oxygen to participate in the formation of diamagnetic complexes. On the other hand, bonding with active coördinated groups containing the elements sulfur, nitrogen and carbon is expected to produce complexes of low paramagnetic susceptibility. An example of the latter is the ferricyanide ion.

The striking color changes which occur upon varying the hydrogen ion concentration are not uncommon for ionic complexes. Similar color changes occur with ferric tartrate complexes.[7] The latter are yellow at low *p*H values and green at high *p*H values. These abrupt color changes at a definite *p*H might be attributed to a replacement on the ferric ion of an active group of the organic complexing agent by a water molecule.

The tendency of the iron complexes, formally studied in this work, to form ferric ions and pyrocatechol disulfonate ions must be very slight for the extreme stability of them has been pointed out by Yoe and Jones.[1a] This is no anomaly for ionic complexes since the ferric fluoride complex, $FeF_6^{\equiv}$, is known to be quite stable. The ferric tartrate complex, $Fe_2(C_4H_4O_6)_3$, showing ionic bonding,[8] has an equilibrium constant of an extremely low value, 10^{-75}.[9] An indication of the order of stability of these iron complex ions is presented in the paper by Yoe and Jones.[1a] They found that the iron complex formed in basic solution by ferric ion and disodium 1,2-dihydroxybenzene-3,5-disulfonate is more stable than the fluoride, oxalate, and tartrate complexes of iron in basic solution; in acid solutions, the results were just the opposite.

In view of the preceding data, assuming that ionic bonds lie at the largest possible angle from one another, it seems likely that the configuration of the red iron complex, $Na_3[Fe(C_6H_2(SO_3Na)_2O_2)_3]$, is ionic octahedral in structure with all the oxygen atoms equivalent. Since the complex $Fe(H_2O)_6^{+++}$ is known to be ionic, possibly the iron in the violet complex maintains a coördination number of six by having one molecule of water replace an active group of the substituted pyrocatechol. This seems even more likely to be true when one recalls that a coördination number of five does not produce a system of high stability, generally speaking, and that such systems are usually covalent ones. Even in the case where a coördination number of four is suggested, that of the blue complex between iron and pyrocatechol disulfonate, there may actually be two ion-dipole bonds existing between ferric ion and two molecules of water, again giving iron a coördination number of six. Weinland and Seuffert[10] have analyzed 2,5-dihydroxynaphthalene ferriate salts, $[Fe(C_{10}H_6O_2)_2]^-$, and have concluded that in these cases iron has a coördination number of four. However, in all but one case their analyses show sufficient water present to satisfy a coördination number of six for iron, assuming two water molecules form ion-dipole bonds with the iron.

Summary

1. Magnetic studies show that iron apparently has five unpaired electrons when in the form of the three complexes studied.
2. This information leads to the conclusion that the bonding is essentially of the ionic type, since the ferric ion is known to have the same number of unpaired electrons.
3. The probability of iron maintaining a coördination number of six is discussed.
4. A consideration of an octahedral structure for the complexes is given.

CLEVELAND, OHIO RECEIVED FEBRUARY 14, 1947

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(7) Franke, *Ann.*, **486**, 282–284 (1931).

(8) Welo, *Phil. Mag.*, **6**, 481–509 (1928).

(9) Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice Hall, Inc., New York, N. Y., 1938, p. 213.

(10) Weinland and Seuffert, *Arch. Pharm.*, **266**, 455–464 (1928).

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF TECHNICAL AND ECONOMICAL SCIENCE, BUDAPEST, HUNGARY]

The Crystal Structure of Sodium Iodate

BY I. NÁRAY-SZABÓ AND J. NEUGEBAUER

Sodium iodate crystallizes according to Eakle[1] in the holohedral class of the orthorhombic system with the axial ratio $a:b:c = 0.9046:1:1.2815$. Its density determined by Kremers[2] and Ditte[3] is $d = 4.277$ and 4.252 g./cc., respectively.

In the course of our systematic examination of the perovskite structure family,[4,5] we examined this compound in order to complete the series of these "sister structures" as defined by one of us.

Zachariasen[6] has studied the lattice of sodium iodate by the aid of powder diagrams; his results were: cell dimensions, $a = 5.75$ Å., $b = 6.37$ Å., $c = 4.05$ Å.; therefore, $a:b:c = 0.903:1:0.636$. Accordingly the ratio $b:c$ of Eakle should be halved. In this unit cell two formula weights of sodium iodate are contained, with a calculated density $d = 4.40$ g./cc. Twenty-six reflections

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(1) Eakle, *Z. Krist.*, **26**, 565 (1896).

(2) Kremers, *Ann.*, **99**, 435 (1856).

(3) Ditte, Thesis, Paris (1870).

(4) I. Náray-Szabó, *Naturwissenschaften*, **31**, 202 (1943); *Matematik. Természcetud. Értesito*, **61**, 913 (1942).

(5) I. Náray-Szabó, *Naturwissenschaften*, **31**, 466 (1943).

(6) Zachariasen, "Untersuchungen über die Kristallstruktur von Sesquioxyden und Verbindungen ABO_3," Oslo, 1928.

only have been observed and from these space group V_h^{19}—Cmmm follows.

The structure deduced from these data shows some unusual features. Iodine ions are stated to have eight neighbors at a distance of 2.95 Å., two at 2.87 Å. and two at 3.18 Å.; these together give a distorted 12-coördination for them. Such has never before been found for pentavalent cations. On the other hand, sodium has in this structure six neighbors, four at 2.15 Å. and two at 2.03 Å. The lattice is characterized as an "anti-perovskite structure." It is not likely, however, that sodium should have smaller radii than the highly charged iodine ions; and the distance sodium–oxygen is also too small, since the sum of the normal radii of sodium and oxygen amounts to 2.30 Å.

We made a careful redetermination of this structure by means of single crystal oscillation diagrams. Suitable crystals of sodium iodate were obtained by evaporation of a solution at about 100°; they were not hygroscopic at all. Their habit was tabular after (001). For the production of reliable intensity data we formed a prism of quadratic cross-section by protracted grinding from a good specimen; its long edge was (010).

Oscillation diagrams about the crystallographic axes gave the following edges for the unit cell: a = 5.75 Å., b = 6.37 Å., c = 8.10 Å.; $a:b:c$ = 0.903:1:1.272. The cell contains four sodium iodate formula weights. Layer lines with weak reflections only appeared and showed that the c axis of Zachariasen must be doubled, therefore Eakle's axial ratio is very nearly correct.

Table I shows all reflections found up to sin δ = 0.480. No reflection ($0kl$) appears if k is odd, nor ($h0l$) if ($h + l$) is odd. The space group is therefore V_h^{16}—Pbnm. Reflections with ($h + k$) odd do appear, although they are very weak, so the space group V_h^{19}—Cmmm adopted by Zachariasen is incorrect.

Our space group V_h^{16}—Pbnm contains these positions

a. 000, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
b. $\frac{1}{2}00$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$
c. $\pm(x. y, \frac{1}{4})$; $(\frac{1}{2} + x, \frac{1}{2} - y, {}^3/_4)$
d. $\pm(x, y, z)$; $(\frac{1}{2} - x, \frac{1}{2} + y, z)$; $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$; $(x, y, \frac{1}{2} - z)$

There are four Na^+, four I^{5+} and twelve $O^=$ ions in our cell. Sodium and iodine ions can be placed in special positions only. An important feature of intensities is that only reflections with ($h + k + l$) even and l even are strong, therefore the strongly scattering iodine ions are near to x = 0 or $\frac{1}{2}$ and y = 0 or $\frac{1}{2}$. They can not lie, however, at the positions (a) or (b) since then their contribution to (501) and (521), for example, would be zero, although these reflections manifest themselves clearly and the contribution of oxygens is small owing to the high glancing angle.[7] We get a good agreement for reflections of high glancing angles for which sodium and oxygen contributions can be neglected if we choose x = 0.01 and y = 0.01 for iodine. All reflections with l odd are weak; the structure factor shows that z must be nearly zero or 0.25 for strongly scattering ions. Iodine ions are consequently on the reflection planes with z = 0.25. Sodium ions will be as far from them as possible, *i. e.*, at position (b). As a matter of fact (006) is not maximally strong, because sodium is working against iodine in this case.

TABLE I

ESTIMATED INTENSITIES AND CALCULATED F-VALUES OF SODIUM IODATE SINGLE CRYSTAL REFLECTIONS (CuKα)

sin δ	hk'	Intensity	F
0.164	101	0	+ 1
.180	110	10	+159
.189	002	10	−132
.204	111	1–2	− 12
.242	020	10[a]	+201
.260	021	9[b]	− 53
.261	112	10	−181
.268	200	10	+199
.277	120	$^1/_2$	− 11
.292	121	0	+ 4
.294	210	1–2	− 39
.307	022	10	−169
.309	211	3	− 44
.316	103	2	+ 47
.328	202	5	−127
.336	122	2–3	− 34
.338	113	0	− 13
.351	212	0	− 19
.360	220	9	+177
.374	221	0	− 14
.374	023	$^1/_2$	+ 12
.379	004	10	+214
.387	130	9	+101
.397	123	$^1/_2$	+ 10
.399	131	2	− 21
.409	222	5	−121
.409	213	0	+ 21
.413	301	3	− 30
.420	310	5	+122
.421	114	5	−121
.431	132	9	−148
.442	311	0	− 11
.449	024	8	+163
.451	230	$^1/_2$	− 8
.460	223	0	+ 13
.461	312	7	−181
.462	231	0	− 11
.466	204	8	+163
.469	320	1	− 22
.471	124	$^1/_2$	+ 4
.478	321	$^1/_2$	− 23
.480	040	6	+139

[a] From powder diagram. [b] Innermost reflection of oscillation diagram, overexposed.

This placement of cations gives a rather good agreement of calculated and observed intensities

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[7] Jonic F values of Zachariasen[6] were used in the calculations.

for the strong reflections, if the glancing angle is not too small, since the oxygen contribution is not considerable for these. But there appear also reflections with $h + k + l$ odd or l odd; in this case sodium contribution is zero and iodine contributes but very slightly, so that it is the oxygens which are mainly determining the F value. Such reflections give the possibility of correct placement of oxygen ions. Twelve $O^=$ ions can be distributed in the following ways: (1) 4 at (a) and 4 + 4 at (c) with different x and y coördinates; (2), 4 at (a) and 8 at (d); (3), 4 at (c) and 8 at (d). Position (b) is already occupied by Na^+ ions.

Case (2) is to be excluded since there is hardly place for two oxygens and two iodine ions on the c axis. Besides, it would give no good agreement for (101) and other reflections. Case (2) can be also excluded by intensities and by geometrical considerations, so that only case (3) remains.

Coördinate ranges for oxygens are restricted by the placing of four Na^+ ions at (b), the minimum sodium–oxygen distance being about 2.2 Å., moreover by the adoption of a minimal iodine–oxygen distance of about 1.9 Å. (the value of Al–O distance) and lastly by the presence of mirror planes parallel to the c face, which means that no oxygen can come nearer than 1.3 Å. to these planes if it is not lying on them.

Parameter values have been systematically varied and the corresponding intensities calculated. From over a hundred combinations only one gives a satisfactory agreement between observed and calculated intensities, where oxygen contribution is considerable. In that way we arrived at a structure which contains no assumptions and is based only on the amply established ionic radii of $O^=$ and Na^+.

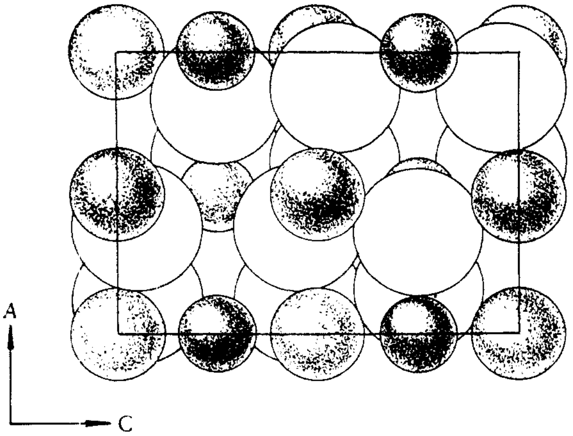

Fig. 1.—The structure of sodium iodate viewed along the b axis: large circles represent oxygen ions; medium sized spheres, sodium ions; and small spheres, iodine ions. The ions lying lower are lighter shaded.

Our final coördinates are

$4Na^+$ at (b)	$\frac{1}{2}00$
$4I^{5+}$ at (c)	$xy\frac{1}{4}$, with $x = 0.01$, $y = 0.01$
$4O^=$ at (c)	$xy\frac{1}{4}$, with $x = 0.656$, $y = 0.080$
$8O^=$ at (d)	xyz, with $x = 0.122$, $y = 0.165$, $z = 0.043$

Figure 1 shows the structure viewed along the b axis. There are definite IO_3 groups in this structure, with a very nearly equilateral triangular base. They can be described as regular tetrahedral of oxygen ions with an iodine at the center and with an oxygen removed. The other neighboring oxygens are much farther apart—together with the former ones they give a strongly deformed octahedral coördination for the pentavalent iodine. An "ionic radius" of about 0.75 Å. can be deduced for the latter, but probably the iodine–oxygen bond is—to some extent, at any rate—homopolar. In the lithium iodate lattice I^{5+} has six oxygen neighbors at the distance of 2.23 Å. which form a nearly regular octahedron.[8] The oxygen parameter of this structure type is, however, not exactly determined, and it is very possible that with a slight modification of it the same result, *i. e.*, IO_3 radicals with an equilateral triangle of oxygens, will come out. Aqueous solutions of iodates undoubtedly contain IO_3^- ions, migrating to the anode if the solution is electrolyzed. Our structure analysis confirms the preformation of these radicals in the lattice.

The following distances of ions in the lattice were found

I–O	2.05 Å. (2 neighbors)
	2.08 Å. (1 neighbor)
	2.89 Å. (1 neighbor)
	3.48 Å. (2 neighbors)
Na–O	2.27 Å. (4 neighbors)
	2.44 Å. (2 neighbors)
Na–I	3.48 Å.
O–O	3.16, 3.35, 3.51, 3.55 Å.

Compared with the perovskite structure we see that to a certain extent sodium iodate forms mixed crystals with ammonium iodate, which belongs undoubtedly to the pervoskite family, although details of its structure are not yet known. But the structure arrived at by us is a G-type since it contains distinct IO_3 radicals. There is an interesting transition from an E-type (perovskite) to a G-type. From the type of perovskite E 2_1 with small cubic cell (a = 3.94 Å.) an orthorhombic unit may be formed if we choose a cell turned with 45° and a doubled c-axis, when $a = b = 5.56$ Å., $c = 7.88$ Å. (taking the sodium columbate, $NaCbO_3$, cell for comparison); the axial ratio of this cell is 1:1:1.414. Sodium columbate was stated to belong to the type E 2_1 (formerly called G 5); the considerable difference of b (5.56 Å. against 6.37 Å. in sodium iodate) and to a smaller degree of c (7.88 Å. against 8.10 Å. in sodium iodate) is the consequence of a change in the structure type. Sodium iodate does not belong to the perovskite family, in spite of the similarity, which

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(8) Zachariasen and Barta, *Phys. Rev.*, **37**, 1626 (1931).

is expressed in the following positions:

	Perovskite (large) cell	"Anti-perovskite" cell (Zachariasen)	Present structure cell
4Na	$\frac{1}{2}00$ (12 neighbors)	$\frac{1}{2}00$ (6 neighbors)	$\frac{1}{2}00$ (6 neighbors)
4I	$00\frac{1}{4}$ (6 neighbors)	$00\frac{1}{4}$ (12 neighbors)	0.01, 0.01 $\frac{1}{4}$ (3 + 2 + 1 neighbors)
4O	000	$\frac{1}{2}0\frac{1}{4}$	0.656, 0.08, $\frac{1}{4}$
8O	$\frac{1}{4}\frac{1}{4}\frac{1}{4}$	$\frac{1}{4}\frac{1}{4}0$	0.122, 0.165, 0.043

It is interesting to compare the dimensions of XO_3 groups in chlorates, bromates and sodium iodate

	Halogen–oxygen, Å.	Oxygen–oxygen, Å.	Regular tetrahedral radical, Å.
$KClO_3$	1.42	2.33 2.48	2.33
$KBrO_3$	1.68	2.73	2.73
$NaIO_3$	2.05 2.08	3.35 3.55	3.35

Summary

Sodium iodate, $NaIO_3$, has an orthorhombic lattice with space group V_h^{16}—Pbnm, a = 5.75 Å., b = 6.37 Å., c = 8.10 Å., z = 4. The structure has been completely determined by the aid of oscillation diagrams. It contains distinct IO_3 radicals with iodine–oxygen distance 2.05 and 2.08 Å., respectively. For parameter values see the text.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Function of Fluxes in the Preparation of Infrared Sensitive Phosphors of the Alkaline Earth Sulfides and Selenides[1,2]

BY WILLIAM PRIMAK,[3] R. KEITH OSTERHELD AND ROLAND WARD

The development of infrared-sensitive phosphors with remarkable capacities for energy storage has been described in a cursory manner elsewhere.[4] A more detailed description of the properties of these phosphors has been given by Urbach[5] who shows the relationship of the infrared-sensitive phosphors to the Lenard phosphors.

The empirical methods used by Lenard and adapted by Urbach to the preparation of infrared sensitive phosphors lead to products of rather uncertain composition.[5,6] The alkaline earth sulfides were prepared in this process by the reaction of the carbonate with sulfur at 1000 to 1100°. A mixture of sulfide with about 30% sul-

$$4MCO_3 + S \longrightarrow 3MS + MSO_4 + 4CO_2$$

fate and smaller amounts of carbonate and oxide was obtained. To this about 6% of a fluxing agent such as calcium fluoride or lithium fluoride containing activators was added along with additional quantities of sulfur. This mixture was again heated at 900 to 1000°. The luminescent properties of materials prepared in this way were subject to wide variations which apparently depended upon the heating cycles and upon the atmosphere to which the samples were exposed at high temperatures.

Strontium sulfide was prepared by the method of Tiede[7] or by heating the carbonate or sulfate in hydrogen sulfide so that it was substantially free from sulfate. The activators, samarium and europium, and the flux, calcium fluoride, were added to this preparation and the mixture was heated at 1000° in nitrogen saturated with carbon disulfide. The product had rather low infrared sensitivity. Subsequent addition of about 6 weight per cent. of strontium sulfate and reheating, however, increased the sensitivity.[5]

To arrive at a better understanding of the fluxing process so that more reproducible phosphors could be obtained, the composition of the flux and its interaction with the base material were studied in some detail. While this investigation was going on, another phosphor, SrSe(Sm,Eu) was developed,[4] the properties of which will be given in a subsequent article.[8] The fluxing of the selenide phosphor was also studied. In this paper attention is directed mainly to the physical and chemical action of the fluxes. The luminescent characteristics of the products are described only to show their dependence on the changes in base material.

Experimental

Pure strontium sulfide was prepared by complete reduction of strontium sulfate with hydrogen. Mixtures of this with either strontium sulfate or calcium fluoride when heated at 1000° showed no evidence of fusion but a mixture of all three substances, when similarly treated, appeared to have been partly fused. It seems obvious, therefore, that the mixture of calcium fluoride and strontium sulfate was acting as a flux.

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[1] This paper is based on work done for the Office of Scientific Research and Development under contract No. OEMsr 982 with the Polytechnic Institute of Brooklyn.

[2] Abstracted from part of a thesis submitted by William Primak in partial fulfilment of the degree of Doctor of Philosophy to the Graduate School of the Polytechnic Institute of Brooklyn, 1946.

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[4] Proceedings Winter Meeting of Optical Society, session on infrared sensitive phosphors, *J. Optical Soc. Am.*, **36**, 351 (1946).

[5] F. Urbach, D. Pearlman and H. Hemmendinger, *J. Optical Soc. Am.*, **36**, 372 (1946).

[6] N. Riehl, "Physik und technische Anwendung der Lumineszenz," J. Springer, Berlin, 1941.

[7] E. Tiede and F. Richter, *Ber.*, **55B**, 69 (1922).

[8] A. L. Smith, R. D. Rosenstein and R. Ward, paper in preparation.