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The Crystal Structure of $NaIO_3$ at 293 K

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The crystal structure of $NaIO_3$ at 293 K has been refined from Mo$K\alpha$ data in space group $Pbnm$, $Z = 4$, M_r 197.89, $a = 5.7500(3)$, $b = 6.3953(4)$, $c = 8.1280(4)$ Å, $V = 298.89(5)$ Å^3. Three thousand eighty-five (857 unique) reflections refined to $R(F) = 0.018$. The iodate group forms a pyramid with I as one apex; the I–O bond distances are 1.8016(8) and 1.8112(7) Å, and the O–I–O angles are 96.43(4)° and 102.60(3)°. Including next-nearest neighbors at distances 2.95–3.30 Å the I–O coordination is described as a two-capped trigonal prism. $NaIO_3$ is of the anti-cementite type, with Na occupying octahedral interstices (empty in cementite) and with the I lone pair approximately in the cementite C position.

Introduction

The crystal structures, stable at room temperature, of all the known simple alkali metal iodates, none of which is a hydrate, have been described in noncentrosymmetric space groups. This includes α-$LiIO_3$ (*1, 2*), $NaIO_3$ (*3*), KIO_3-III (*4*), and α-$RbIO_3$ (*5*). The $CsIO_3$ is still only known qualitatively (*5*), but the list may be augmented by α-HIO_3 (*6, 7*) and NH_4IO_3 (*8*). Most of the compounds have also been shown to be pyroelectric or piezoelectric and, e.g., α-HIO_3 and α-$LiIO_3$ have notable nonlinear optical properties (*9*). However, to the best of our knowledge the lack of centrosymmetry has not yet been demonstrated for any physical property of $NaIO_3$. On the contrary, it was found in a test for nonlinear optical properties that powdered $NaIO_3$ at room temperature did not generate any detectable second harmonic signal (*10*). The structure of $NaIO_3$ was first determined independently by MacGillavry and van Eck (*11*) and Naray-Szabo and Neugebauer (*12*) in space group $Pbnm$, with some doubts remaining as to the exact positions of the oxygen atoms. A recent refinement by Sorokina *et al.* (*3*) arrived at the result that the true space group is the polar $Pbn2_1$, but there are still some irregularities in that work. Our present investigation settles all questions about the details of the structure and shows that space group $Pbnm$ is very adequate.

Experimental

Single crystals of $NaIO_3$, prepared by slow evaporation of a saturated water solution at 85°C, were received from Dr. M. Koralewski (*13*). Part of a large transparent crystal was ground to a sphere with diameter 0.35(1) mm. It was bathed in ethanol to remove surface powder, and then investigated on a Huber four-circle X-ray diffractometer (*14*) with graphite-monochromated

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Mo$K\alpha$ radiation. The unit cell dimensions were determined from the accurately measured Bragg angles of 80 reflections with properly resolved α_1–α_2 peaks.

Three-dimensional intensity data, from a hemisphere of reciprocal space ($-10 \leq h \leq 10$, $0 \leq k \leq 11$, $-14 \leq l \leq 14$) were collected in two data sets. The $\omega - 2\theta$ scan technique was used with scan angles $\Delta\omega = 0.8° + 0.4° \tan\theta$ and scan rate 2° min^{-1}. The rate was lowered to 0.4° min^{-1} in a second additive scan if, initially, $3 \leq I/\sigma_c(I) < 40$. The scans were continuous but were divided into 255 steps by a high-speed multichannel scaler. The outer 30 steps on each side were taken as background. The intensities of three standard reflections measured every 2 hr decreased by a total of 10% during the 103 hr of exposure time, due to X-ray tube decay. They could be fitted by two functions linear in time, which were used to rescale all intensities and to put the two data sets on a common scale. The 3799 intensities were corrected for Lp and absorption effects. The absorption correction factors were interpolated according to Dwiggins (*15*) after calculation of the correction table by Gaussian integration over the sphere on a 40 × 40 × 40 grid. With a linear absorption coefficient 105.2 cm^{-1} the range of transmission factors was 0.086–0.130.

TABLE I

Crystal Data, Data Collection, and Least-Squares Refinement Details for $NaIO_3$, Space Group *Pbnm*, $Z = 4$, M_r 197.89

Temperature (K)	293(1)
a (Å)	5.7500(3)
b (Å)	6.3953(4)
c (Å)	8.1280(4)
V (Å^3)	298.89(5)
D_x (g cm^{-3})	4.398
No. of symmetry allowed reflections	
Collected	3417
In final L.S. cycle	3085
Unique in final L.S. cycle	857
$R(F)$	0.0818
$R(F^2)$	0.0263
$R_w(F_2)$	0.0441
$S(\Sigma w(\Delta F^2)^2/(n - m))^{1/2}$	1.94

The symmetry is orthorhombic with systematic extinctions indicating space groups *Pbnm* or *Pbn*2_1. After exclusion of the extinct data there were 3417 reflections to a resolution of $\sin\theta/\lambda = 0.89$ Å^{-1}. The internal agreement factor ($R_{int} = \Sigma|F^2_{obs} - F^2_{aver}|/\Sigma F^2_{obs}$) when averaging symmetry equivalent reflections was 0.017.

Further information concerning crystal data and least-squares refinements is given in Table I.

Structure Refinements

The full-matrix least-squares refinements minimized $\Sigma w(F_o^2 - F_c^2)^2$, where $w = (\sigma_c^2(F_o^2) + (c_1 F_o^2)^2 + c_2)^{-1}$ with $\sigma_c(F_o^2)$ from counting statistics and $c_1(= 0.012)$ and $c_2(= 4.0)$ adjusted to give constant $\langle w\Delta F^2\rangle$ in different F_o^2 and $\sin\theta$ intervals. Following the IUCr recommendation (*24*) the unaveraged data set was used in the refinements starting with parameters from (*3*). One isotropic extinction parameter (type I, Lorentzian mocaicity (*16*)) was refined in the initial least-squares cycles, $q = 5.1(1) \times 10^3$. Due to large extinction (max correction on F_o^2, $y = 4.19$), data below $\sin\theta/\lambda = 0.3$ Å^{-1} were excluded in the final refinement together with reflections having y greater than 1.3. In order to avoid overestimates of the extinction corrections, q was kept constant in the final refinements. Furthermore, unobserved data with $I < 3\sigma_c(I)$ were omitted. The 28 parameters used in the final least-squares cycles included positional and anisotropic thermal parameters and one scale factor. The largest (parameter shift)/(parameter e.s.d.) in the final cycle was less than 0.01. The largest differences in the final difference Fourier synthesis were -0.59 and $+0.47$ eÅ^{-3}, both near iodine.

Refinements in the noncentric space

group $Pbn2_1$ only lowered $R_w(F^2)$ from 0.0441 to 0.0425, while the number of parameters increased from 28 to 45. To test the choice of the noncentric space group by Sorokina *et al.* (*3*) a model calculation was performed. The 1800 largest structure factors were generated using the structural parameters from (*3*). One centric and one noncentric isotropic structure model was refined against these calculated structure factors resulting in $R(F)$ 0.043 and 0.039, respectively. In neither case can the use of a noncentric space group for $NaIO_3$ be justified. Sorokina *et al.* claimed that the centric model gave an R factor of 0.17, but in light of our test calculation that was obviously due to human error.

Scattering factors for neutral atoms and anomalous scattering corrections were taken from (*17*). The crystallographic computer programs have been described by (*18*). Final atomic parameters are given in Table II.[1]

TABLE II

FINAL ATOMIC COORDINATES, ANISOTROPIC TEMPERATURE FACTOR COEFFICIENTS ($\times 10^5$), AND R.M.S. COMPONENTS OF THERMAL DISPLACEMENTS ALONG PRINCIPAL AXES WITH ESTIMATED STANDARD DEVIATIONS FOR $NaIO_3$

	x	y	z	B_{iso} (Å^2)	Wyckoff position
Na	0.5	0.0	0.0	1.37(2)	4b
I	0.01137(1)	0.01360(1)	0.25	0.886(2)	4c
O(1)	−0.28739(13)	0.09848(14)	0.25	1.23(1)	4c
O(2)	0.13664(11)	0.16501(11)	0.08384(8)	1.48(1)	8d

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	930(19)	893(16)	534(10)	−33(7)	49(5)	−29(6)
I	560(2)	452(2)	445(1)	23(1)	0	0
O(1)	640(16)	884(16)	527(9)	171(11)	0	0
O(2)	1080(15)	888(13)	596(8)	32(9)	226(8)	191(8)

	r.m.s.[1] (Å)	r.m.s.[2] (Å)	r.m.s.[3] (Å)
Na	0.123(1)	0.132(1)	0.139(1)
I	0.0946(2)	0.0990(1)	0.1221(2)
O(1)	0.098(1)	0.133(1)	0.140(1)
O(2)	0.110(1)	0.133(1)	0.164(1)

Note. $B_{iso} = 4\Sigma_i\Sigma_j\beta_{ij} * (a_i * a_j)/3$. The temperature factor is of the form: $\exp - (\beta_{ii} * h_i^2 + \ldots + 2 * \beta_{ij} * h_i * h_j + \ldots)$.

TABLE III

SELECTED DISTANCES (Å) AND ANGLES (°) IN $NaIO_3$

NaO_6 octahedron (Na at inversion center)			
Na–O(1)	2.4536(4)	O(2)–O(2)′	3.3623(7)
Na–O(2)	2.3815(7)	O(1)–O(2)	3.6799(10)
Na–O(2)′	2.4379(7)	O(1)–O(2)′	3.3097(8)
O(1)–O(2)	3.1371(8)	O(2)–O(2)′	3.4532(5)
O(1)–O(2)′	3.6018(10)		
IO_8 two-capped trigonal prism (I and O(1) in mirror plane)			
I–O(1)	1.8016(8)	O(1)–I–O(2)	102.60(3)
I–O(2)	1.8112(7)	O(2)–I–O(2)	96.43(4)
I–O(1)′	2.9507(9)		
I–O(2)′	3.3001(7)		
I–O(2)″	3.0646(7)		
O(1)–O(2)	2.8195(9)	O(1)′–O(2)′	3.6018(10)
O(2)–O(2)	2.7011(13)	O(2)′–O(2)′	2.7011(13)
O(1)–O(1)′	3.2264(3)		
O(2)–O(2)′	3.4532(5)		
O(1)–O(2)″	3.3097(8)	O(1)′–O(2)″	3.1371(8)
O(2)–O(2)″	2.9633(13)	O(2)′–O(2)″	3.3623(7)
Na–O–I and Na–O–Na bridging angles			
Na–O(1)–I	113.44(2)	Na–O(2)–I	108.53(3)
Na–O(1)–Na	111.82(3)	Na–O(2)–Na	126.31(3)

Discussion

The geometrical details of the $NaIO_3$ structure are given in Table III. The iodate ion geometry is pyramidal with the lone pair of electrons of iodine pointing at the fourth vertex of a tetrahedron (*19, 20*). In

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[1] See NAPS document No. 04620 for 24 pages of supplementary material. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $8.95 for microfiche copy or for photocopy. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material, $1.50 for postage of any microfiche orders.

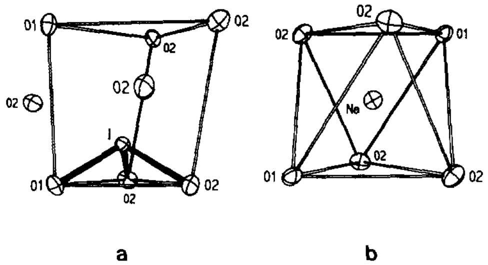

FIG. 1. Perspective views of the coordination polyhedra around (a) iodine and (b) sodium in $NaIO_3$.

room temperature $NaIO_3$ the ion has *m* symmetry with I–O bond distances of 1.8016(8) and 1.8112(7) Å. The mirror related oxygen atoms are those with the longest I–O distances and with the smaller O–I–O angle of 96.43(4)°. Apart from these distortions the geometry is quite similar to that of the regular IO_3^- ion in α-$LiIO_3$ (*1, 2*) with I–O 1.8034(3) Å and O–I–O 100.13(2)° at 295 K. After corrections for thermal motion, assuming O to ride on I, the bond distances are 1.8051 and 1.8176, respectively, with an average 1.813 Å instead of 1.808 Å as in α-$LiIO_3$ (*1*). The height of the iodine atom above the plane formed by the three oxygen atoms is 0.830 Å compared to 0.838 Å in α-$LiIO_3$.

The crystal structures of iodates are usually described in terms of a coordination polyhedron around iodine that includes next-nearest neighbors. Thus, the alkali metal iodate structures with the large cations K^+, Rb^+, Cs^+, as well as NH_4^+, can all be thought of as distorted perovskite-type structures (*4, 5, 8*). With the smaller cations, on the other hand, the capped trigonal prism, with the lone pair approximately at the center of the prism, has been used as a structural building element. Svensson *et al.* (*21*) described a whole series of isostructural iodates with α-$LiIO_3$ as parent structure, in terms of packing of these tricapped trigonal prisms together with octahedra centered by small cations, e.g., 3d transition metals. Andersson (*22*) showed that $NaIO_3$ is of the anti-cementite type with the iodine lone pair approximately at the C position of Fe_3C, near the center of a two-capped trigonal prism. The α-HIO_3 (*6, 7*) is also closely related to this structure (*22*).

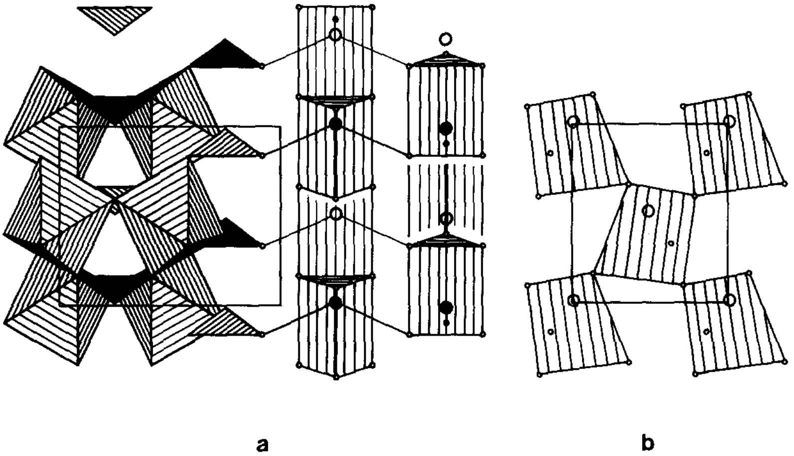

FIG. 2. Crystal packing in $NaIO_3$. (a) Projected on the *bc* plane. To the left the NaO_6 octahedra and IO_3 pyramids are shown. The atomic positions are extended to the right-hand side of the figure, where the connected two-capped trigonal prisms around iodine are shown. (b) Projected on the *ab* plane. A view perpendicular to the sheet of connected trigonal prisms; large circles are iodine, small circles oxygen.

Figure 1a shows the neighbors of iodine in $NaIO_3$ for I–O distances up to 3.30 Å. (cf. Table III) forming a distorted two-capped trigonal prism. The closest next-nearest neighbor at 2.951(1) Å is unusually far away. In α-$LiIO_3$, the other trigonal prism structure, that distance is 2.908(1) Å, but it is shorter in the distorted perovskite structures, e.g., 2.753(3) Å in α-$RbIO_3$ (*5*). The trigonal prisms are connected by edge and corner sharing to sheets on the mirror planes of the space group as shown in Fig. 2. These mirror planes correspond to the unit cell twin planes between blocks of hexagonal close packing as described by Andersson and Hyde for cementite (*23*). The net of corner-sharing octahedral interstices between the sheets, which are empty in cementite, are shown to the left in Fig. 2a. This fairly regular octahedral sodium coordination has Na–O distances in the range 2.382 to 2.454 Å (cf. Fig. 1b).

Acknowledgments

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References

1. C. Svensson, J. Albertsson, R. Liminga, Å. Kvick, and S. C. Abrahams, *J. Chem. Phys.* **78,** 7343 (1983).
2. E. Coquet, J. M. Crettez, J. Pannetier, J. Bouillot, and J. C. Damien, *Acta Crystallogr. Sect. B* **39,** 408 (1983).
3. M. I. Sorokina, V. V. Ilyukhin, V. I. Pakhomov, and N. V. Belov, *Sov. Phys. Dokl.* **24,** 881 (1979).
4. V. V. Ilyukhin, V. R. Kalinin, I. N. Ivanova-Korfini, and V. I. Pakhomov, *Koord. Khim.* **5,** 1549 (1979).
5. N. W. Alcock, *Acta Crystallogr. Sect. B* **28,** 2783 (1972).
6. M. T. Rogers and L. Helmholz, *J. Amer. Chem. Soc.* **63,** 278 (1941).
7. B. S. Garrett, USAEC Report, ORNL-1745, 97 (1954).
8. E. T. Keve, S. C. Abrahams, and J. L. Bernstein, *J. Chem. Phys.* **54,** 2556 (1971).
9. Landolt-Börnstein, *in* "Numerical Data and Functional Relationships in Science and Technology" (K.-H. Helwege and A. M. Hellwege, Eds.), Vols. 7b2, 11, 18, Springer, Berlin (1979).
10. J. G. Bergman, Jr., G. D. Boyd, A. Ashkin, and S. K. Kurtz, *J. Appl. Phys.* **40,** 2860 (1969).
11. C. H. MacGillavry and C. L. Panthaleon van Eck, *Rec. Trav. Chim. Pays-Bas* **62,** 729 (1943).
12. I. Naray-Szabo and J. Neugebauer, *J. Amer. Chem. Soc.* **69,** 1280 (1947).
13. M. Koralewski, Personal communication (1987).
14. C. Svensson, *Acta Crystallogr. Sect. A* **43,** C270 (1987).
15. C. W. Dwiggins, Jr., *Acta Crystallogr. Sect. A* **31,** 146 (1975).
16. P. J. Becker and P. Coppens, *Acta Crystallogr. Sect. A* **30,** 129 (1974).
17. J. A. Ibers and W. C. Hamilton (Eds.), "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1974).
18. J.-O. Lundgren, "Crystallographic Computer Programs," Report No. UUIC-B13-4-05, University of Uppsala (1983).
19. S. Andersson, A. Åström, J. Galy, and G. Meunier, *J. Solid State Chem.* **6,** 187 (1973).
20. J. Galy, G. Meunier, S. Andersson, and A. Åström, *J. Solid State Chem.* **13,** 142 (1975).
21. C. Svensson, S. C. Abrahams, and J. L. Bernstein, *J. Solid State Chem.* **36,** 195 (1981).
22. S. Andersson, *Acta Crystallogr. Sect. B* **35,** 1321 (1979).
23. S. Andersson and B. G. Hyde, *J. Solid State Chem.* **9,** 92 (1974).
24. D. Schwarzenbach, *Acta Crystallogr. Sect. A* **43,** C281 (1987).