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POTASSIUM PERXENATE NONAHYDRATE

Berkeley, California

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POTASSIUM PERXENATE NONAHYDRATE

Allan Zalkin, J. D. Forrester, David H. Templeton, Stanley M. Williamson
and Charles W. Koch

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Potassium Perxenate Nonahydrate[1]

Sir:

Several salts of the unstable perxenic acid have been isolated and identified. Sodium perxenate[2,3] exists in several crystalline forms, and the structures of $Na_4XeO_6 \cdot 8H_2O$[4,5] and $Na_4XeO_6 \cdot 6H_2O$[6] have been determined. Perxenate salts of barium[7,8] and of calcium, lithium, and cesium[8] have been prepared, but their structures are unknown. We have now prepared a potassium salt and characterized it as $K_4XeO_6 \cdot 9H_2O$ by determination of its crystal structure.

The solubility of potassium perxenate appears to be much greater than that of the sodium perxenates at a given concentration of OH^-. The disproportionation reaction of xenic acid in potassium hydroxide solution failed to give crystals under conditions analogous to those at which $Na_4XeO_6 \cdot 8H_2O$ was easily crystallized. Appelman and Malm[7] have described other failures to obtain potassium perxenate. We obtained the potassium salt by the following procedure. A concentrated solution of reagent grade KOH was treated with a small amount of $KMnO_4(s)$ and was heated at 70° for three days, i. e. until the purple color was no longer present. The solution (10.04 M) was decanted from the sediment and was used without further treatment. Prolonged exposure to the atmosphere was avoided, and all experiments were carried out in Pyrex ware. After thorough degassing, 200 μl of the base and 750 μl of 0.1082 M xenic acid, prepared by dissolution of $XeO_3(s)$, were mixed in vacuum at 0°. By gas evolution measurements similar to those previously described[9] it was determined that 26.06 μmole of Xe(VIII)

was prepared. No crystals were obtained by cooling the solution to 0°. We removed 400 μl of H_2O via vacuum distillation and added 200 μl of the xenic acid. This increment of 21.64 μmole of xenic acid produced only an additional 5.61 μmole of Xe(VIII). When this solution was cooled slowly to 5°, well-defined, colorless, transparent crystals appeared. After equilibrium at 5° was established, about three-fourths of the mother liquor was removed. The crystals in the remaining solution were stable and insoluble at room temperature. Before crystallization the concentrations were [Xe(VIII)] = 0.042 and $[K^+]$ = 3.39.

Crystals were studied by the same X-ray techniques which we used for sodium perxenate.[6] The crystals of the potassium salt are considerably more stable in X-rays than $Na_4XeO_6 \cdot 6H_2O$, but less so than $Na_4XeO_6 \cdot 8H_2O$. Thus we were able to collect intensity data by direct counting with a single specimen (diameters 0.3 mm. or less), but the intensity scale had to be adjusted by a factor 1.85 between the start and finish of the measurements. We used Mo$K\alpha$ radiation (λ = 0.70926 Å. for $K\alpha_1$). The measurements include all 1412 independent reflections permitted by the space group with 2θ less than 50°; of these, we recorded 95 as zero. No correction was made for absorption or extinction.

The symmetry is orthorhombic, space group $Pbc2_1$ (C_{2v}^5), with a = 9.049 ± 0.004, b = 10.924 ± 0.004, c = 15.606 ± 0.006 Å., Z = 4, d_x = 2.35 g./ml. Each atom is in general positions 4(a):

$$x, y, z; \quad -x, -y, \tfrac{1}{2} + z; \quad -x, \tfrac{1}{2} + y, z; \quad x, \tfrac{1}{2} - y, \tfrac{1}{2} + z.$$

By alternate Fourier and least-squares methods we reduced the unreliability factor[6] R to 0.063, with anisotropic thermal parameters for Xe and isotropic ones for K and O. A Fourier synthesis of (F_{obs} - F_{cal}) at this stage showed no peaks larger than 2.2 electrons per Å.^{3} (near a potassium atom)

and 1.4 electrons per Å.^{3} (near an oxygen atom). Further refinement with potassium atoms assigned anisotropic thermal parameters reduced R to 0.058.

The composition is assigned as $K_4XeO_6 \cdot 9H_2O$ on the basis of the good agreement with the X-ray data.

Atomic coordinates are listed in Table I. The XeO_6^{-4} ion is in the

TABLE I

ATOMIC COORDINATES AND THERMAL PARAMETERS[a]

Atom	x	y	z	B, Å.^{2}
Xe	0.249	0.988	0.250	1.1[b]
K(1)	.628	.987	.339	2.1[b]
K(2)	.846	.238	.958	2.9[b]
K(3)	.307	.227	.026	3.2[b]
K(4)	.877	.989	.139	1.9[b]
O(1)	.403	.101	.251	2.4
O(2)	.094	.878	.253	2.4
O(3)	.138	.096	.316	2.0
O(4)	.176	.058	.151	2.2
O(5)	.323	.918	.351	1.6
O(6)	.360	.881	.188	2.3
W(1)[c]	.654	.839	.190	1.9
W(2)	.850	.136	.297	1.9
W(3)	.873	.829	.369	2.2
W(4)	.692	.046	.506	3.0
W(5)	.997	.243	.111	2.0
W(6)	.967	.980	.972	2.7
W(7)	.376	.470	.002	3.1

W(8)	.493	.262	.886	3.1
W(9)	.606	.150	.124	2.8

[a]Standard deviations correspond to 0.02 Å. or less for coordinates and 0.3 Å.^{2} or less for B. [b]Value equivalent to average of anisotropic parameters. [c]"W" indicates oxygen atom of water molecule.

shape of a regular octahedron within experimental accuracy, with average Xe-O distance 1.86 ± 0.01 Å., in excellent agreement with 1.864 ± 0.012 Å.[5] and 1.84 ± 0.02 Å.[6] found in the two sodium salts. The bond angles that would be 90° for a regular octahedron range from 88.8° to 91.2° (σ = 0.7°). The four independent potassium atoms have respectively 6, 6, 7, and 7 water molecules and 2, 1, 1, and 2 oxygen atoms of perxenate as neighbors as indicated in Fig. 1 at distances ranging from 2.67 to 3.22 Å. These neighbors are at the corners of very irregular polyhedra, and some other neighbors are not much more distant. An intricate network of hydrogen bonds connects the entire structure.

DEPARTMENT OF CHEMISTRY AND
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

ALLAN ZALKIN
J. D. FORRESTER
DAVID H. TEMPLETON
STANLEY M. WILLIAMSON
CHARLES W. KOCH

(1) Work done in part under the auspices of the U. S. Atomic Energy Commission.

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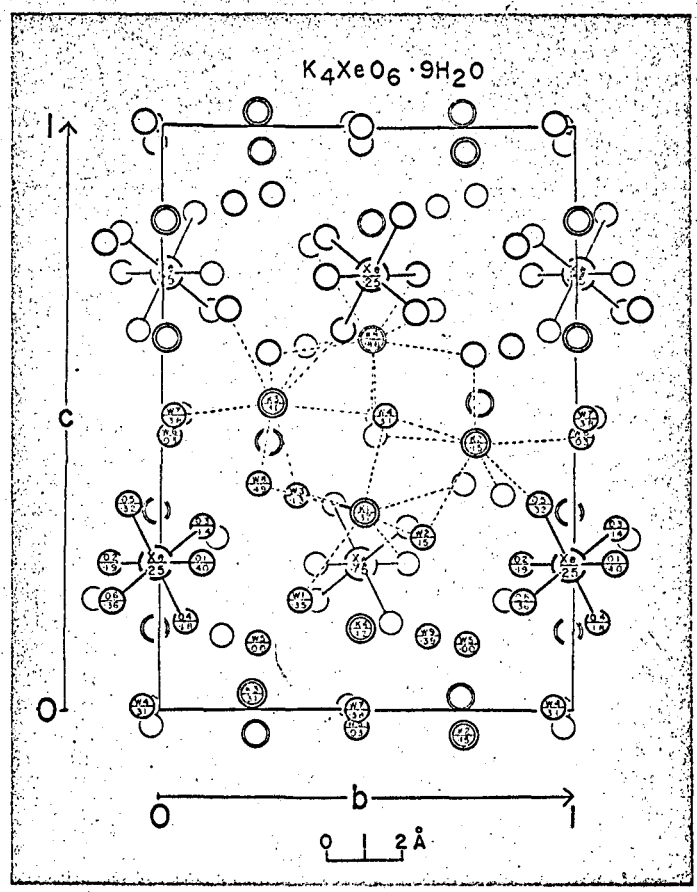

Fig. 1.—Crystal structure of $K_4XeO_6 \cdot 9H_2O$ viewed down the a axis. The designation and x coordinate are indicated on some of the atoms. Broken lines connect potassium atoms to their neighbors.

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