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The Crystal Structure of Boron Triiodide[1]

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The crystal structure of boron triiodide has been determined by the powder method. The structure is hexagonal with $a = 7.00 \pm 0.01$, $c = 7.46 \pm 0.02$ Å., and two molecules per cell. The boron–iodine bond distance has been found to be 2.10 ± 0.04 Å.

Introduction

From the similarity of the pure nuclear quadrupole spectrum of iodine in boron triiodide to that of chlorine in boron trichloride and that of bromine in boron tribromide, Laurita and Koski[2] inferred that the structure of boron triiodide is similar to that of the other two known[3a,b] boron trihalides. The present work was undertaken to check their inference by seeing if a crystal structure based on the assumption of isostructurality with boron trichloride would give acceptable agreement between observed and calculated intensities and, if so, to determine the boron–iodine bond length.

Experimental

Boron triiodide, obtained from the General Electric Corporation, was deposited *in vacuo* at −196° as a powder onto a cold finger suspended over a Pyrex capsule. Tapping the vessel caused the powder to drop into the capsule, which was sealed off and inserted into the camera. A powder pattern was obtained in a Philips-type camera using Ni-filtered Cu radiation [$\lambda(K\alpha) = 1.5418$ Å.], 45 kv., 12 mamp., 24-hr. exposure. Indexing the film showed that the structure is hexagonal with $a = 7.00 \pm 0.01$ and $c = 7.46 \pm 0.02$ Å., 2 molecules per cell, and a diffraction aspect $P6_3{*}{*}$ which is compatible with space groups $P6_322$ ($= D_6^6$), $P6_3/m$ ($= C_{6h}^2$), and $P6_3$ ($= C_6^6$).

A structure isotype of that of BCl_3 can be described in either $P6_3$, with $z_B = z_I = 0$ or any arbitrary value, or $P6_3/m$ (Table I), with $z_B = z_I = {}^1/_4$ fixed by symmetry.

In $P6_3$ the planarity of the molecule is assumed on the basis of isostructurality with BCl_3 and justified by agreement of intensities; in $P6_3/m$ the space-group symmetry requires the molecule to be planar. (Note that we have no evidence for the existence of a center of symmetry, so that $P6_3$ cannot be ruled out.) As to $P6_322$ it is ruled out by the available 6-fold positions, as well as by the Laue class 6/m observed[3a] for BCl_3.

TABLE I

DESCRIPTION OF CRYSTAL STRUCTURE OF BORON TRIIODIDE

Atoms	Positions in $P6_3$	Position in $P6_3/m$	Atomic coördinates[a]		
			x	y	z
2B	x, y, z;	1/3, 2/3, 1/4;	1/3	2/3	0
	$\bar{x}, \bar{y}, 1/2 + z$	2/3, 1/3, 3/4			
6I	x, y, z;	x, y, 1/4;	0.03	0.37	0
	$\bar{y}, x\text{-}y, z$;	$\bar{y}, x\text{-}y$, 1/4;			
	$y\text{-}x, \bar{x}, z$;	$y\text{-}x, \bar{x}$, 1/4;			
	$\bar{x}, \bar{y}, 1/2 + z$;	$\bar{x}, \bar{y}$, 3/4;			
	$y, y\text{-}x, 1/2 + z$;	$y, y\text{-}x$, 3/4;			
	$x\text{-}y, x, 1/2 + z$	$x\text{-}y, x$, 3/4			

[a] The value of z in $P6_3$ is 0 or any arbitrary quantity; it is a question of choice of origin.

For iodine, the parameters x and y of the general position were obtained by plotting the calculated relative intensities, LpI_{calcd}, *versus* the y coördinate ($0.36 \leq y \leq 0.38$) for several values of x ($x = 0.025$, 0.030, and 0.035) for reflections No. 7, 10, 13, 23, and 27. (The reflections referred to are listed in numerical order from 1 to 45 in Table II.) These curves are very dependent on small

TABLE II

X-RAY DIFFRACTION DATA FOR BORON TRIIODIDE[a] (POWDER METHOD)

No.	hkl	$Q_{\text{obsd.}}$	$Q_{\text{calcd.}}$	$I_{\text{obsd.}}$	$LpI_{\text{calcd.}}$
1	100	~0.027	0.02713	0.02	0.022
2	101	*b*	.04509	*b*	.030
3	002	.07325	.07184	.40	.34
4	110	.08215	.08139	.20	.20
5	102	.09973	.09897	1.00	.01
	111		.09935		.99
6	200		.10852	N.O.	.014
7	201	.12694	.12648	0.02	.025
8	112	.15309	.15324	.10	.17
9	202		.18036	N.O.	.015
10	103		.18877		.008
	210	.18982	.18991	0.05	.014
	120				.023
11	211		.20787	N.O.	.012
	121				.006
12	113	.24229	.24303	0.40	.27
	300		.24417		.15
13	212	.26181	.26175	.05	.019
	122				.029

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[1] Work supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

[2] W. G. Laurita and W. S. Koski, *J. Am. Chem. Soc.*, **81**, 3179 (1959).

[3] (a) M. Atoji and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 195 (1957); (b) M. A. Rollier and A. Riva, *Gazz. chim. ital.*, **77**, 361 (1947).

TABLE II (*Continued*)

No.	*hkl*	$Q_{\text{obsd.}}$	$Q_{\text{calcd.}}$	$I_{\text{obsd.}}$	$LpI_{\text{calcd.}}$
14	301		.26513	N.O.	.002
15	203		.27016	N.O.	.009
16	004	.28722	.28736	0.10	.066
17	104	.31502	.31449	.10	.002
	302		.31601		.14
18	220		.32556	N.O.	.022
19	310		.32621	N.O.	.016
	130				.002
20	221	.34090	.34352	0.10	.12
21	311		.35021	N.O.	.001
	131				.022
22	213		.35455	N.O.	.008
	123				.004
23	113	.36894	.36865	0.05	.045
24	204	.39252	.39588	.02	.004
	222		.39740		.028
25	312		.40046	N.O.	.014
	132				.μ02
26	303		.40581	N.O.	.001
27	400	.43101	.43408	0.01	.010
28	401	.44936	.45208	.02	.033
29	105		.47613	N.O.	.002
30	214		.47727	N.O.	.008
	124				.012
31	223	.48678	.48720	0.02	.048
32	402		.50592	N.O.	.007
33	230		.51502	N.O.	.001
	320				.017
34	115		.53039		.078
	304	.53027	.53153	0.15	.082
	231		.53230		.008
	321				.001
35	410		.56940	N.O.	.007
	140				.006
36	411		.58669		.016
	141	.58276		0.02	.018
	232		.58702		.001
	322				.012
37	403		.59572	N.O.	.017
38	224	.61723	.61292	0.02	.021
39	215		.63891	N.O.	.007
	125				.003
40	412		.64157		.006
	142	.64339		0.02	.005
	006				.014
41	106		.67369	N.O.	.001
42	500		.67825		.028
	233	.68587		0.02	.006
	323		.67952		.001
43	501		.69621	N.O.	.018
44	404		.72144	N.O.	.005
45	116		.72795		.010
	412	.72609		0.02	.013
	143		.73129		.015

[a] Legend: *hkl* = Bravais-Miller 4-index symbols with the superabundant third index omitted; *Lp* = Lorentz and polarization factor; *I* = Intensity; N.O. = Not Observed; $Q_{\text{obsd.}} = (4 \sin^2 \theta)/\lambda^2$; $Q_{\text{calcd.}} = (h^2 + hk + k^2)a^{*2} + lc^{*2}$. [b] Inaccessible to observation; hidden by diffraction from Pyrex capsule.

changes in the values of x and y and therefore were useful in limiting the possible ranges of x and y. At $x = 0.03$ and $y = 0.37$, the relative values for $LpI_{\text{calcd.}}$ for the different reflections were closer to $I_{\text{obsd.}}$ than at any other point. These graphs also were used to obtain an estimate of the possible error in the boron–iodine bond length. The values for $I_{\text{obsd.}}$ (Table II) were obtained by visual estimation.

Unfortunately, the powdered sample gave spotty lines which decreased the accuracy of the estimated intensities and prevented the use of a microphotometer.

Results

The boron–iodine bond length calculated from the data gives a value of 2.10 ± 0.04 Å. The limits of error are given in Table III. For the value of the x coördinate listed, the best fit for y and the possible maximum and minimum values are given, along with the corresponding bond lengths.

Even at $x = 0.035$ and $x = 0.025$ it is impossible to find a y value for which the calculated intensities fulfill the conditions imposed by the observed relative intensities (Table IV).

The c/a ratio for BI_3 is 1.066 as compared with 1.071 and 1.077 reported for BBr_3[3b] and BCl_3,[3a,4] respectively. The unit cell is shown in Fig. 1.

Discussion

The value for the covalent radius of boron has been reported by Hedberg[5] to lie between 0.80 and 0.88 Å. This uncertainty may be due to different hybridizations for boron. Levy and

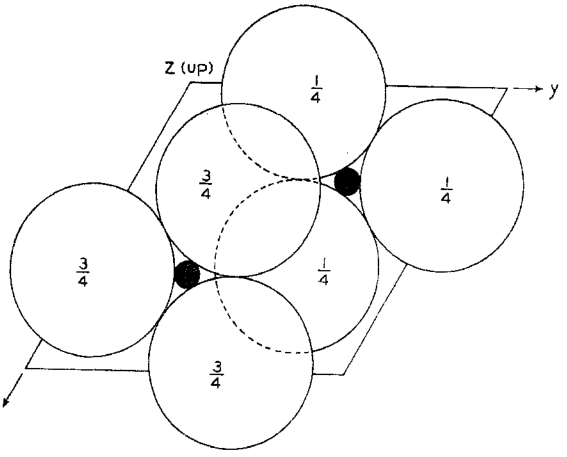

Fig. 1.—Crystal structure of boron triiodide in $P6_3/m$ projected on the xy plane. Heights of atoms shown by fractions of c. Mirror planes of symmetry at heights $^1/_4$ and $^3/_4$.

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(4) C. Spencer and W. N. Lipscomb, *J. Chem. Phys.*, **28**, 355 (1958).

(5) K. Hedberg, *J. Am. Chem. Soc.*, **74**, 3486 (1952).

TABLE III

BOND-LENGTH DATA FOR BORON TRIIODIDE

x	$y_{\text{(best fit)}}$	Bond length	$y_{\text{max.}}$	Bond length	$y_{\text{min.}}$	Bond length
0.025	0.373	2.11 Å.	0.380	2.08 Å.	0.365	2.13 Å.
.030	.370	2.10 Å.	.375	2.08 Å.	.365	2.12 Å.
.035	.367	2.09 Å.	.375	2.07 Å.	.360	2.06 Å.

TABLE IV

CONDITIONS FROM OBSERVED INTENSITIES[6]

Reflection 23 $>$ 10 $\sim$ 13
Reflection 27 $<$ 7 $\ll$ 10 $\sim$ 13

Brockway[7] find 0.79 Å. as the trigonal radius and 0.89 Å. as the tetragonal radius. They interpret these results by remarking that the covalent radius for boron should change as the double bond character varies: when the boron–halogen π-bond character increases from 0 to $^1/_3$, the hybridization changes from trigonal to tetragonal and the boron covalent radius increases from 0.79 to 0.89 Å.

Nuclear quadrupole data can be used to obtain the π bonding in these compounds. This method gives 0.06, 0.12, and 0.16 as the halogen double-bond character in BCl_3,[8] BBr_3,[8] and BI_3,[2] respectively. Note that the two parameters—the nuclear quadrupole coupling constant and the asymmetry parameter—were obtained directly in BBr_3 and BI_3. In BCl_3, however, the parameters were determined on the assumption of a value for the ionic character of the B–Cl bond, which might lead to some error in this case. The preceding π-bond characters yield boron covalent radii of 0.82, 0.83, and 0.84 Å. for the trichloride, tribromide, and triiodide, respectively. With Coulson's values[9] for the halogen covalent radii and taking into account the electronegativity and π-bond contractions,[9] we calculate these bond lengths for BCl_3, BBr_3, and BI_3: 1.71, 1.88, and 2.09 Å., which compare well with the experimental values of 1.75 (Lipscomb[3a,4]), 1.87 (Levy and Brockway[7]), and 2.10 Å. (this paper).

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[6] I_{obs} for reflections 23 and 27 weakened more by thermal motion than for the other three reflections.

[7] H. A. Levy and L. O. Brockway, *J. Chem. Soc.*, **59**, 2085 (1937).

[8] T. Chiba, *J. Phys. Soc. Japan*, **13**, 860 (1958).

[9] C. A. Coulson, "Valence," Oxford Press, 1952.

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The Electronic Structure of the Vanadyl Ion[1]

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The bonding in the molecule ion $VO(H_2O)_5^{2+}$ is described in terms of molecular orbitals. In particular, the most significant feature of the electronic structure of VO^{2+} seems to be the existence of considerable oxygen to vanadium π-bonding. A molecular orbital energy level scheme is estimated which is able to account for both the "crystal field" and the "charge transfer" spectra of $VO(H_2O)_5^{2+}$ and related vanadyl complexes. The paramagnetic resonance g factors and the magnetic susceptibilities of vanadyl complexes are discussed.

Introduction

The high oxidation states of metal ions occurring at the beginning of the transition and actinium series usually are found in complex oxycations of the types MO^{n+} and MO_2^{n+}. The remarkable stability of these complexes, along with their interesting spectral and magnetic properties, has aroused considerable theoretical speculation concerning their electronic structures. The uranyl ion, UO_2^{2+}, has been discussed most often,[3] but partly due to the lack of good wave functions for

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[1] Presented at the Symposium on Ligand Field Theory, 140th National A.C.S. Meeting, Chicago, September, 1961.

[2] National Science Foundation Postdoctoral Fellow, 1960–61.

[3] For example, see R. L. Belford and G. Belford, *J. Chem. Phys.*, **34**, 1330 (1961).