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The Crystal Structure of Neodymium Bromate Enneahydrate, $\text{Nd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$

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Introduction

The structure of neodymium bromate enneahydrate has been determined with the purpose of establishing the nature of the coordination of water molecules about the rare earth ion, and of determining the dimensions of the bromate group.

It has been found that all nine of the water molecules are coordinated about the neodymium ion, as suggested by the work of Ketelaar¹ in his study of the rare earth ethyl sulfates and also by the existence of the compound $\text{NdCl}_3 \cdot 9\text{H}_2\text{O}$. The determination of the space group fixes the minimum symmetry of the environment of the Nd ion as C_{3v} and a determination of the parameters involved in the structure indicates that the immediate environment (that of the coordinated water molecules) has approximately the symmetry D_{3h} .

The limits of error which must be attributed to the determination of the configuration of the bromate group are so large that the second object of this work can scarcely be said to have been achieved. However, the Br-O distance found, $1.74 \pm 0.07 \text{ \AA}$., lends support to the results of the recent investigation of Hamilton² on sodium bromate and indicates that the interatomic distance is larger than has been reported in previous work.

The consideration of the nature of the structure and the existence of some intensity discrepancies lead fairly directly to the conclusion that a certain degree of randomness exists in the crystal. The intensities as well as the result of a pyroelectric experiment indicated that this randomness cannot be complete.

Preparation of Crystals.—Single crystals of $\text{Nd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ were prepared by adding hot barium bromate solution to neodymium sulfate, filtering, and allowing the resulting solution to evaporate slowly. $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ was obtained by treating crude commercial neodymium oxalate with sulfuric acid and crystallizing several times. Unquestionably this preparation did not yield samples of great purity, but since the rare earth bromates are isomorphous, and so presumably have the same structure, it was felt that the pres-

ence of some rare earth impurity would not materially influence the structure determination.

This preparation yielded chiefly fine pink hexagonal prisms showing prominent (10·0) faces and usually terminated by (10·1) faces. The interfacial angle (10·0):(10·1) was $56^\circ 45'$, giving an axial ratio $a:c = 1.74$.

The crystals occasionally grew in prisms as large as $4 \times 4 \times 10 \text{ mm}$. They were quite stable in air and melted at 68° . The melting point reported by James and Langelier³ is 66.7° . The density of the sample was found to be 2.79 g./cc. at 20° .

Space Group and Unit Cell.—Laue photographs taken with the X-ray beam normal and parallel to the c -axis showed that the crystal possesses the Laue symmetry D_{6h} . The regular absence of reflections from the planes ($h\bar{h}l$) with l odd was observed. These data limit the choice of space groups to three: D_{6h}^4 , D_{3h}^4 and C_{6v}^4 . As mentioned previously a pyroelectric experiment showed the c -axis to be polar, thus eliminating the first two possibilities and establishing the space group as $C_{6v}^4 - C6mc$.

The size of the unit cell was found from ($h0\cdot0$) and ($00\cdot l$) reflections to be

$$\begin{aligned} a_0 &= 11.73 \pm 0.02 \text{ \AA} \\ c_0 &= 6.76 \pm 0.02 \text{ \AA} \\ a:c &= 1.736:1 \end{aligned}$$

The data giving these results are found in Table I.

The size of the unit cell and the observed density lead to the number of molecules in the unit $1.98 \approx 2$.

Determination of the Structure.—The atoms may be placed in the unit cell with space group C_{6v}^4 in the following sets of equivalent positions⁴

- 2 a) $00x, 00, x + \frac{1}{2}$
 2 b) $\frac{1}{2}\frac{1}{2}z, \frac{3}{2}\frac{1}{2}z + \frac{1}{2}$
 6 c) $x\bar{x}z; x, 2x, z; 2\bar{x}, \bar{x}z; \bar{x}, xz + \frac{1}{2}; \bar{x}2\bar{x}, z + \frac{1}{2}; 2xx, z + \frac{1}{2}$
 12 d) $xyz; \bar{y}, x - y, z; y - x, \bar{x}z; \bar{x}\bar{y}, \frac{1}{2} + z; y, y - x, \frac{1}{2} + z; x - y, x, \frac{1}{2} + z; \bar{y}xz; x, x - y, z; y - x, y, z; y, x, \frac{1}{2} + z; \bar{z}, y - x, \frac{1}{2} + z; x - y, \bar{y}, \frac{1}{2} + z$.

The two neodymium ions were assigned to the positions 2b with the parameter z arbitrarily given the value 0.25. The choice of positions 2a may be

(1) J. A. A. Ketelaar, *Physica*, **4**, 619 (1937).

(2) Jane E. Hamilton, *Z. Krist.*, **100**, 104 (1938).

(3) James and Langelier, *THIS JOURNAL*, **31**, 913 (1909).

(4) "Int. Tab. Bestimmung Kristallstrukturen."

TABLE I

(<i>h</i> 0·0)	sin θ	<i>d</i> _{obsd.} , Å.	<i>d</i> _{calcd.} , Å.	<i>a</i> ₀ , Å.
(10·0)	0.0761	10.11	10.16	11.73
(20·0)	.1516	5.076	5.080	11.72
(30·0)	.2265	3.397	3.387	11.77
(40·0)	.3031	2.539	2.540	11.73
(50·0)	.3783	2.032	2.032	11.73
(60·0)	.4535	1.697	1.695	11.75
(70·0)	.5285	1.456	1.453	11.74
(80·0)	.6040	1.274	1.271	11.74
(90·0)	.6797	1.132	1.131	11.75
(100·0)	.7541	1.020	1.017	11.74
Average				11.74
(00· <i>l</i>)				<i>a</i> ₀
(00·2)	0.2276			6.76
(00·4)	.4559			6.75
(00·6)	.6842	1.125	1.126	6.75
(00·8)	α_1 .9100	0.8447	0.8450	6.76
	α_2 .9123	.8447		
Average				6.755

eliminated since it would lead to an unreasonable distribution of the highly positive ions. It may also be noted that for the positions 2a the contribution of the neodymium atoms to the intensity of reflections from planes of the type (*hkl*) with *l* odd would be zero and so these reflections would in general be weaker than those with *l* even. This is not observed.

The six bromine atoms were placed in the six-fold positions 6c and the positions of the thirty-six oxygen atoms were assigned on the basis of a two-dimensional Fourier projection as will be shown later.

The experimental intensities used in the structure determination were obtained from oscillation photographs taken with CuK α radiation. A fine needle-like prism of neodymium bromate approximately 0.05 mm. in diameter was used.⁵ Photographs of different exposure times were taken and the relative intensities determined visually by comparing reflections of equal intensity and varying exposure times in the usual way.

The influence of absorption was neglected and this unquestionably has led to some error. The observed intensities do not fall off as rapidly with increasing sin θ as those calculated, an effect which would be anticipated with absorption neglected.

The intensities given in Tables II and III were calculated using the expression

$$I^{\frac{1}{2}} = C \left(\frac{1 + \cos^2 2\theta}{\sin 2\theta} \right)^{\frac{1}{2}} |S| e^{-\beta(\sin \theta/\lambda)^2}$$

(5) The photographs used to obtain the data for large values of *l* (Table II) were obtained by reflecting CuK α radiation from the end of a relatively large prism and for these intensities only qualitative comparisons are of significance since the intensities are uncorrected for absorption and for the differing fractions of the beam effective in producing the reflection.

where $|S|$ is the absolute value of the structure factor, $e^{-\beta(\sin \theta/\lambda)^2}$ the temperature factor with β

TABLE II

(<i>hkl</i>)	Calcd.	<i>I</i> ^{1/2} Obsd.	(<i>hkl</i>)	Calcd.	<i>I</i> ^{1/2} Obsd.
(10·0)	+ 40	45	(73·0)	- 77	79
(11·0)	+147	164	(90·0)	+ 66	74
(20·0)	+305	306	(82·0)	+ 8	0
(21·0)	-195	193	(65·0)	+ 8	0
(30·0)	- 5	34	(91·0)	- 41	45
(22·0)	+222	227	(74·0)	+ 18	32
(31·0)	+ 1	21	(83·0)	- 30	36
(40·0)	-238	268	(10,0·0)	- 46	45
(32·0)	+ 80	64	(92·0)	- 40	36
(41·0)	+ 76	78	(86·0)	+ 45	55
(50·0)	-112	121	(75·0)	- 15	32
(33·0)	+338	334	(10,1·0)	+ 40	43
(42·0)	+ 20	25	(84·0)	- 39	43
(51·0)	- 93	111	(93·0)	+ 47	53
(60·0)	+ 14	23	(11,0·0)	- 50	50
(43·0)	- 80	76	(10,2·0)	+ 21	25
(52·0)	+ 42	55	(76·0)	- 40	40
(61·0)	- 55	52	(85·0)	+ 7	0
(44·0)	+ 73	54	(11,1·0)	- 15	0
(70·0)	+ 61	61	(94·0)	- 22	0
(53·0)	-119	116	(10,3·0)	+ 40	45
(62·0)	- 69	52	(12,0·0)	+ 14	29
(71·0)	+112	121	(77·0)	+ 81	100
(54·0)	+ 11	16	(11,2·0)	+ 97	127
(63·0)	+ 9	25	(86·0)	- 34	45
(80·0)	+ 36	43	(95·0)	- 43	52
(72·0)	- 31	45	(10,4·0)	+ 49	56
(81·0)	+ 16	0	(12,1·0)	- 45	56
(55·0)	+140	148	(11,3·0)	- 2	0
(64·0)	+ 13	0	(13,0·0)	- 88	91

	<i>I</i> ^{1/2} , <i>l</i> = 1		<i>I</i> ^{1/2} , <i>l</i> = 2		Obsd.	
	Random	Polar	Obsd. Random	Polar		
(20· <i>l</i>)	514	514	522	312	314	321
(21· <i>l</i>)	13	55	33	69	72	72
(30· <i>l</i>)	261	276	305	163	165	126
(22· <i>l</i>)	255	258	214
(31· <i>l</i>)	128	134	128	127	127	114
(40· <i>l</i>)	89	93	91	78	79	64
(32· <i>l</i>)	178	178	187	71	79	71
(41· <i>l</i>)	75	75	75	105	105	111
(50· <i>l</i>)	12	29	0	137	139	136
(33· <i>l</i>)	157	160	136
(42· <i>l</i>)	101	101	91	9	10	0
(51· <i>l</i>)	121	123	121	83	84	72
(60· <i>l</i>)	112	115	116	67	67	56
(43· <i>l</i>)	5	10	0	64	66	55
(52· <i>l</i>)	97	97	87	1	13	0
(61· <i>l</i>)	63	67	62	5	5	0
(44· <i>l</i>)	7	11	0
(70· <i>l</i>)	51	53	74	4	20	0
(53· <i>l</i>)	143	147	137	84	85	72
(62· <i>l</i>)	1	12	0	56	56	46
(71· <i>l</i>)	21	21	23	130	130	112
(54· <i>l</i>)	27	27	27	30	31	0
(63· <i>l</i>)	9	19	0	10	10	0

TABLE III

(hkl)	$I^{\frac{1}{2}}$ Obsd.	$I^{\frac{1}{2}}$ (Partially random)	$I^{\frac{1}{2}}$ (Polar)	$I^{\frac{1}{2}}$ (Complete random)
(10·3)	75	75.5	75.5	76
4	20	12	35	1
5	59	47.5	49	47.5
6	0.0	7.6	20.5	4
7	51	25	26	25
8	20	13	29	8
(20·3)	198	222	223	222
4	104	87	90	86
5	118	109	119	108
6	79	56	59	55
7	79	66	72	65
8	47	40	35	34
(30·3)	114	146	147	146
4	40	16	35	14
5	79	57	77	55
6	63	41	46	40
7	55	47	56	46
8	51	28	39	25
(40·3)
4	102	95	96	95
5	51	31	31	31
6	39	29	32	28
7	47	31	33	31
8	63	51	56	50
(50·5)	0	13	41	2
6	75	48	52	47
7	31	17	42	9
(60·5)	44	43	52	42
6	55	35	35	35
7	28	43	54	43

set equal to 1.5. The atomic f -values were taken from the tables of Pauling and Sherman.⁶

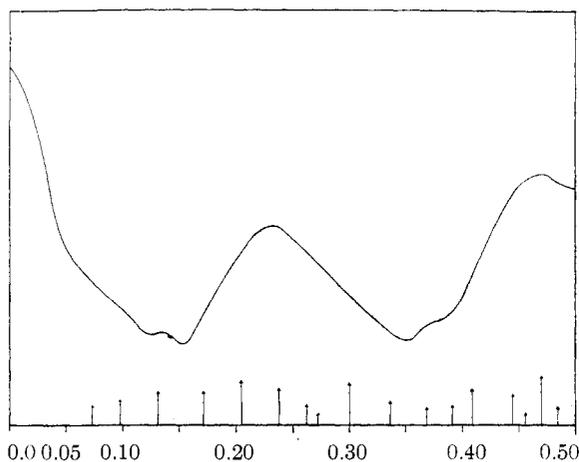


Fig. 1.

An approximate value for the Br x -parameter was found as the first step in the structure deter-

(6) Pauling and Sherman, *Z. Krist.*, **81**, 1 (1932).

mination. For this purpose a one-dimensional Patterson projection was made on the line [12.0] using the thirteen available $F^2_{(h0\cdot0)}$'s. This projection, shown in Fig. 1, may be accounted for qualitatively by the assumption of a value of the bromine parameter in the neighborhood of $x = 0.12$. The components of the various interatomic distances parallel to (10·0) in the final structure are shown in Fig. 1 by vertical arrows, the height of the arrows indicating the weight to be attached to each interatomic distance.

By a consideration of the intensities of reflection from planes of the type $(hh\cdot0)$ it was further possible to establish $x = 0.12$ as a lower limit for the parameter in question.

With a knowledge of the bromine parameter x , it was possible to calculate the signs of the F 's for most of the reflections from the prism planes. A two-dimensional Fourier projection on the basal plane was then made using this information. This projection gave approximate values for the oxygen parameters and thus permitted the calculation of the signs for all but a few of the very weak reflections. A second projection was then made including these new terms.

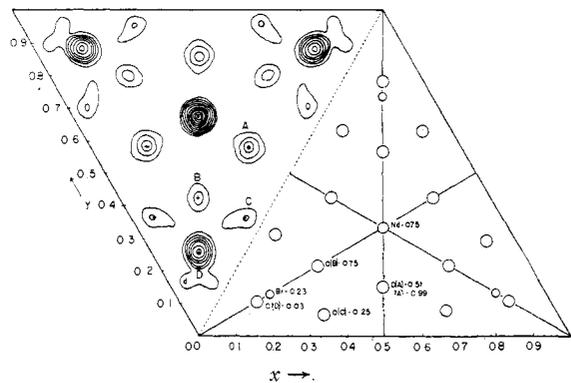


Fig. 2.

This process was repeated again to give the final projection shown in Fig. 2. The crosses mark the positions assigned to the atoms in the final structure, determined by varying the parameters slightly in order to obtain the best fit with the experimental intensities.

The right-hand half of the figure shows the positions of the atoms in the projection with the z -parameter given after the letter designating the particular atom shown. A plane of symmetry *in the projection* is shown by a dotted line. Planes of symmetry *in the crystal* are shown by full lines in this half of the cell.

The projection shows large maxima of the right relative magnitudes at positions assumed for bromine and neodymium. Three maxima, designated by A, distinctly larger than those remaining, appear at the corners of an equilateral triangle of which the neodymium ion is the center. At a somewhat greater distance from the neodymium ions in the projection three smaller maxima B occur at the corners of an equilateral triangle turned through 180° from the first.

The magnitudes of these maxima A and B correspond to two and one oxygen atoms, respectively. A consideration of the components of interatomic distances given by the projection makes it clear that the oxygen atoms A must be associated with the neodymium ion. From the position of two of the bromate oxygen atoms which may be identified with the maxima C and that of oxygen B it can be seen that for no value of the z -parameters of the oxygen atom at B can this atom be considered to belong to the bromate group.

The conclusion must be that all these oxygen atoms A and B correspond to water molecules coordinated about the neodymium ion as shown in Fig. 3, that the strong maxima A correspond to two oxygen atoms (superimposed in the projection) at the corners of a triangular prism, and that the maxima B correspond to oxygen atoms located out from the prism faces. The fact that the Nd-O separation from Nd to O (B) is nearly the sum of the ionic radii with some correction for coordination number lends support to this view.

This analysis of the Fourier projection leads to the assignment of the oxygen atoms (water molecules) to the six-fold set of positions for the space group C_{6v}^4 in the following way

- A $6\text{H}_2\text{O}$ at $x\bar{x}z$, etc.
- A' $6\text{H}_2\text{O}$ at $x'\bar{x}'z'$, etc.
- B $6\text{H}_2\text{O}$ at $x''\bar{x}''z''$, etc.

The parameter values satisfy the relations $x = x'$, $z = \frac{1}{2} - z'$, $z'' = \frac{1}{4}$ if the coordination polyhedron suggested above is correct. Other evidence supporting this conclusion will be brought forward later.

Two of the three bromate oxygen atoms appear very definitely at the positions C. These atoms readily may be assigned to the twelve-fold positions of C_{6v}^4 . The slight asymmetry of the bromine maximum suggests that the third bromate oxygen D lies above (or below) the bromine atom in the same plane of symmetry and may be assigned to

the six-fold set of positions for C_{6v}^4 with a parameter $x \approx 0.10$.

The maxima d are felt to be spurious and due to the incompleteness of the data. The positions of these maxima cannot correspond to the positions of any atoms since if the space group determination is correct the symmetry plane which bisects the line connecting them would place the atoms only about 0.50 \AA . apart.

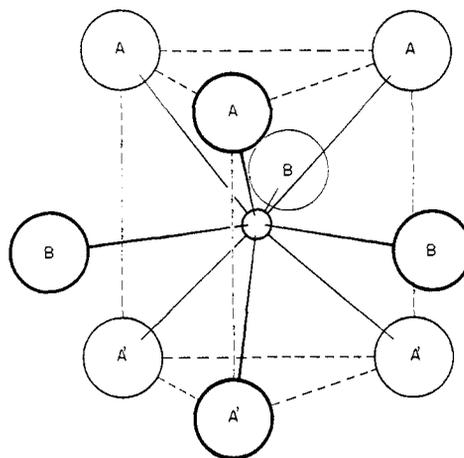


Fig. 3.

The determination of the z -parameters was begun by observing that the intensities of the reflections from $(hk-l)$, $(hk-l + 4)$, etc., show very nearly normal decline for l not too large, indicating that the atoms must lie very nearly in planes parallel to the basal plane at $z = 0, 0.25, 0.50$ and 0.75 . The fact that $I_{(00.2)} \approx I_{(00.4)}$ and $I_{(00.6)} \approx I_{(00.8)}$ shows that there must be a considerable concentration of scattering matter in the planes at $z = 0.0$ and 0.50 .

The z -parameters of certain of the oxygen atoms were fixed by the following structural arguments. If it is assumed that the nine Nd-OH₂ distances are equal (or approximately equal), the six molecules A and A' are calculated to have z -parameters very close to 0.50 and 0.0 . With the positions of these molecules fixed by this assumption and the x - and y -parameters of oxygen atoms C given by the Fourier projection, it follows that these bromate oxygen atoms C cannot lie far from the plane $z = 0.75$ without coming into too close contact with oxygens A. With $z = 0.75$ for these atoms C the interatomic distance O(A) - O(C) and O(A') - O(C) is 2.77 \AA ., which corresponds closely to a hydrogen-bonded contact. Any deviation from $z = 0.75$ leads to difference in length

of these hydrogen bonds and since there seems to be no physical reason for this and the intensities do not require such a deviation, the z -parameter for oxygen C has been assumed to be 0.75. The value of z for oxygen atoms A and A' has been determined from the intensity data after making the assumption that it must lie in the neighborhood of 0.50 (and 0.0). It will be seen that these structural arguments lead to positions for the oxygen atoms in agreement with the conclusions of the previous paragraph.

Intensity relationships among the reflections ($hk\cdot l$) eliminate the possibility that the parameter z for the bromine atom can vary more than two or three hundredths from 0.75. The final value for this parameter was arrived at on the basis of the intensities of reflection for large values of l , as will be discussed later. With the positions of two of the bromate oxygens established and the x -parameter of the third fixed, the assumption of a triangular pyramidal shape for the bromate group determines the z -parameter for the third. Since the peak ascribed to O(D) is not resolved, its x -parameter is not well determined and the values of x and z for O(D) were then found by varying these parameters to obtain the best fit with intensities.

The final parameter values are:

Nd	$x=0.333$	$y=0.666$	$z=0.25$
Br	$x=0.130 \pm 0.002$		$z=0.73 \pm 0.03 - 0.01$
O(A)	$x=0.425 \pm 0.01$		$z=0.49 \pm 0.01$
O(A')	$x=0.425 \pm 0.01$		$z=0.01 \pm 0.01$
O(B)	$x=0.215 \pm 0.01$		$z=0.25 \pm 0.01$
O(C)	$x=0.065 \pm 0.005$	$y=0.365 \pm 0.005$	$z=0.75 \pm 0.01$
O(D)	$x=0.105 \pm 0.01$		$z=0.53 \pm 0.03$

The square roots of the intensities calculated from these parameter values and those observed are found in Tables II and III. In Table II two

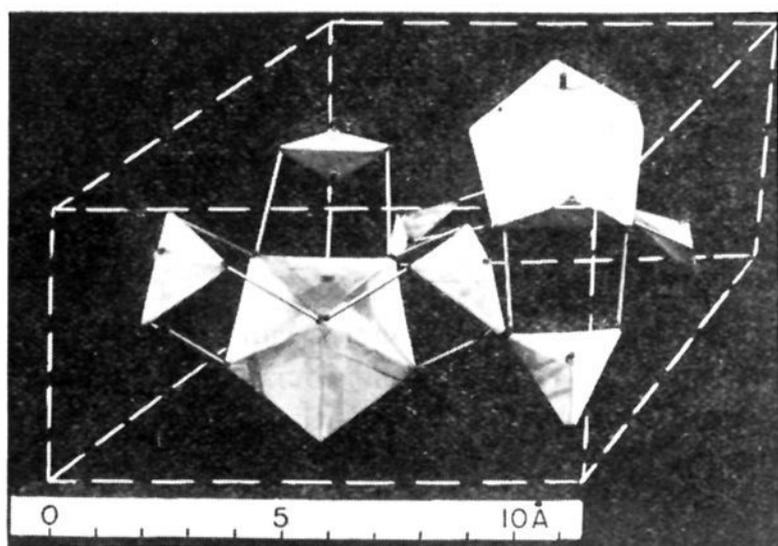


Fig. 4.

sets of calculated intensities are given for reflections with $l = 0$. The first column gives the intensity calculated for a completely random structure of a type to be discussed. In Table III calculated intensities are tabulated for the polar structure, for complete randomness, and for a structure with "one-third randomness."

The agreement is in general satisfactory. The fact that the calculated intensities fall off more rapidly with $\sin \theta$ than those observed may be attributed to neglect of the absorption factor.

The intensities given in Table III are uncorrected for absorption and the varying cross section of the crystal in the X-ray beam and are hence considered to have only qualitative significance.

Discussion of the Structure

The parameters given above lead to the structure shown in Fig. 4, in which the $\text{Nd}(\text{OH}_2)_9^{+++}$ group is indicated by the large fourteen-sided polyhedron with a Nd^{+++} ion at the center and a water molecule at each of the nine corners. The bromate groups are shown as flattened triangular pyramids. Probable hydrogen-bonded contacts as deduced from O-O separations are indicated by metal tubes connecting the bonded oxygen atoms.

1. The $\text{Nd}(\text{OH}_2)_9^{+++}$ Group.—The neodymium ions as shown in Fig. 3 are surrounded by nine water molecules: six at the corners of a trigonal prism at a distance $2.47 \pm 0.05 \text{ \AA}$. and three out from the prism faces at a distance $2.51 \pm 0.05 \text{ \AA}$. from the central ion. These distances are equal within the error of the determination, and they are seen to be somewhat larger than the sum of the ionic radii, approximately 2.35 \AA ., obtained from the structure of Nd_2O_3 .⁷ This increase in interatomic distance may be ascribed partially to an increase in coordination number and partially to the difference in the character of the bond.

The water molecules in positions A (and A') have five near oxygen neighbors: two A (or A') at $3.22 \pm 0.10 \text{ \AA}$.; two of type B at $2.72 \pm 0.10 \text{ \AA}$.; and one at A' (or A) at $3.25 \pm 0.10 \text{ \AA}$. The three water molecules at positions B have four near neighbors (types A and A') all at $2.72 \pm 0.10 \text{ \AA}$.

It can be seen that this arrangement of water molecules about the neodymium ion gives the group the approximate symmetry D_{3h} . It is true

(7) L. Pauling, *Z. Krist.*, **75**, 128 (1930).

that the parameters determining this arrangement have not been derived exclusively from the X-ray data; the intensity relationships and the nature of the structure, however, suggest no deviations from this symmetry. It is only the orientation of the bromate groups that destroys the symmetry D_{3h} for the environment of the neodymium ion in the crystal as a whole.

2. The Bromate Group.—As mentioned previously, the parameter determination is not accurate enough to give an entirely satisfactory description of the bromate group. A triangular pyramid has been assumed as the configuration of the group and the interatomic distances and angles given below were then found. The second column gives the corresponding values reported by Hamilton.

	Helmholz	Hamilton
Br-O, Å.	1.74 ± 0.07	1.78
O-O, Å.	2.75 ± 0.10	2.95
O-Br-O	105 ± 10°	112°

3. Hydrogen Bonds.—Each oxygen atom (water molecule) A and A' has two bromate oxygens C at a distance 2.77 ± 0.10 Å. from it, and it seems reasonable to place hydrogen bonds between these pairs of atoms. The oxygen atoms C belong to different bromate groups in the same plane parallel to the basal plane and are related to each other by a plane of symmetry, as can be seen in the right side of Fig. 2 and Fig. 4, where this distribution of hydrogen bonds is shown.

Each bromate oxygen C has two oxygen atoms of 2.77 Å., one of type A and one of type A'. These oxygens belong to different $\text{Nd}(\text{OH}_2)_9^{+++}$ groups, one above the other in a line parallel to the C-axis.

The location of the hydrogen bonds formed by the water molecule B is subject to considerable uncertainty because of the relatively large error in the determination of the position of bromate oxygen D. There are two possibilities which may be discussed. The interatomic distance O(B)-O(D) is 2.63 ± 0.20 Å., suggesting that both hydrogen atoms of water molecule B may be directed toward O(D), forming a strong bond. Within the limits of error of the determination another possibility exists: at 2.79 ± 0.10 Å. from the water molecule B and in the same plane parallel to the basal plane there lie two bromate oxygens of the type C to which two hydrogen bonds have been formed already as described above. It may

be that these bromate oxygen atoms C form three hydrogen bonds, one to A, one to A', and one to B, and that the bromate oxygen D forms none; in which case the interatomic distance O(B)-O(D) should be 2.63 ± 0.20 Å. The intensity data obtained in this work are not sufficiently accurate to decide this question.

The following hydrogen bond angles may be listed

Nd-OH ₂ (A)-O(C)	- 130 ± 10°
Nd-OH ₂ (B)-O(D)	- 150 ± 10°
Nd-OH ₂ (B)-O(C)	- 120 ± 5°
O(C)-OH ₂ (A)-O(C)	- 90 ± 10°

4. The Structure as a Whole and its Degree of Randomness.—The structure as a whole is seen to consist of vertical strings of $\text{Nd}(\text{OH}_2)_9^{+++}$ groups passing through the positions $\frac{1}{3} \frac{2}{3} 0$ and $\frac{2}{3} \frac{1}{3} 0$, and columns of bromate groups about a line parallel to the c-axis through the position $x = y = 0$. These vertical strings of hydrated cations are in relatively close contact, and fill a good part of the volume of the unit, but they leave holes about the line $x = y = 0$. The bromate groups fit into these holes in positions governed by the formation of hydrogen bonds as discussed above, and by the packing of the bromate oxygen atoms.

The closest approach of oxygen atoms in adjacent strings is 3.05 Å. The separation of the closest oxygen atoms of different $\text{Nd}(\text{OH}_2)_9^{+++}$ groups in the same string is 3.52 Å. The bromine atoms have in addition to the bromate oxygens two oxygen atoms of neighboring bromate groups at the distance 3.01 Å.

Inspection of the structure shows that if the bromine atoms and the oxygen atoms D were ignored there would exist horizontal planes of symmetry through the neodymium ions. It would seem possible then that the bromate group in entering the crystal could orient itself with the oxygen atom D pointing either up or down the c-axis; that is, with z equal to either 0.53 or 0.97, and the corresponding bromine z -parameter either 0.73 or 0.77. The distance of 6-7 Å. between the columns of bromate groups might well be large enough so that the interaction between the different columns of BrO_3 groups would be slight. If one bromate ion had taken up either the first or second position the rest of the bromate groups in that particular column would be forced to take up a similar orientation with respect to the c-axis, since otherwise the bromate oxygen atoms D of

two opposed bromate groups would interfere with each other, their interatomic distance being only 2.10 Å. This behavior would give rise to a type of randomness in which all bromate groups in the same column had the same orientation but might differ in orientation from other columns isolated from it by the intervening chains of hydrated neodymium ions.

This type of randomness is suggested by the intensity relationships. The fact that $I_{(03.8)}$ is observed to be greater than $I_{(02.8)}$ demands that z for bromine differ from 0.75 by more than 0.015. This comparison cannot be accounted for by errors in the oxygen parameter, since at the angle at which this reflection occurs the scattering power of oxygen is too small. If the bromine z -parameter is adjusted to give agreement with this comparison the calculated intensity of (50.1) becomes greater than those of many reflections readily observed. However, the reflection (50.1) has never been observed on any photographs. Deviations from z -bromine = 0.75 lead to similar discrepancies for many planes. If the type of randomness suggested above is postulated and introduced into the intensity calculations, these discrepancies disappear. This evidence makes it probable that randomness of this reasonable type exists in the crystal.

Tables II and III give calculated intensities for the polar and for the completely random structure. Table III gives also intensities calculated assuming one-third of the bromate groups to be

oriented in one direction and two-thirds in the opposite direction.

The positive result of the pyroelectric experiment and the fact that it would seem that the best agreement between calculated and observed intensities is obtained with only partial randomness suggest that the orientation of bromate groups in one column may influence that in adjacent columns to some extent, and that consequently the randomness is not complete.

Summary

The structure of $\text{Nd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ has been determined, and it has been found that the nine water molecules are coordinated about the rare earth ion, six at the corners of a trigonal prism and three out from the prism faces. The $\text{Nd}-\text{OH}_2$ distance has been found to be the same within the limits of error for all water molecules and equal to 2.50 ± 0.05 Å.

The symmetry of the isolated $\text{Nd}(\text{OH}_2)_9^{+++}$ group is approximately that of D_{3h} . The space group determination gives the point group symmetry at the Nd ion C_{3v} .

The Br-O separation in the bromate group has been determined to be 1.74 ± 0.07 Å., lending support to the interatomic distance reported by Hamilton, 1.78 Å., which is considerably larger than earlier published values.

The existence of randomness in the crystal structure is suggested and discussed.

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The Thermodynamics of Hyponitrous Acid

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The heat of formation of hyponitrous acid given by Berthelot¹ indicates that the potential of the $\text{N}_2-\text{H}_2\text{N}_2\text{O}_2$ couple in acid solution is about equal to that of the fluorine couple. Since experimentally the reduction of hyponitrous acid to nitrogen is very difficult in water solution, it seemed desirable to redetermine the heat of formation of the acid and its ions.

The Calorimeter.—The calorimeter was essentially that described by Pitzer.² The main object in its construction was that it should permit accurate measurement of small

amounts of heat so that dilute solutions could be employed which would minimize the correction to infinite dilution.

The reaction vessel was a 1-liter Dewar jar to which was fitted an evacuated glass stopper. A tube of small diameter through the center of this stopper accommodated the stirrer, the leads to heating coil and resistance thermometer. The material which was to react with the solution in the calorimeter was placed in a thin-walled glass bulb, sealed to the end of the stirrer, and could be broken against the bottom of the vessel.

The heater consisted of 102.30 ohms of no. 40 manganin wire with leads of no. 24 copper wire. Approximately 100 ohms of no. 40 wire, with leads of no. 24 manganin, formed the thermometer. The latter was enclosed in the upper part, and the heater in the lower, of a closely

(1) Berthelot, *Ann. chim. phys.*, [6] **18**, 571 (1889).

(2) K. S. Pitzer, *This Journal*, **59**, 2365 (1937).