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SODIUM PEROXENATE HEXAHYDRATE

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Sodium Perxenate Hexahydrate

Abstract. Sodium perxenate hexahydrate ($\text{Na}_4\text{XeO}_6 \cdot 6\text{H}_2\text{O}$) has been identified by determination of the crystal structure by x-ray diffraction. The perxenate ion (XeO_6^{-4}) has the shape of a regular octahedron with Xe-O bond distance 1.84 Å.

Some hydrated sodium salts of xenon in the +8 oxidation state were produced by Malm, Bane, and Holt (1) by hydrolysis of XeF_6 in the presence of sodium hydroxide. Crystal data were reported by Siegel and Gebert (2) for three phases produced in this way. By determination of the crystal structure Hamilton, Ibers, and Mackenzie (3) have shown that one of these phases is $\text{Na}_4\text{XeO}_6 \cdot 8\text{H}_2\text{O}$, containing perxenate ion (XeO_6^{-4}) in the shape of a regular octahedron.

We have produced another salt which is characterized as $\text{Na}_4\text{XeO}_6 \cdot 6\text{H}_2\text{O}$ by determination of the crystal structure. We find the same shape for the perxenate ion with dimensions close to those reported in the work on the octahydrate (3). This hexahydrate is not one of the phases reported by Siegel and Gebert (2).

The crystals of $\text{Na}_4\text{XeO}_6 \cdot 6\text{H}_2\text{O}$ were obtained from the reaction of pure xenic acid (aqueous XeO_3) (4,5) and sodium hydroxide. When 0.100 ml of 0.208 M XeO_3 (Aq) and 0.060 ml of 6 M NaOH were mixed the resulting solution was pale yellow. After one day in a refrigerator at 5° crystals grew as very thin fragile sheets. The production of crystals from the reaction is

much more rapid at elevated temperatures, ca. 60° , but at this higher temperature the product is the octahydrate. It was identified by its cell dimensions which we measured as $\underline{a} = 11.864$, $\underline{b} = 10.358$, $\underline{c} = 10.426$ Å (each ± 0.005 Å), in agreement with the previous work (2,3).

The hexahydrate is much less stable than the octahydrate. The x-ray study was made of crystals sealed in thin-walled glass capillaries containing some of the mother liquor. Most crystals survived only a few hours in the capillaries, and several preparations were necessary before adequate data were obtained. Photography of one crystal by the Weissenberg technique gave some preliminary information. Intensity data with $\text{MoK}\alpha$ radiation were gathered by direct counting with a scintillation counter for about 1250 reflections (including about 250 absent because of the space group) on one or more of 10 different crystals. At higher angles many of the reflections with mixed (even and odd) indices were too weak to be observed reliably. The structure refinement was based on 491 reflections from one or another of 5 different crystals, including 14 reflections which were assigned zero intensity. These crystals were 0.3 mm or less in the largest dimension with thicknesses too thin to be measured with our microscope. Experiments by a technique described elsewhere (6) showed that absorption reduced some intensities about 20 percent, but was negligible for most of the data.

The crystals are orthorhombic, space group \underline{Pbca} , with $\underline{a} = 18.44 \pm 0.01$, $\underline{b} = 10.103 \pm 0.007$, $\underline{c} = 5.873 \pm 0.005$ Å. The density is calculated as 2.59 g/ml with 4 molecules per unit cell. The crystals were observed to sink in ethylene bromide (density 2.17 g/ml). Xenon atoms are on centers of inversion at the origin and face centers. All other atoms are in general 8-fold sets of positions.

All atoms (except hydrogen, which is not detected with these data) were recognized in the Patterson function. The refinement never changed the main features of the structure, but it was circuitous because change of sign of several of the coordinates has little effect on most of the intensities and because strong correlation among some of the parameters results from pseudosymmetry of the structure. Refinement by least squares eventually reduced $R = \sum ||\underline{F}_o| - |\underline{F}_c|| / \sum |\underline{F}_o|$ to 0.072 with the atomic parameters listed in Table 1. Standard deviations of coordinates correspond to 0.01 Å for sodium and 0.02 Å for oxygen. A three-dimensional Fourier synthesis of $\underline{F}_o - \underline{F}_c$ showed no peaks as high as 2 electrons/Å³.

Table 1. Atomic coordinates and thermal parameters in Na₄XeO₆·6H₂O.

Atom	<u>x</u>	<u>y</u>	<u>z</u>	<u>B</u> , Å ²
Xe	0	0	0	(0.85 ± 0.04)*
Na(1)	0.009	0.164	0.492	1.4 ± 0.2
Na(2)	.252	.155	.539	1.7 ± 0.2
O(1)	.060	.005	.252	1.2 ± 0.2
O(2)	.064	.115	.854	1.8 ± 0.4
O(3)	.951	.136	.127	1.0 ± 0.4
O(W1)	.169	.200	.242	1.6 ± 0.3
O(W2)	.339	.183	.836	1.5 ± 0.3
O(W3)	.192	.518	.242	2.2 ± 0.4

*Isotropic B equivalent to average of anisotropic temperature factor.

The perxenate ion is centric by the space-group symmetry. The three independent Xe-O distances are:

Xe-O(1)	$1.85 \pm 0.02 \text{ \AA}$
Xe-O(2)	$1.86 \pm 0.02 \text{ \AA}$
Xe-O(3)	$1.81 \pm 0.02 \text{ \AA}$

The deviations from the average value 1.84 \AA are not significant. Our data concerning thermal motion are incomplete, but we estimate that the correction for thermal motion would increase this distance less than 0.01 \AA . The bond angles O-Xe-O which would be 90° for regular octahedral shape range from 87.1° to 92.9° with standard deviations of about 1° . We do not consider these deviations from 90° to be significant. These results are in accord with those from the octahydrate (3) in which the angles were found closer to 90° and the average bond distance was reported as $1.875 \pm 0.021 \text{ \AA}$, with somewhat more scatter from the average than in the hexahydrate.

Each Na(1) has six oxygen neighbors belonging to perxenate ions at an average distance 2.46 \AA . Each Na(2) has six oxygen neighbors (water molecules) at an average distance 2.44 \AA . In each case the six neighbors are at the corners of an irregular octahedron.

The overall structure is quite different from that of the octahydrate. It consists of layers perpendicular to the a axis. Layers containing the perxenate and half of the sodium alternate with layers containing the rest of the sodium and all of the water. The six independent hydrogen atoms are assigned to hydrogen bonds which all have reasonable distances and angles. Five of these bonds, between water and oxygen of perxenate, hold the layers to each other. (7)

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References and Notes

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7. This work was done in part under the auspices of the U. S. Atomic Energy Commission.

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