3. Sulfur and selenium behave in liquid ammonia as weak nitridizing (oxidizing, de-electronizing) agents.

4. Solutions of cyanides in liquid ammonia react very readily with sulfur and selenium, much more slowly with tellurium, and not at all with arsenic. The following new compounds have been prepared: $Al(SCN)_3$·-$5NH_3$, $Mg(SCN)_2$·$4NH_3$, $Mg(SeCN)_2$·4 and 6(?)NH_3, $Zn(SeCN)_2$·$4NH_3$, $Al(SeCN)_3$·$5NH_3$.

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THE CRYSTAL STRUCTURE OF SODIUM PERIODATE

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Introduction

The similarity of crystal form of sodium periodate, $NaIO_4$, and calcium tungstate, $CaWO_4$, as well as of some periodates of other univalent metals and tungstates and molybdates of other bivalent metals, was recognized by Hiortdahl.[1] To these Barker[2] added the compounds $KRuO_4$ and $KOsO_3N$ and discussed the bearing of such cases of isomorphism on valence theory. These crystals are all tetragonal[3] and have axial ratios ranging from 1:1.521 to 1:1.634. Crystallographers have not, however, assigned all of these compounds to the same *class* of symmetry. Thus sodium periodate is given[3] as ditetragonal bipyramidal (D_{4h}), calcium tungstate as tetragonal bipyramidal (C_{4h}), and lead molybdate as tetragonal pyramidal (C_4). The present work casts doubt upon the reality of these differences in symmetry.

From some x-ray-spectrometer measurements it was concluded[4] that in wulfenite, $PbMoO_4$, and scheelite, $CaWO_4$, the metal atoms were placed on two interpenetrating "diamond" arrangements elongated in the direction of the tetragonal axis. These data were theoretically discussed by Niggli and Faesy,[5] and an attempt was made to determine the space-group symmetry; owing, however, to an omission[6] in the space-group tables used, the space group C_{4h}^6 was incorrectly eliminated. In some unpublished work in this Laboratory, Dr. R. M. Bozorth and one of us (R. G. D.) found that symmetrical, basal-plane Laue photographs of wulfenite showed

[1] Hiortdahl, *Z. Kryst. Min.*, 12, 411 (1887).

[2] Barker, *J. Chem. Soc.*, 101, 2487 (1912).

[3] Groth, "Chemische Krystallographie," Engelman, Leipzig, 1908, vol. 2, pp. 175, 393.

[4] Dickinson, THIS JOURNAL, 42, 85 (1920).

[5] Niggli and Faesy, *Z. Kryst.*, 59, 473 (1924).

[6] This omission has since been corrected by K. Weissenberg, *ibid.*, 63, 173 (1926).

a tetragonal axis and, except for the spots nearest the central image, four symmetry planes;[7] it was further found that, except for this small hemihedry, the intensities of spots occurring on slightly unsymmetrical basal-plane Laue photographs were in accord with the structure factors calculated from the arrangement previously given,[4] completely omitting the oxygen atoms. These facts may be given the following interpretation: (1) the metal atoms have a highly symmetrical arrangement; (2) the slight hemihedry is due to the positions of the oxygen atoms; (3) the hemihedry is noticeable only in the case of simple planes because the reflecting power of the oxygen atoms relative to that of the heavy atoms decreases, as would be expected, with decreasing interplanar distance.

Sodium periodate has been chosen for the present work partly because of its reported higher symmetry, and partly because of the relatively greater weight of the oxygen atoms in it. Moreover, its *structural* similarity to the tungstates and molybdates remained to be demonstrated.

Preparation of the Crystals

Sodium periodate was prepared[8] by passing chlorine into a hot solution of iodine in sodium hydroxide, made by dissolving 20 g. of iodine and 80 g. of sodium hydroxide in 300 cc. of water. After several hours a fine crystal meal separated which, after being filtered and washed, was found to liberate iodine from a slightly basic solution of potassium iodide—a test for periodate.[9] The product was further purified by dissolving it in dil. sulfuric acid and slowly reprecipitating by adding sodium hydroxide. It was then dissolved in water to which a small amount of sulfuric acid had been added, and allowed to crystallize at a temperature of 40° to 45°. The crystals were 3–6 mm. long with the forms $(111)_c$ and $(101)_c$ developed. Throughout this paper the subscript "c" designates those indices which are referred to the crystallographic axes; indices without subscript refer to the space-group axes. The faces were identified by interfacial angle measurements on a reflection goniometer.

A density determination made by displacement of carbon tetrachloride[10] in a pycnometer gave the value 4.12 g./cc. This value is considerably higher than that previously given,[11] 3.865 g./cc. Three analyses were made by adding an excess of potassium iodide to an acid solution of the

[7] The weakness of the hemihedry of such photographs has also been found by Haga and Jaeger, *Proc. Acad. Sci. Amsterdam*, **18**, II, 1350 (1916), and by Aminoff, *Geol. Fören. Förh.*, **42**, 296 (1920).

[8] See Gmelin-Kraut, "Handbuch der anorganische Chemie," Carl Winter, Heidelberg, 1909, vol. 1 (2), p. 364.

[9] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, New York, 1911, vol. 2, p. 670.

[10] A. E. H. Tutton, "Crystallography and Practical Crystal Measurement," Macmillan Co., 1911, pp. 518–534.

[11] Ref. 3, p. 176.

periodate and titrating the free iodine with standard thiosulfate solution. These gave 58.0, 58.4 and 58.7% of iodine; calcd. for $NaIO_4$: 59.3.

Experimental Procedure

Spectral photographs were made by reflecting the K radiation of molybdenum from $(111)_c$, $(110)_c$ and $(001)_c$, using a rotating crystal; to insure precision in the measurements, a reference spectrum of calcite was photographed simultaneously with the spectrum of the periodate. The spectral data are given in Table I.

TABLE I

SPECTRAL DATA FROM SODIUM PERIODATE

hkl	Line[a]	Angle of reflection	$\dfrac{\lambda}{2 \sin \theta}$	Order (true unit)	Estimated intensity
(001)	γ	$5° 59'$	2.978	n_1	0.05
	β	$6° 5'$	2.977	n_1	.4
	α	$6° 49'$	2.990	n_1	1.8
	β	$12° 10'$	1.489	$2n_1$	0.2
	α_1	$13° 43'$	1.492	$2n_1$	1.0
	α_2	$13° 48'$	1.493	$2n_1$	0.3
	β	$18° 32'$	0.993	$3n_1$	.3
$(110)_c$	β	$6° 51'$	2.644	n_2	.2
	α	$7° 39'$	2.666	n_2	.9
	β	$13° 43'$	1.330	$2n_2$	.25
	α_1	$15° 25'$	1.331	$2n_2$	1.0
	α_2	$15° 31'$	1.331	$2n_2$	0.6
$(111)_c$	α	$4° 12'$	4.846	n_3	1
	α	$8° 24'$	2.432	$2n_3$	0.1
	β	$11° 17'$	1.612	$3n_3$	.05
	α_1	$12° 39'$	1.616	$3n_3$	.3
	α_2	$12° 44'$	1.616	$3n_3$	.1
	γ	$14° 51'$	1.209	$4n_3$	.05
	β	$15° 7'$	1.210	$4n_3$	.3
	α_1	$17° 1'$	1.210	$4n_3$	.8
	α_2	$17° 8'$	1.209	$4n_3$	.5

[a] The letters refer to the K lines of molybdenum, whose wave lengths are: $\gamma = 0.6197$ Å.; $\beta = 0.6311$; $\alpha_1 = 0.7078$; $\alpha_2 = 0.7121$; when α_1 and α_2 are unresolved they are designated as α and the wave length taken as 0.710 Å.

Laue photographs were taken with the white radiation from a tungsten anticathode; the tube was operated at a peak voltage of 51.5 kv., hence the lower wave-length limit of the x-rays was 0.24 Å. Symmetrical and unsymmetrical photographs were taken through sections ground parallel to $(001)_c$, $(111)_c$ and $(110)_c$. Gnomonic projections of the Laue photographs were made to assist in the assignment of indices to the reflecting planes. Data from these photographs are listed in Table II.

The Unit of Structure

It is convenient first to find the smallest unit of structure compatible with these spectral measurements. From the hemihedry of the Laue

photographs, demonstrated below, it follows that the crystal has insufficient symmetry to fix the position of the true H axis as one of two alternatives, but that any possible crystal edge perpendicular to the tetragonal axis must be considered a possible position of the H axis. Let the indices of $(110)_c$ become $(h'k'0)$ when referred to the space-group axes, and those of $(111)_c$ become $(h''k''l'')$. The spectral measurements of Table I lead to the following values: $d_{001} = n_1 \times 2.982$; $d_{h'k'0} = n_2 \times 2.661$; $d_{h''k''l''} = n_3 \times 4.841$; hence $d_{100} = n_2 \sqrt{h'^2 + k'^2} \times 2.661$. Taking $1:1.590$ as the axial ratio defining the position of $(111)_c$, it can be shown (for example by considering the intercepts of $(111)_c$ on the original and rotated axes) that $h'':k'':l''=h'\sqrt{2}\,d_{hk0}:k'\sqrt{2}\,d_{hk0}:d_{001}/1.590\,d_{001}=3.76\,n_2h':3.76\,n_2k':1.875n_1 = 2n_2h':2n_2k':n_1$. If r is the highest integral common divisor of $2n_2h'$, $2n_2k'$ and n_1, then $(h''k''l'') = \left(\dfrac{2n_2h'}{r}\ \dfrac{2n_2k'}{r}\ \dfrac{n_1}{r}\right)$. Substituting these indices and the above values for d_{100} and d_{001}, in the formula: $d_{h''k''l''} = \left[\left(\dfrac{h''}{d_{100}}\right)^2 + \left(\dfrac{k''}{d_{100}}\right)^2 + \left(\dfrac{l''}{d_{001}}\right)^2\right]^{-\frac{1}{2}}$, we get $d_{h''k''l''} = 1.215r$. Since this is equal to $n_3 \times 4.841$, it follows that $r = 4n_3$. We now have only to assign integral values to n_1, n_2, n_3, h and k subject to the restrictions that (1) h and k shall be prime integers, (2) $n_2h'/2n_3$, $n_2k'/2n_3$ and $n_1/4n_3$ shall be prime integers and (3) $n_1n_2^2\ (h'^2 + k'^2)$ shall be as small as possible (since this is proportional to the size of the unit). These conditions are satisfied when and only when $n_1 = 4$, $n_2 = 2$, $n_3 = 1$, $h' = 1$ (or 0), and $k' = 0$ (or 1).

It is thus shown that the smallest possible unit compatible with the spectral data is one having its H and K axes at $45°$ with the crystallographic axes and having $d_{100} = d_{010} = 5.322$ Å., and $d_{001} = 11.93$ Å. The number of molecules in this unit calculated from our density is 3.94 or evidently 4. When values of $n\lambda$ were calculated for spots occurring on the Laue photographs using this unit and indices referred to it, none was found smaller than 0.26 Å. There is, then, no evidence that the true unit is other than the one described.

The Space Lattice

From the Laue photographs no value of $n\lambda$ was found below 0.48 Å. for any plane having $h + k + l$ odd; thus no such planes gave first-order reflections. This shows that the atomic arrangement is derivable from a space-group based on the body-centered lattice Γ'_t.

The Space Group

A Laue photograph taken with the incident beam nearly perpendicular to (001) showed that spots due to $\{hkl\}$ were not always equal in intensity to those due to $\{khl\}$. The best example of this is shown in Fig. 1, in which the ordinates are estimated intensities and the abscissas $n\lambda$'s. The sharp change in intensity around 0.37 Å. is obviously due to the K absorp-

tion edge of iodine. Planes of the form {321} clearly reflect more strongly than those of the form {231}. These data show that there are no planes of symmetry containing the tetragonal axis and that the point-group symmetry is accordingly S_4, C_4 or C_{4h} and *not* D_{4h}.

With the above restrictions as to point group and space lattice, the possible space groups are S_4^2, C_4^5, C_4^6, C_{4h}^5 and C_{4h}^6. In addition to reflections in odd order from planes having $h + k + l$ odd, reflections are required to be absent in the following cases.[12]

S_4^2, C_4^5, C_{4h}^5: none.

C_4^6: reflections from (001) when n is not a multiple of four.

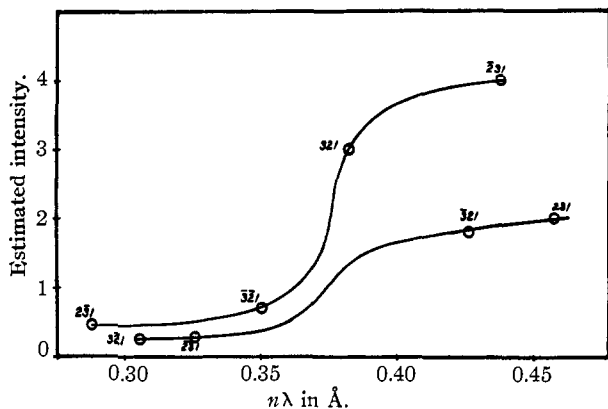C_{4h}^6: reflections from (001) when n is not a multiple of four; reflections from $(hk0)$ when n is odd.

Fig. 1.—Intensities of reflection of {321} {231}.

It has already been shown that for the reflections found from (001) n is a multiple of four. Furthermore, no planes of the type $(hk0)$ were found to reflect in the first order on the Laue photographs although (150), (170), (370) and (350) were in position to do so; and on a transmission spectral photograph where the reflections (110), (330) and (130) had opportunity to appear, these were absent. All of these absences are required by the space group C_{4h}^6, but are not by the others.

The Atomic Arrangement

The coördinates of the general and special positions of C_{4h}^6 are:[13]
Four equivalent positions:

(a) $(0 \frac{3}{4} \frac{1}{8})$ $(0 \frac{1}{4} \frac{7}{8})$ $(\frac{1}{2} \frac{1}{4} \frac{5}{8})$ $(\frac{1}{2} \frac{3}{4} \frac{3}{8})$

(b) $(0 \frac{3}{4} \frac{5}{8})$ $(0 \frac{1}{4} \frac{3}{8})$ $(\frac{1}{2} \frac{1}{4} \frac{1}{8})$ $(\frac{1}{2} \frac{3}{4} \frac{7}{8})$

12 Astbury and Yardley, *Phil. Trans.*, **223A**, 238 (1924).

13 Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," *Carnegie Inst. Publ.*, No. **318** (1922).

Eight equivalent positions:

(c) $(0\ 0\ 0)$ $(\frac{1}{4}\ \frac{1}{4}\ \frac{3}{4})$ $(\frac{1}{2}\ 0\ \frac{1}{2})$ $(\frac{1}{4}\ \frac{3}{4}\ \frac{1}{4})$ $(0\ \frac{1}{2}\ 0)$ $(\frac{3}{4}\ \frac{3}{4}\ \frac{1}{4})$ $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ $(\frac{3}{4}\ \frac{1}{4}\ \frac{3}{4})$

(d) $(0\ 0\ \frac{1}{2})$ $(\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4})$ $(\frac{1}{2}\ 0\ 0)$ $(\frac{1}{4}\ \frac{3}{4}\ \frac{3}{4})$ $(0\ \frac{1}{2}\ \frac{1}{2})$ $(\frac{3}{4}\ \frac{3}{4}\ \frac{3}{4})$ $(\frac{1}{2}\ \frac{1}{2}\ 0)$ $(\frac{3}{4}\ \frac{1}{4}\ \frac{1}{4})$

(e) $(0\ \frac{1}{4}\ u)$ $(\frac{1}{2}, \frac{1}{4}, \frac{3}{4} + u)$ $(\frac{1}{2}, \frac{3}{4}, \frac{1}{2} + u)$ $(0, \frac{3}{4}, \frac{1}{4} + u)$ $(0, \frac{3}{4}, \bar{u})$ $(\frac{1}{2}, \frac{3}{4}, \frac{1}{4} - u)$ $(\frac{1}{2}, \frac{1}{4}, \frac{1}{2} - u)$ $(0, \frac{1}{4}, \frac{3}{4} - u)$

Sixteen equivalent positions:

(f) $(x\ y\ z)$ $(\frac{1}{4} + y, \frac{1}{4} - x, \frac{3}{4} + z)$ $(\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z)$ $(\frac{1}{4} - y, \frac{3}{4} + x, \frac{1}{4} + z)$

$(x, \frac{1}{2} + y, + \bar{z})$ $(\frac{1}{4} + y, \frac{3}{4} - x, \frac{1}{4} - z)$ $(\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z)$ $(\frac{1}{4} - y, \frac{1}{4} + x, \frac{3}{4} - z)$

$(\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z)$ $(\frac{3}{4} + y, \frac{3}{4} - x, \frac{1}{4} + z)$ $(\bar{x}, \frac{1}{2} - y, z)$ $(\frac{3}{4} - y, \frac{1}{4} + x, \frac{3}{4} + z)$

$(\frac{1}{2} + x, y, \frac{1}{2} - z)$ $(\frac{3}{4} + y, \frac{1}{4} - x, \frac{3}{4} - z)$ $(\bar{x}\ \bar{y}\ \bar{z})$ $(\frac{3}{4} - y, \frac{3}{4} + x, \frac{1}{4} - z)$

There is only one distinct way in which the sodium and iodine atoms can be placed, namely Na at (a) and I at (b). In these positions the sodium and iodine atoms contribute nothing to the first-order reflections from the planes (114), (118), (138), (338) and (154), which were found to reflect in the first order; these reflections must be due to the oxygen atoms alone. If the sixteen oxygen atoms are in any combination of the positions (c), (d) and (e) the structure factor for the planes just mentioned remains zero. The only remaining arrangement for the oxygen atoms is (f); the oxygen atoms are thus all in equivalent positions.

A considerable amount of confirmatory evidence is obtainable from the Laue photographs. In order to consider this, it is convenient to divide the first-order reflections into three classes according to their structure factors.

Class 1. h and k both odd; l twice an odd number.
$S = 4\ (\overline{\text{Na}} + \overline{\text{I}})$ + oxygen terms.

Class 2. $h + k$ odd; l odd.
$S = 2\ \sqrt{2}(\overline{\text{Na}} - \overline{\text{I}})$ + oxygen terms.

Class 3. h and k both odd, l twice an even number.
$S = 0$ + oxygen terms.

Neglecting the contribution of the oxygen atoms, the structure factor for Class 1 is much greater than that for Class 2; while that for Class 3 is zero. This is in agreement with the observations; under comparable conditions of $n\lambda$ and interplanar distance, reflections of Class 1 were always found to be stronger than those of Class 2, and those of Class 2 stronger than those of Class 3. Instances of this are shown by the Laue data of Table II. The spectral and Laue data thus lead to the conclusion that sodium periodate has the space-group symmetry C_{4h}^6 with the sodium atoms at (a), the iodine atoms at (b) and the oxygen atoms at (f).

TABLE II

LAUE PHOTOGRAPHIC DATA FROM SODIUM PERIODATE

INCIDENT BEAM THROUGH (100) = (110)$_0$

hkl	Class	d_{hkl}, Å.	$n\lambda$, Å.	Estimated intensity
219	2	1.160	0.42	5
1.1.10	1	1.139	.44	9
41$\bar{5}$	2	1.137	.42	3
31$\bar{8}$	3	1.116	.43	0.05
0.1.$\overline{11}$	2	1.063	.45	2.5
$\bar{2}$.1.$\overline{11}$	2	0.987	.41	2.2
$\bar{5}$1$\bar{4}$	3	.985	.45	0.02
$\bar{3}$.1.$\overline{10}$	1	.975	.42	6
$\bar{5}$1$\bar{6}$	1	.935	.40	5
$\bar{4}$1$\bar{9}$	2	.934	.39	1.8
52$\bar{9}$	2	.793	.44	0.8
3.2.$\overline{13}$	2	.780	.45	.9
1.2.$\overline{15}$	2	.756	.44	.4
$\bar{1}$.2.15	2	.756	.41	.7
$\bar{5}$.2.$\overline{11}$	2	.732	.45	.3
$\bar{7}$21	2	.730	.45	.7
$\bar{7}$23	2	.720	.44	.3
$\bar{7}$2$\bar{5}$	2	.701	.42	.5
734	3	.679	.47	.00
$\bar{5}$.2.$\overline{13}$	2	.672	.39	.2
736	1	.659	.43	.9
5.3.$\overline{14}$	1	.632	.43	.5
83$\bar{1}$	2	.623	.39	.25
83$\bar{3}$	2	.616	.39	.1
7.3.$\overline{10}$	1	.603	.38	.5
$\bar{8}$3$\bar{7}$	2	.585	.43	.2
$\bar{8}$3$\bar{9}$	2	.564	.40	.15

Discussion of the Structure

The arrangement of the sodium and iodine atoms in the unit of structure as well as the general character of the arrangement of the oxygen atoms is shown by the left parallelopiped of Fig. 2. Each iodine atom is surrounded by four equidistant oxygen atoms at the corners of a tetragonal bisphenoid.[14] All of the bisphenoids are alike, but half of them are rotated 90° about a vertical axis from the position of the other half. The bisphenoids may approximate closely to regular tetrahedra but are not required by symmetry to do so. The sodium and iodine atoms form two interpenetrating "diamond" arrangements. This is shown by the right-hand part of Fig. 2, which is a drawing of a unit containing eight molecules of sodium periodate and having its axes parallel to the crystallographic axes; its relation to the

[14] This remark applies equally well to the sodium atoms; however, on chemical grounds, it is more natural to consider the association of the oxygen atoms to be with the iodine atoms rather than the sodium atoms.

true unit of structure is shown by the numbering of the corresponding sodium atoms.

The sodium and iodine atoms are thus arranged in just the same manner as previously given[4] for the analogous atoms in lead molybdate and calcium tungstate. The fact that sodium periodate, instead of being holohedral, turns out to be tetragonal bipyramidal, strengthens the presumption that the periodates, tungstates and molybdates mentioned in the introduction are structurally even more closely similar than had been supposed.
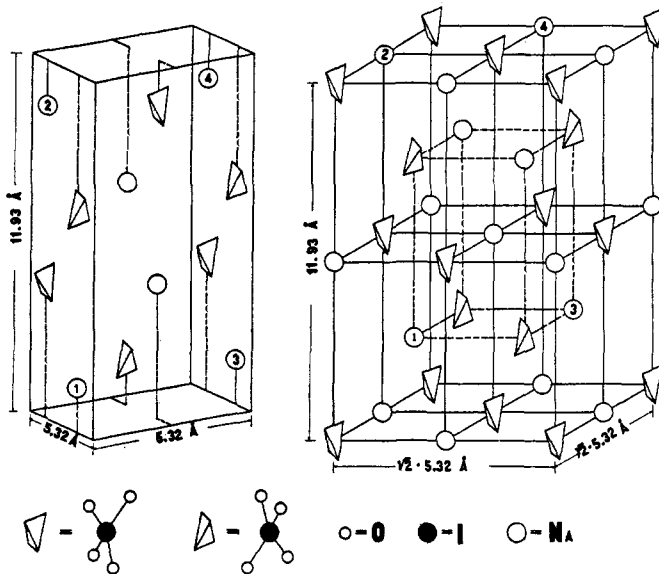

Fig. 2.—Left: the unit of structure of $NaIO_4$. Right: a larger unit which contains 8 $NaIO_4$ and whose axes are the crystallographic axes.

Incidentally, this structure shows that it is unjustifiable to write the formula of solid sodium periodate as $Na_2I_2O_8$, as has sometimes been done.

Summary

The structure of the tetragonal crystal sodium periodate has been investigated using spectral and Laue photographs. The crystal is found not to be holohedral; its space-group symmetry is C_{4h}^6. There are four molecules in a unit having $d_{100} = 5.322$ and $d_{001} = 11.93$ Å. The sodium and iodine atoms are in the no-parameter positions (a) and (b), respectively (see text); the oxygen atoms are all equivalent and in the general three-parameter positions (f).

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