identical. Analytical results at Argonne[2] indicate a Na:Xe ratio of and an oxidation number of eight for Xe. The density observed here is in poor agreement with four formula weights of the pentahydrate in the units cell ($\rho_c = 2.10$ g. cm.$^{-3}$). However, it is in excellent agreement with the formula $Na_4XeO_6 \cdot 8H_2O$ ($\rho_c = 2.38$ g. cm.$^{-3}$) which was deduced here from the structure determination.

Solution of the Structure

The multiplicity of the general positions in Pbcn is 8 and the four Xe atoms must therefore lie in special positions. It was clear from examination of the intensities of several reflections and from the three-dimensional Patterson function that the Xe atoms are in positions (4c), $\pm(0, y, {}^1/_4)$, $({}^1/_2, {}^1/_2 + y, {}^1/_4)$, with y approximately 0.20. From the Patterson function the positions of six atoms bonded to the Xe were readily found. Two of these were placed in two sets of special positions (4c) along the twofold axis, and four were placed in two sets of general positions $\pm(x, y, z)$, $({}^1/_2 - x, {}^1/_2 - y, {}^1/_2 + z)$, $({}^1/_2 + x, {}^1/_2 - y, \bar{z})$, $(\bar{x}, y, {}^1/_2 - z)$. Successive least-squares and difference electron-density syntheses led to the placement of six more atoms in general positions in the asymmetric unit. From their coordination and peak heights in the electron density maps, two of the atoms were identified as sodium, and the four remaining were assigned as oxygen, presumably as water molecules. In a final series of least-squares refinements the Xe was allowed to vibrate anisotropically, while the other atoms were constrained to vibrate isotropically. In these refinements, which were carried out on F, unit weights were assigned for $F < 50$ electrons, and weights were taken as $(50/F)^2$ for $F \geqslant 50$ electrons. The atomic scattering factors used were those of Watson and Freeman[8] for Xe, Berghuis, *et al.*,[9] for Na, and Hoerni and Ibers for O.[10] Proper account was taken of the effects of anomalous dispersion by applying corrections to F_c.[11] The final parameters derived from these refinements are given in Table I. The conventional R factor $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ is 0.105. In Table II the final values of observed and calculated structure amplitudes are given. A final difference Fourier, based on the data of Table II, shows one peak of height 6.6 e/Å.^{3} at the Xe site; the next peak is of height 2.7 e/Å.^{3}, approximately 25% of the height of an oxygen peak in this structure and about 15% of the height of a sodium atom. The residual density at the Xe site presumably arises from improper treatment of the Xe scattering or vibrations, but is only about 4% of the Xe peak height of 178 e/Å.^{3}. Since the Xe lies

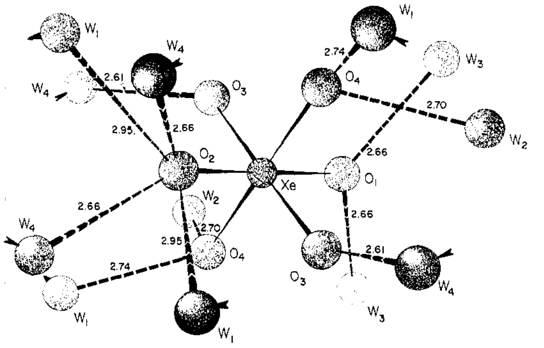

Fig. 1.—Perxenate ion with surrounding water molecules. A twofold axis coincides with the line O_1–Xe–O_2. The dashed lines are hydrogen bonds. The sodium ions coordinated to the perxenate ion and the water molecules are not shown. Distances are in Å.

TABLE I

PARAMETERS IN SODIUM PERXENATE OCTAHYDRATE[a]

Atom	Position	x	y	z	B, Å.^{2}
Xe	4c	0	0.20199 (14)	$^1/_4$	Anisotropic
O_1	4c	0	0.3836 (23)	$^1/_4$	2.0 (4)
O_2	4c	0	0.0233 (22)	$^1/_4$	2.0 (4)
O_3	8d	0.1079 (18)	0.2041 (20)	0.3766 (22)	2.2 (4)
O_4	8d	0.1190 (14)	0.2051 (15)	0.1301 (17)	0.8 (3)
Na_1	8d	0.1188 (9)	0.4299 (10)	0.4368 (10)	1.8 (2)
Na_2	8d	0.2811 (15)	0.2139 (10)	0.2644 (12)	1.9 (3)
W_1	8d	0.3153 (17)	0.4159 (17)	0.4090 (17)	2.2 (3)
W_2	8d	0.4364 (18)	0.1456 (17)	0.4255 (17)	2.0 (3)
W_3	8d	0.3259 (16)	0.0174 (17)	0.1558 (17)	2.0 (3)
W_4	8d	0.3823 (17)	0.3486 (17)	0.1245 (18)	2.0 (3)

[a] The numbers in parentheses are estimated standard deviations. W indicates the oxygen atom in a water molecule.

TABLE Ia

ANISOTROPIC THERMAL PARAMETERS FOR XENON

$\beta_{11} = 0.00117\ (45)$

$\beta_{22} = 0.00181\ (17)$

$\beta_{33} = 0.00182\ (17)$ $\langle r_1^2 \rangle^{1/2} = 0.087 \pm 0.015$[a]

$\beta_{12} = 0$ by symmetry $\langle r_2^2 \rangle^{1/2} = 0.099 \pm 0.005$

$\beta_{13} = 0.00023\ (17)$ $\langle r_3^2 \rangle^{1/2} = 0.104 \pm 0.007$

$\beta_{23} = 0$ by symmetry

[a] Root mean square amplitudes of vibration. The deviations from isotropy are so insignificant that the derived directions of the principal axes of the motion are meaningless.

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(5) These are the cell constants quoted in ref. 4 (λ Mo Kα_1 = 0.70926 Å.); they are in satisfactory agreement with our less precise values quoted in ref. 3, where an accidental transposition of b and c was made.

(6) "International Tables for X-Ray Crystallography," Vol. 1, The Kynoch Press, Birmingham, 1952.

(7) S. Siegel and E. Gebert, ref. 2, p. 193.

(8) R. E. Watson and A. G. Freeman, private communication, 1963.

(9) J. Berghuis, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, **8**, 478 (1955).

(10) J. A. Hoerni and J. A. Ibers, *ibid.*, **7**, 744 (1954).

(11) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

TABLE II

Observed and Calculated Structure Amplitudes (in Electrons) for $Na_4XeO_6 \cdot 8H_2O$

K	L	OBS	CAL
****H= 0*****			
0	0	904	838
0	2	185	244
0	4	55	67
0	6	247	270
0	8	183	167
0	10	130	145
0	12	83	86
2	0	150	199
2	1	124	115
2	2	199	206
2	3	177	147
2	4	131	119
2	5	68	58
2	6	138	126
2	7	76	75
2	8	177	163
2	9	70	76
2	10	68	71
2	11	53	46
2	12	41	40
4	0	65	66
4	1	260	271
4	2	177	141
4	3	58	55
4	4	76	74
4	5	216	195
4	7	159	147
4	8	78	70
4	9	95	89
4	10	54	51
4	11	91	90
4	12	27	24
6	0	36	37
6	1	235	254
6	2	71	63
6	3	200	177
6	5	96	88
6	7	181	160
6	8	51	51
6	9	150	146
6	10	21	23
6	11	66	66
8	0	123	124
8	1	95	99
8	2	58	58
8	3	92	103
8	4	66	62
8	5	47	43
8	6	88	90
8	7	103	87
8	8	59	59
8	9	90	85
8	10	55	55
10	0	126	122
10	1	57	61
10	2	124	123
10	4	64	87
10	5	36	30
10	6	73	79
10	8	98	99
12	0	83	85
12	1	46	48
12	2	88	94
12	3	31	18
12	4	69	71
****H= 1*****			
0	4	107	96
0	6	72	76
0	8	61	65
1	2	125	97
1	3	196	175
1	4	29	28
1	5	129	122
1	6	25	25
1	7	133	127
1	8	79	82
1	9	129	124
1	11	75	78
2	1	38	33
2	2	11	1
2	3	29	21
2	4	92	73
2	5	22	21
2	9	21	24
3	0	161	181
3	1	122	117
3	2	160	116
3	3	39	42
3	4	19	21
3	6	58	55
3	7	88	89
3	8	113	110
3	9	61	65
3	10	76	71
3	11	28	29
3	12	33	35
4	1	108	95
4	2	42	36
4	3	21	19
4	4	16	19
4	5	26	26
4	7	39	43
4	8	21	16
4	10	27	25
5	0	211	227
5	1	49	47
5	2	151	146
5	3	68	59
5	4	138	118
5	5	36	32
5	6	155	140
5	7	16	13
5	8	120	120
5	10	111	99
6	1	30	34
6	2	61	69
6	4	18	19
6	5	22	26
6	9	19	23
7	0	129	123
7	1	71	67
7	2	99	107
7	3	55	54
7	4	67	65
7	5	56	57
7	6	76	80
7	7	51	56
7	8	90	90
7	9	40	44
7	10	62	59
8	1	22	26
8	2	28	30
8	5	28	36
9	0	55	56
9	1	109	118
9	3	37	43
9	4	22	27
9	5	75	72
9	6	38	42
9	7	70	75
9	8	25	22
9	9	60	68
10	7	25	27
11	0	24	22
11	1	100	104
11	3	73	80
11	5	67	65
11	6	21	23
****H= 2*****			
0	2	127	153
0	4	162	161
0	6	139	145
0	8	105	106
0	10	96	96
0	12	70	73
1	4	49	71
1	6	26	31
2	1	89	86
2	2	69	67
2	4	32	30
2	5	77	72
2	6	63	62
2	7	76	64
2	8	68	67
2	9	39	31
2	10	55	62
2	11	38	44
2	12	53	57
3	1	34	38
3	2	99	87
4	3	129	94
4	2	26	22
4	3	107	94
4	4	29	30
4	5	92	86
4	6	34	29
4	7	81	77
4	8	33	32
4	9	86	82
4	11	65	72
5	1	34	33
5	2	25	18
5	3	33	30
5	7	37	34
6	0	74	65
6	1	119	106
6	2	27	27
6	3	126	119
6	4	29	32
6	5	103	96
6	6	59	57
6	7	105	98
6	8	29	25
6	9	87	88
6	11	54	63
8	0	82	67
8	1	48	46
8	2	73	72
8	3	32	33
8	4	57	61
8	5	28	25
8	6	41	49
8	7	43	42
8	8	63	57
8	9	40	41
10	0	77	72
10	2	96	89
10	4	68	84
10	6	72	68
12	0	74	69
12	1	40	38
12	2	71	59
12	3	41	45
12	4	54	52
****H= 3*****			
0	4	95	86
0	6	40	35
0	10	43	46
1	3	205	230
1	4	79	76
1	5	202	170
1	6	20	18
1	7	157	143
1	9	120	106
1	10	55	56
1	11	90	87
1	12	31	29
2	2	34	31
2	3	28	25
2	5	43	39
2	6	23	21
2	7	16	15
3	1	59	61
3	2	114	117
3	3	130	116
3	4	199	175
3	5	134	132
3	6	104	103
3	7	40	45
3	8	61	66
3	9	46	50
3	10	52	54
3	11	63	62
3	12	63	59
4	1	64	57
4	3	22	19
4	4	22	17
4	5	39	37
4	6	35	32
4	7	21	15
4	9	27	23
5	0	223	193
5	1	26	22
5	2	208	197
5	3	34	33
5	4	206	168
5	6	152	137
5	8	117	109
5	10	94	91
6	1	40	39
6	7	22	22
7	0	126	114
7	1	64	64
7	2	91	101
7	8	83	67
7	4	119	135
7	5	49	44
7	6	116	114
7	7	36	38
7	8	60	62
7	9	47	47
7	10	71	72
9	0	38	44
9	1	64	71
9	2	52	58
9	3	84	97
9	4	43	44
9	5	99	98
9	6	32	31
9	7	74	76
9	8	27	37
11	1	114	98
11	3	101	97
11	5	101	100
****H= 4*****			
0	4	265	326
0	6	143	156
0	8	112	123
0	10	88	91
0	12	109	108
1	2	130	95
1	3	22	23
1	4	31	29
1	5	14	7
1	6	18	10
1	9	23	25
1	10	22	20
1	11	13	11
2	1	139	111
2	2	157	125
2	3	51	53
2	4	199	185
2	5	119	118
2	6	147	128
2	7	51	60
2	8	49	44
2	9	47	44
2	10	83	85
2	11	53	57
2	12	82	79
3	1	22	14
3	3	21	16
3	4	57	48
3	5	31	29
4	0	86	74
4	1	138	117
4	2	66	59
4	3	211	217
4	4	76	69
4	5	126	115
4	6	65	66
4	7	112	109
4	8	31	36
4	9	89	90
4	10	37	32
4	11	71	68
5	1	31	31
5	4	23	24
5	5	20	19
5	6	24	12
5	7	37	34
5	8	27	33
6	0	34	34
6	1	144	134
6	3	223	180
6	4	44	49
6	5	197	191
6	6	47	46
6	7	100	95
6	9	70	74
6	10	24	25
8	0	32	34
8	1	63	61
8	2	90	94
8	3	83	92
8	4	82	84
8	5	93	98
8	6	52	49
8	7	32	40
8	8	61	61
8	9	35	34
9	1	24	31
10	0	94	95
10	2	94	95
10	3	37	45
10	4	93	107
10	6	80	91
12	0	74	73
12	2	66	72
****H= 5*****			
0	2	58	52
0	4	43	40
1	3	163	159
1	4	63	63
1	5	121	117
1	6	87	88
1	7	95	83
1	9	75	76
1	10	15	22
1	11	75	76
1	12	35	32
2	2	22	27
2	3	10	8
2	4	32	30
2	5	16	19
2	6	18	15
2	7	37	37
2	8	21	24
3	0	15	17
3	1	43	40
3	2	86	72
3	3	18	17
3	4	120	106
3	5	98	92
3	6	53	56
3	7	27	26
3	8	30	30
3	9	14	15
3	10	49	56
3	11	53	58
4	1	30	25
4	4	30	25
4	5	21	17
5	0	16	18
5	1	56	53
5	2	137	134
5	3	54	58
5	4	208	167
5	6	94	90
5	8	74	80
5	10	72	72
6	1	16	14
6	2	49	51
6	3	25	23
6	4	26	26
7	0	91	95
7	1	43	49
7	2	52	53
7	3	58	56
7	4	81	72
7	5	56	64
7	6	86	79
7	7	45	49
7	8	33	38
7	9	33	30
8	2	21	21
9	1	59	44
9	2	26	27
9	3	110	112
9	4	27	29
9	5	60	63
9	7	37	44
9	8	27	24
11	0	20	30
11	1	63	61
11	2	23	19
11	3	67	79
11	4	12	15
****H= 6*****			
0	4	123	147
0	6	95	104
0	8	87	106
0	10	81	90
1	4	37	36
2	2	84	77
2	3	105	92
2	4	130	123
2	5	48	48
2	6	85	85
2	7	33	37
2	8	58	57
2	9	49	57
2	10	47	57
2	11	25	40
3	1	77	67
3	5	53	44
3	6	41	35
4	0	57	62
4	1	98	89
4	2	39	36
4	3	139	116
4	4	33	25
4	5	120	102
4	7	91	91
4	9	65	68
4	11	52	60
6	0	24	25
6	1	140	119
6	2	53	44
6	3	129	110
6	4	50	37
6	5	130	113
6	7	91	81
6	9	73	72
7	4	57	45
8	0	50	54
8	1	29	32
8	2	62	60
8	3	52	56
8	4	65	68
8	5	63	65
8	6	62	66
8	7	54	37
8	8	44	47
10	0	87	94
10	2	82	77
10	4	73	76
10	6	73	78
****H= 7*****			
0	6	24	32
0	8	24	20
1	1	125	205
1	2	50	59
1	3	153	141
1	4	53	41
1	5	208	164
1	6	41	39
1	7	127	128
1	8	44	44
1	9	92	96
1	10	23	23
1	11	87	88
2	2	37	37
2	3	37	31
3	0	184	163
3	1	100	93
3	2	108	95
3	3	142	114
3	4	87	75
3	5	58	53
3	6	109	98
3	7	79	73
3	8	71	74
3	9	72	71
3	10	69	66
4	1	17	17
4	2	42	40
4	3	18	15
5	0	195	186
5	1	26	28
5	2	185	152
5	3	16	17
5	4	161	135
5	5	22	14
5	6	174	133
5	8	101	108
5	10	86	88
7	0	88	90
7	1	51	53
7	2	141	130
7	3	51	51
7	4	110	104
7	5	42	49
7	6	74	70
7	7	39	43
7	8	101	97
9	0	49	53
9	1	96	91
9	2	47	46
9	3	63	73
9	4	39	45
9	5	61	66
9	6	38	40
****H= 8*****			
0	2	111	139
0	4	114	114
0	6	123	120
0	8	128	124
0	10	104	99
1	2	26	27
1	5	17	26
2	0	81	129
2	1	51	52
2	2	115	113
2	3	97	88
2	4	56	41
2	5	32	30
2	6	62	57
2	7	63	64
2	8	105	103
2	9	52	52
2	10	66	58
4	0	47	47
4	1	113	125
4	2	29	27
4	3	91	84
4	4	33	36
4	5	108	92
4	6	53	53
4	7	77	75
4	8	36	26
4	9	103	87
6	1	125	133
6	2	37	39
6	3	102	91
6	5	99	82
6	7	125	107
6	8	46	44
8	0	89	97
8	1	89	84
8	2	53	49
8	3	22	24
8	4	46	46
8	5	29	30
8	6	60	58
8	7	63	61
10	0	74	85
****H= 9*****			
0	6	24	20
1	1	69	120
1	2	43	53
1	3	38	46
1	5	90	85
1	7	101	85
1	8	46	47
1	9	80	71
1	10	25	23
2	2	30	20
3	0	107	106
3	1	29	34
3	2	40	40
3	3	65	57
3	4	33	27
3	8	71	64
3	9	61	56
4	2	13	14
5	0	205	153
5	1	17	19
5	2	104	85
5	3	26	23
5	4	58	52
5	6	103	84
5	7	19	2
5	8	103	85
7	0	31	31
7	1	61	57
7	2	90	77
7	3	42	41
7	4	58	56
7	5	35	34
7	6	43	38
7	7	43	37
9	0	30	34
9	1	66	74
9	3	42	41
****H=10*****			
0	2	95	129
0	4	99	99
0	6	129	115
0	8	138	108
1	2	33	47
1	3	16	12
1	4	26	11
2	0	69	97
2	1	46	52
2	2	86	97
2	3	73	78
2	4	76	70
2	5	35	38
2	6	83	66
2	7	53	47
2	8	95	81
2	9	52	57
3	1	35	42
3	5	19	19
3	7	32	23
4	0	46	45
4	1	138	114
4	2	40	39
4	3	90	78
4	4	35	36
4	5	92	86
4	6	37	35
4	7	94	84
4	8	35	28
5	3	19	20
5	4	41	28
6	1	130	119
6	2	32	32
6	3	98	89
6	4	16	20
6	5	108	84
6	7	109	92
7	2	11	19
7	4	20	24
7	6	18	15
8	0	73	75
8	1	67	62
8	2	47	50
8	3	45	45
8	4	39	45
****H=11*****			
1	1	76	119
1	2	15	20
1	3	104	120
1	4	25	35
1	5	109	104
1	6	59	50
1	7	107	91
2	2	13	24
2	3	19	16
2	4	13	15
2	7	17	18
3	0	72	87
3	1	70	77
3	2	83	81
3	3	47	49
3	4	79	70
3	5	77	65
3	6	77	62
3	7	68	53
4	2	13	16
5	0	108	92
5	2	144	115
5	3	29	27
5	4	126	115
5	6	112	90
6	4	24	21
7	0	104	98
7	1	38	40
7	2	85	77
7	3	41	37
7	4	83	68
****H=12*****			
0	2	66	104
0	4	94	102
0	6	76	68
1	3	29	7
2	0	30	44
2	1	40	49
2	2	40	46
2	3	27	30
2	4	91	77
2	5	59	50
2	6	92	66
2	7	43	33
4	0	31	32
4	1	65	57
4	2	27	24
4	3	101	86
4	4	17	19
4	5	82	63
6	0	40	31
6	1	83	69
6	3	88	77
****H=13*****			
1	2	10	18
1	3	76	88
1	4	35	36
1	5	85	72
3	0	18	24
3	1	28	32
3	2	56	57
3	3	41	40
3	4	84	73
3	5	68	58
5	0	55	58
5	2	84	79

on a twofold axis, the electron density error may be expected to be $\sqrt{2}$ times larger than in a general position.[12] It is clear that no other atoms (except hydrogen) remain to be found in this structure.

Description of the Structure

From the electron density maps it is not possible to distinguish among the three species oxygen, hydroxyl, and fluorine. Chemical analysis indicates that the material is fluoride-free and that the oxidation number is 8. The presence of hydroxyl groups would be hard to explain in view of this oxidation number and the clear stereochemical evidence that there are four sodium atoms per molecule. Moreover, as we shall indicate, there are a number of O···O distances in the range 2.63 to 3.05 Å. which can be interpreted in terms of a very reasonable over-all hydrogen bonding scheme for water molecules and XeO_6^{-4} ions. Finally, the volume per oxygen atom is 23.1 Å.^{3}, a typical value for hydrates. From these arguments, as well as from the reasonableness of all interatomic distances, we conclude that the material studied here is $Na_4XeO_6 \cdot 8H_2O$.

The parameters of Table I, together with the cell dimensions and symmetry of the space group, describe a structure in which XeO_6^{-4} ions and Na ions are linked together by water molecules in a complicated three-dimensional network. Figure 1 is a perspective drawing of the XeO_6^{-4} ion, together with the principal hydrogen-bonded interactions between the oxygens of the perxenate ion and of the water molecules. In Table III the principal interatomic distances and angles and their estimated standard deviations are listed.

Both the Xe atom and the two sodium ions are octahedrally coordinated. The ion is required by its position on the crystallographic twofold axis to have a twofold axis passing through Xe, O_1, and O_2; the results here indicate that the perxenate ion has approximately the form of a regular octahedron. The hypothesis that the four independent Xe–O bond lengths are equal cannot be rejected at the 5% level. One of the O–Xe–O angles is 87.4° with an estimated standard deviation of 0.8°. Such a distortion from the ideal symmetry is not surprising in view of the different environments of the oxygen atoms in the crystal structure.

The mean Xe–O distance in the perxenate ion is estimated from the four independent distances to be 1.864 ± 0.012 Å. This value is in good agreement with that found for the hexahydrate, 1.840 ± 0.015 Å.[4] This distance is about 0.11 Å. longer than the average Xe–O distance in XeO_3.[13] This difference is exactly the difference found between the I–O distances in the IO_6^{-5} ion in $(NH_4)_2H_3IO_6$[14] (1.93 Å.) and in the IO_3^- ion (1.82 Å.)[15]; these ions are isoelectronic with XeO_6^{-4} and XeO_3. Te–O distances ranging from 1.83 to 1.95 Å. have been found in what is assumed to be the $Te(OH)_5O^-$ ion by Raman.[16]

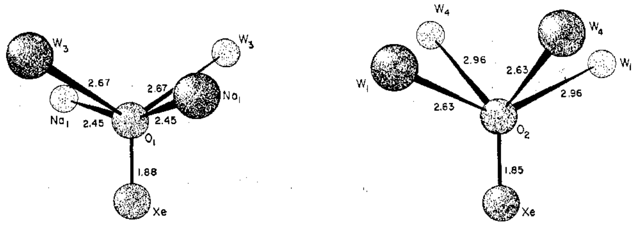

Fig. 2.—O_1 and O_2 each lie near the center of a square pyramid with the bonded Xe at the apex and sodium and/or water on the corners of the base.

TABLE III

INTERATOMIC DISTANCES (Å.) AND ANGLES[a]

Perxenate ion

Xe–O_1	1.88	∠O_1–Xe–O_3	89.3°
Xe–O_2	1.85	∠O_2–Xe–O_3	90.7°
Xe–O_3	1.84	∠O_1–Xe–O_4	89.0°
Xe–O_4	1.89	∠O_2–Xe–O_4	91.0°
Mean Xe–O	1.864	∠O_3–Xe–O_4	87.4°
σ (of mean)	0.012	∠O_3–Xe–O_4'	92.6°

Na_1 octahedron

Na_1–O_1	2.45	∠O_1–Na_1–O_3	65°	∠O_3–Na_1–W_2'	154°
Na_1–O_3	2.43	∠O_1–Na_1–W_1	117°	∠O_3–Na_1–W_3	118°
Na_1–W_1	2.35	∠O_1–Na_1–W_2	85°	∠W_1–Na_1–W_2	147°
Na_1–W_2	2.71	∠O_1–Na_1–W_2'	89°	∠W_1–Na_1–W_2'	109°
Na_1–W_2'	2.33	∠O_1–Na_1–W_3	161°	∠W_1–Na_1–W_3	82°
Na_1–W_3	2.44	∠O_3–Na_1–W_1	88°	∠W_2–Na_1–W_2'	95°
		∠O_3–Na_1–W_2	79°	∠W_2–Na_1–W_3	77°
				∠W_2'–Na_1–W_3	85°

Na_2 octahedron

Na_2–O_3	2.37	∠O_3–Na_2–O_4	66°	∠O_4–Na_2–W_3	82°
Na_2–O_4	2.38	∠O_3–Na_2–W_1	83°	∠O_4–Na_2–W_4	94°
Na_2–W_1	2.61	∠O_3–Na_2–W_2	107°	∠W_1–Na_2–W_2	75°
Na_2–W_2	2.59	∠O_3–Na_2–W_3	113°	∠W_1–Na_2–W_3	157°
Na_2–W_3	2.39	∠O_3–Na_2–W_4	141°	∠W_1–Na_2–W_4	79°
Na_2–W_4	2.35	∠O_4–Na_2–W_1	120°	∠W_2–Na_2–W_3	85°
		∠O_4–Na_2–W_2	161°	∠W_2–Na_2–W_4	102°
				∠W_3–Na_2–W_4	96°

Water molecules (position of H inferred)

W_1–H····O_2	2.96		
W_1–H····O_4	2.74	∠O_2–W_1–O_4	116°
W_2–H····O_4	2.72		
W_2–H····W_4	3.05	∠O_4–W_2–W_4	85°
W_3–H····O_1	2.67		
W_3–H····W_4	3.04	∠O_1–W_3–W_4	112°
W_4–H····O_2	2.63		
W_4–H····O_3	2.64	∠O_2–W_4–O_3	127°
W_4····H–W_2	3.05	∠O_2–W_4–W_2	101°
		∠O_3–W_4–W_2	70°
W_4····H–W_3	3.04	∠O_3–W_4–W_3	105°
		∠O_2–W_4–W_3	89°
		∠W_2–W_4–W_3	170°

[a] Estimated standard deviations are about 0.02 Å. and 0.6–0.8° for all quantities in the table.

The geometry found is in agreement with the most obvious electronic structure for the perxenate ion, that involving six single electron pair bonds from Xe to O at the corners of a regular octahedron. Such a structure would lead to formal charges of −1 on each

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[12] See, for example, D. W. J. Cruickshank and J. S. Rollett, *Acta. Cryst.*, **6**, 705 (1953).

[13] D. H. Templeton, A. Zalkin, J. D. Forrester, and S. M. Williamson, *J. Am. Chem. Soc.*, **85**, 817 (1963).

[14] L. Helmholz, *ibid.*, **59**, 2036 (1937).

[15] J. A. Ibers, *Acta Cryst.*, **9**, 225 (1956).

[16] S. Raman, *Inorg. Chem.*, **3**, 634 (1964).

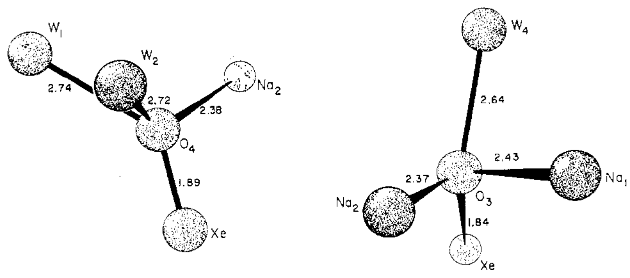

Fig. 3.—O_3 and O_4 are surrounded by slightly distorted tetrahedra composed of the bonded Xe and sodium and water.

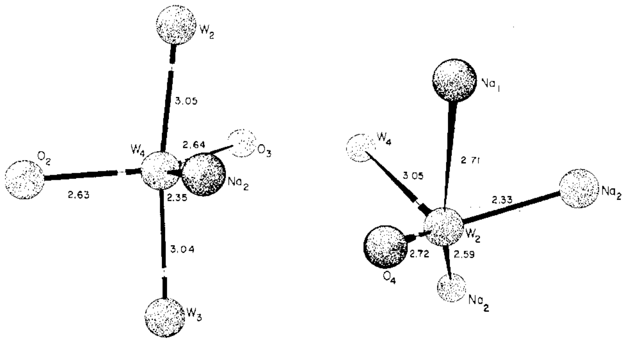

Fig. 4.—The nearest neighbors of W_4 and W_2 (sodium and H-bonded oxygens) are arranged about these molecules in approximate trigonal bipyramids. Suggested positions of hydrogen atoms are indicated by the breaks in the bonds.

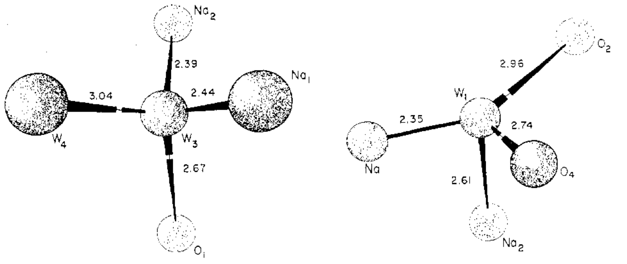

Fig. 5.—The nearest neighbors of W_3 and W_1 (sodium and H-bonded oxygen) are at the corners of distorted tetrahedra. Suggested positions of hydrogen atoms are indicated by the breaks in the bonds.

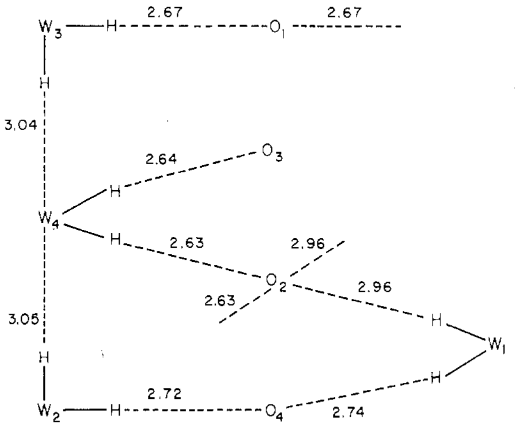

Fig. 6.—Topological diagram of hydrogen bonding in sodium perxenate octahydrate. Atoms indicated may be related by symmetry operations of the space group to those atoms whose coordinates are given in Table I.

oxygen and +2 on Xe; there is probably some additional shift of electronic charge into the bonds from oxygen, thus leading to a small amount of double-bond character. This is consistent with the bond length found.

The geometry of the perxenate ion thus offers no surprises and adds further weight to the accumulating body of evidence that the rare gas compounds have molecular structures which are readily understood in terms of conventional ideas of structural chemistry. In particular, there are marked similarities to the structures of compounds of the neighboring halogens.

The sodium octahedra are severely distorted, as an examination of Table III will indicate.

Hydrogen Bonding

Hydrogen atoms have been assigned to the water molecules to form a complex three-dimensional hydrogen-bonded network which may be partially comprehended by an examination of Fig. 2–6, as well as Fig. 1. Six of the independent hydrogen atoms are involved in hydrogen bonds from water to perxenate oxygen at distances of 2.63, 2.64, 2.67, 2.72, 2.74, and 2.96 Å. The two other hydrogen atoms may reasonably be assigned to hydrogen bonds between water molecules at distances of 3.04 and 3.05 Å. Although these distances may be too large to provide conclusive evidence for hydrogen bonds, they are the shortest nonbonded distances aside from the six above, and the bond angles (Table III) would be reasonable if these are indeed hydrogen bonds.[17] It is interesting that W_4, which contributes hydrogen to the two shortest hydrogen bonds (2.63 and 2.64 Å.), is also the acceptor in the postulated hydrogen bonds from W_2 and W_3. The coordination about W_4 is an almost regular trigonal bipyramid, W_2 and W_3 being at the apices (Fig. 4).

The extensive strong hydrogen bonding is consistent with the low temperature factors on all the atoms in the structure[18] and is perhaps also in part responsible for the stability of the crystals, protecting the perxenate ions from reducing agents. The four shortest interperxenate ion O···O distances are 4.73, 4.83, 4.29, and 5.00 Å.

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(17) A O–H···O hydrogen bond with a length of 3.35 Å. has been described by J. A. Ibers, J. Kumamoto, and R. G. Snyder, *J. Chem. Phys.*, **33**, 1164 (1960).

(18) That the temperature factor on O_4 is lower than that for the other light atoms is viewed as an artifact, perhaps due to the same sort of systematic errors in the data which may be responsible for the large peak at the Xe position in the difference Fourier.