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The Crystal Structure of $Zr(IO_3)_4$*

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$Zr(IO_3)_4$ is tetragonal, space group $P4/n$, with $a=8{\cdot}38\pm0{\cdot}01$, $c=7{\cdot}49\pm0{\cdot}01$ Å and has two formula units per unit cell. The complete structure has been determined from single crystal data obtained with a Geiger counter. The zirconium atoms are coordinated to eight oxygen atoms at the corners of a nearly perfect antiprism with an average Zr–O distance of 2·206 Å. An interesting feature of the structure is that there are voids extending completely through the crystal along the fourfold inversion axis.

Introduction

Several years ago the structure of $Ce(IO_3)_4$ was reported by Cromer & Larson (1956). This work was done because of interest in the structure of $Pu(IO_3)_4$, which is isomorphous with $Ce(IO_3)_4$. At that time some $Zr(IO_3)_4$ was prepared in the hope that it too would be isomorphous with $Pu(IO_3)_4$. Because zirconium has a smaller scattering power than cerium, $Zr(IO_3)_4$ would have been a more favorable compound to study. However, $Zr(IO_3)_4$ is not isomorphous with the other compounds, so its study was not pursued further at that time.

The zirconium/oxygen radius ratio is slightly smaller than that predicted for a stable Archimedean antiprism coordination (Pauling, 1948). Nevertheless, an antiprism coordination of oxygen about zirconium has been observed in $Zr(SO_4)_2.4\,H_2O$ (Singer, 1951; Singer & Cromer, 1959). Because $Ce(IO_3)_4$ has an antiprism coordination and $Zr(IO_3)_4$ was observed to have a different unit cell and space group, it was thought that in this compound zirconium might not have this type of coordination. For this reason, the study of $Zr(IO_3)_4$ was resumed. In anticipation we might say now that an antiprism was found.

Experimental

Stoichiometric amounts of $NaIO_3$ and $Zr(SO_4)_2.4H_2O$ were dissolved in water and the two solutions were mixed. A white precipitate formed immediately. The precipitate, presumably $Zr(IO_3)_4$, or a hydrate thereof, was dried in air. An X-ray powder photograph of the precipitate had no crystalline diffraction lines. The precipitate was placed in the thimble of a Soxhlet extractor, and concentrated HNO_3 was refluxed through it for a day. During this time, a considerable number of small, very well-formed crystals were produced at the bottom of the flask. The crystals were tetragonal prisms showing the forms {001} and {110}.

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Weissenberg and precession photographs were taken. The Laue symmetry of $4/m$ and the systematic extinctions ($hk0$ absent if $h+k=2n+1$) observed in these photographs uniquely established the space group to be $P4/n$. The lattice constants are

$$a=8{\cdot}38\pm0{\cdot}01,\ c=7{\cdot}49\pm0{\cdot}01\ \text{Å},$$

as determined from measurement of the 006 and 071 lines on a powder photograph taken with Cr radiation ($K\alpha_1$, $\lambda=2{\cdot}2896$ Å). The calculated density, with two formula units per unit cell, is 4·99 g.cm.$^{-3}$. The density, measured by displacement of 1,1,2,2-tetrabromoethane, was found to be 5·01 g.cm.$^{-3}$. A chemical analysis of the compound showed 11·66% Zr and 64·0% I. The calculated amounts are 11·57% Zr and 64·16% I. These calculated quantities take account of the fact that the Zr contained 0·36 at.% Hf as determined spectrographically. No water was found.

For intensity measurements, a crystal of dimensions $42\times42\times96\mu$ was mounted on the c axis. This axis coincided with the long dimension of the crystal. Intensities of levels from $l=0$ through $l=10$ were measured with a Geiger counter attached to a Weissenberg camera (Evans, 1953). Intensities were measured to $\sin\theta/\lambda\approx1{\cdot}0$, using Mo $K\alpha$ radiation. Of the 1930 reflections in this sphere, 1176 were observed to be greater than zero. Lorentz-polarization corrections were applied to give a set of relative F^2 for each layer with constant l. No absorption corrections were made.

Determination of the trial structure

With $Z=2$, one would expect to find zirconium in a twofold set and the iodine and three different oxygens in the eightfold general positions. A three-dimensional Patterson was first computed. For this purpose, all l layers were assumed to have the same scale factor. The iodine atom was found to be at

$$x\approx-0{\cdot}01,\ y\approx0{\cdot}03,\ z\approx0{\cdot}27\ .$$

Of the three possible twofold sets in which to place the zirconium atom, only the set 2c, with $z\approx0{\cdot}06$,

Table 1. *Results of least-squares refinement of* $Zr(IO_3)_4$

The origin is at $\bar{1}$

Atom	x	y	z	$B \times 10^{16}$ cm.^{2}
Zr	$\frac{1}{4}$	$\frac{1}{4}$	0.0603 ± 0.0003	0.095 ± 0.024
I	-0.0061 ± 0.0001	-0.0302 ± 0.0001	0.2699 ± 0.0001	0.510 ± 0.011
O_1	0.1547 ± 0.0014	-0.0022 ± 0.0014	0.5578 ± 0.0018	1.55 ± 0.16
O_2	0.0404 ± 0.0011	0.1787 ± 0.0011	0.2173 ± 0.0015	0.95 ± 0.12
O_3	-0.1589 ± 0.0016	-0.0430 ± 0.0016	0.0929 ± 0.0020	1.92 ± 0.19

gave a self-consistent vector set. Structure factors were calculated with the above heavy atom positions. Next, a three-dimensional Fourier was calculated using about two-thirds of the observed structure factors. Three small peaks were observed about 1·8 Å from the iodine atom. These peaks were presumed to be the oxygen atoms.

Refinement of the structure

The atomic positions obtained from the three-dimensional Fourier were used as the initial values in a least-squares refinement calculated on an IBM 704. Also, temperature factors for each atom, and separate scale factors for each value of l, were included as parameters. The full 29×29 matrix was computed and solved for each cycle. The observed reflections were weighted equally, and the unobserved reflections were omitted. McWeeney's (1951) oxygen form factor and the zirconium and iodine form factors from the *Internationale Tabellen* (1935) were used. Anomalous dispersion corrections of -1.3 electrons for iodine and -3.4 electrons for zirconium were applied to the form factors (James, 1948).

The final position and temperature factor parameters are listed in Table 1. The zirconium temperature factor is rather low and suggests that the anomalous dispersion correction of -3.4 electrons was somewhat large. The standard deviations were computed from the expression

$$\sigma(\xi_i) = \left[\frac{\Sigma(\Delta F)^2}{(m-s)} D_{ii}\right]^{\frac{1}{2}},$$

where m is the number of observations, s the number of parameters, and D_{ii} is the diagonal element of the inverse matrix. The list of calculated and observed structure factors, for which $R = 7.05\%$, is given in Table 2.

Discussion of the structure

The structure projected on (001) is shown in Fig. 1 and the important interatomic distances and bond angles are listed in Table 3. The zirconium atom is surrounded by four O_2 and four O_3 atoms at the corners of a nearly perfect Archimedean antiprism. The average Zr–O distance of 2·206 Å compares favorably with the value of 2·178 Å recently reported for $Zr(SO_4)_2 . 4\,H_2O$ (Singer & Cromer, 1959) in which a nearly perfect Archimedean antiprism also exists. In zircon (Krstanović, 1958) a rather distorted antiprism is found with four Zr–O distances of 2·15 Å and four of 2·29 Å. In the monoclinic ZrO_2 baddeleyite, the zirconium atom has seven oxygen neighbors (McCullough & Trueblood, 1959). Six of the neighbors lie approximately at the corners of an antiprism and the seventh neighbor lies intermediate between the two remaining antiprism corners. In the high temperature form of ZrO_2 the zirconium has eight oxygen neighbors at the corners of a cube at a distance of 2·20 Å (Passerini, 1930).

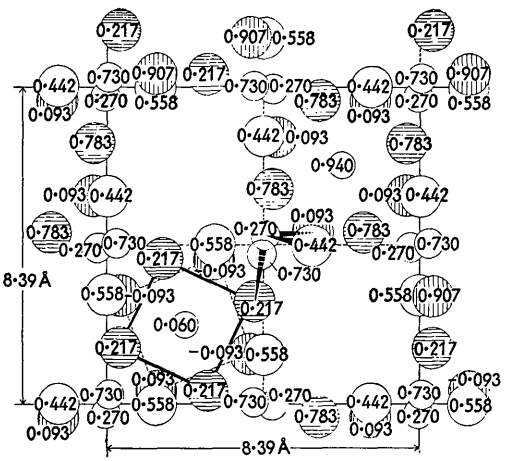

Fig. 1. $Zr(IO_3)_4$ projected on (001). The large circles are oxygen, medium circles are iodine, and the small circles are zirconium. The O_1 atoms are open circles, the O_2 atoms are shaded with horizontal lines, and the O_3 atoms are shaded with vertical lines. The z coordinates are given beside each atom.

The dimensions of the iodate group agree well with those found in $Ce(IO_3)_4$ (Cromer & Larson, 1956) and in $Ce(IO_3)_4 . H_2O$ and other iodates (Ibers, 1956). The three I–O bonds do not differ significantly but the O–I–O angles do; thus in this compound the iodate group shows a small but significant departure from trigonal symmetry. It is unfortunate that the accuracy of this analysis does not permit rigorous statements concerning differences in the I–O bonds. The shortest apparent distance is I–O_1 and it involves the oxygen that is not shared with a metal atom. A situation of this sort occurs in both $Ce(IO_3)_4$ and $Ce(IO_3)_4 . H_2O$. There is a short non-bonded I–O distance of 2·55 Å in $Zr(IO_3)_4$. A short non-bonded I–O distance of 2·45 Å was first observed by Rogers & Helmholtz (1941) in their study of HIO_3. Garrett

Table 2. *Observed and calculated structure factors for* $Zr(IO_3)_4$

The column headings are h, k, l, F_o and F_c. Where $F_o = 0$, the reflection was at too small an angle to be observed. Where F_o is negative, it was unobserved and the value listed is the estimated maximum

Table 2 (*cont.*)

3	1	5	-9	3
3	2	5	40	39
3	3	5	26	23
3	4	5	138	135
3	5	5	20	21
3	6	5	63	61
3	7	5	54	48
3	8	5	98	98
3	9	5	38	37
3	10	5	32	35
3	11	5	61	57
3	12	5	56	53
3	13	5	49	41
3	14	5	-21	-1
3	15	5	43	48
4	1	5	74	-71
4	2	5	108	-108
4	3	5	43	36
4	4	5	95	-92
4	5	5	26	-16
4	6	5	56	-57
4	7	5	62	59
4	8	5	55	-56
4	9	5	-17	12
4	10	5	-18	-8
4	11	5	36	38
4	12	5	-20	-14
4	13	5	-21	-7
4	14	5	-22	3
4	15	5	-22	15
5	1	5	10	-15
5	2	5	117	126
5	3	5	20	-19
5	4	5	83	86
5	5	5	43	23
5	6	5	128	133
5	7	5	24	22
5	8	5	64	63
5	9	5	57	56
5	10	5	89	87
5	11	5	46	45
5	12	5	29	25
5	13	5	56	53
5	14	5	32	35
6	1	5	-12	-5
6	2	5	90	-89
6	3	5	43	-37
6	4	5	36	-36
6	5	5	27	24
6	6	5	35	-43
6	7	5	-16	-13
6	8	5	-17	-15
6	9	5	37	36
6	10	5	-19	-10
6	11	5	20	-21
6	12	5	-21	5
6	13	5	-21	9
6	14	5	-22	-3
7	1	5	55	-47
7	2	5	74	78
7	3	5	-14	-4
7	4	5	141	145
7	5	5	-16	-9

12	7	5	-21	19
12	8	5	-21	17
12	9	5	-22	-20
12	10	5	29	26
13	1	5	43	-41
13	2	5	71	74
13	3	5	37	-36
13	4	5	42	46
13	5	5	-21	-18
13	6	5	83	79
13	7	5	-22	-15
13	8	5	53	40
14	1	5	21	27
14	2	5	-21	2
14	3	5	-21	-2
14	4	5	-22	17
14	5	5	21	28
14	6	5	-22	15
14	7	5	-22	-2
15	1	5	43	-42
15	2	5	-21	25
15	3	5	-22	-21
15	4	5	61	58
0	0	6	0	-217
0	1	6	0	-65
0	2	6	116	-134
0	3	6	36	-27
0	4	6	142	-145
0	5	6	91	-85
0	6	6	92	-81
0	7	6	70	-61
0	8	6	76	-70
0	9	6	79	-84
0	10	6	-17	-7
0	11	6	23	-32
0	12	6	27	-23
0	13	6	49	-51
0	14	6	-20	12
0	15	6	-21	-8
1	1	6	0	29
1	2	6	19	-20
1	3	6	18	-15
1	4	6	86	-80
1	5	6	54	53
1	6	6	36	-37
1	7	6	45	38
1	8	6	57	-60
1	9	6	72	73
1	10	6	-17	-7
0	11	6	-18	-32
1	12	6	28	-34
1	13	6	74	74
1	14	6	-20	13
1	15	6	39	41
2	1	6	19	16
2	2	6	139	-151
2	3	6	49	-45
2	4	6	83	-80
2	5	6	-11	-9
2	6	6	107	-105
2	7	6	80	-75
2	8	6	35	-34
2	9	6	26	-26

7	1	6	57	-53
7	2	6	107	-105
7	3	6	-14	-3
7	4	6	73	-76
7	5	6	15	-14
7	6	6	107	-112
7	7	6	42	45
7	8	6	49	-52
7	9	6	-18	26
7	10	6	88	-71
7	11	6	54	56
7	12	6	24	-26
7	13	6	34	37
8	1	6	-15	3
8	2	6	28	-30
8	3	6	35	33
8	4	6	51	-48
8	5	6	19	-18
8	6	6	-17	1
8	7	6	19	16
8	8	6	26	-19
8	9	6	-19	-14
8	10	6	17	17
8	11	6	-20	17
8	12	6	-20	0
8	13	6	-21	1
9	1	6	24	-27
9	2	6	54	-53
9	3	6	47	-44
9	4	6	106	-106
9	5	6	-17	6
9	6	6	67	-69
9	7	6	-18	-1
9	8	6	84	-83
9	9	6	32	35
9	10	6	42	-46
9	11	6	24	21
9	12	6	48	-51
10	1	6	30	36
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10	4	6	-17	5
10	5	6	-18	14
10	6	6	-18	-8
10	7	6	-19	-12
10	8	6	19	23
10	9	6	-20	18
10	10	6	-20	8
10	11	6	-21	-0
11	1	6	62	-65
11	2	6	65	-70
11	3	6	27	-26
11	4	6	53	-52
11	5	6	39	-33
11	6	6	74	-76
11	7	6	-20	8
11	8	6	37	-39
11	9	6	-20	-1
11	10	6	50	-58
12	1	6	-19	-4
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12	3	6	-19	15
12	4	6	-19	-9

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3	3	7	22	17
3	4	7	38	-44
3	5	7	69	-65
3	6	7	71	-71
3	7	7	22	-24
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3	9	7	75	-78
3	10	7	54	-47
3	11	7	50	-49
3	12	7	-21	-15
3	13	7	74	-72
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4	1	7	-11	10
4	2	7	137	139
4	3	7	-12	9
4	4	7	58	61
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4	6	7	89	89
4	7	7	-16	-10
4	8	7	-17	20
4	9	7	39	-34
4	10	7	26	32
4	11	7	-21	-8
4	12	7	-22	-8
4	13	7	-22	-15
4	14	7	-23	13
5	1	7	68	53
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5	5	7	-15	-4
5	6	7	66	-65
5	7	7	64	-59
5	8	7	81	-78
5	9	7	37	-35
5	10	7	41	-39
5	11	7	78	-77
5	12	7	46	-40
5	13	7	46	-41
6	1	7	43	40
6	2	7	44	50
6	3	7	-15	-11
6	4	7	72	77
6	5	7	-16	3
6	6	7	19	25
6	7	7	29	-21
6	8	7	37	44
6	9	7	-20	-1
6	10	7	-21	-9
6	11	7	-21	-12
6	12	7	-22	20
6	13	7	-22	11
7	1	7	25	19
7	2	7	78	-87
7	3	7	51	47
7	4	7	59	-64
7	5	7	27	-22
7	6	7	83	-89
7	7	7	-19	4

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14	2	7	-22	-20
14	3	7	-22	-15
14	4	7	-23	-1
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0	1	8	0	14
0	2	8	102	114
0	3	8	50	47
0	4	8	45	44
0	5	8	69	64
0	6	8	74	72
0	7	8	85	77
0	8	8	-18	6
0	9	8	57	61
0	10	8	45	38
0	11	8	55	58
0	12	8	-22	-13
0	13	8	37	38
0	14	8	-24	12
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1	4	8	34	35
1	5	8	-14	7
1	6	8	52	53
1	7	8	52	-51
1	8	8	48	44
1	9	8	-19	-19
1	10	8	22	30
1	11	8	52	-60
1	12	8	-22	15
1	13	8	-23	-23
1	14	8	-24	4
2	1	8	14	-9
2	2	8	52	58
2	3	8	-11	6
2	4	8	107	101
2	5	8	47	44
2	6	8	23	23
2	7	8	51	48
2	8	8	65	58
2	9	8	44	44
2	10	8	-20	0
2	11	8	40	39
2	12	8	31	23
2	13	8	27	29
3	1	8	20	-17
3	2	8	81	70
3	3	8	33	22
3	4	8	80	79
3	5	8	36	-39
3	6	8	79	80
3	7	8	-17	-0
3	8	8	74	73
3	9	8	51	-57
3	10	8	41	47
3	11	8	-22	-22
3	12	8	28	33
3	13	8	57	-52
4	1	8	-12	-12
4	2	8	112	101
4	3	8	-13	6
4	4	8	43	36

9	7	8	27	-21
9	8	8	70	72
9	9	8	-23	0
9	10	8	69	65
10	1	8	-20	-12
10	2	8	-20	-3
10	3	8	-21	-6
10	4	8	36	28
10	5	8	-22	6
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11	1	8	-21	17
11	2	8	57	61
11	3	8	34	41
11	4	8	72	76
11	5	8	-22	-3
11	6	8	64	67
11	7	8	-23	18
11	8	8	58	60
12	1	8	-22	-11
12	2	8	23	18
12	3	8	-23	3
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12	7	8	-24	3
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0	1	9	0	12
0	2	9	83	-101
0	3	9	-12	12
0	4	9	134	-133
0	5	9	37	37
0	6	9	48	-49
0	7	9	29	25
0	8	9	82	-75
0	9	9	35	34
0	10	9	-23	-12
0	11	9	25	22
0	12	9	23	-23
0	13	9	26	22
1	1	9	0	24
1	2	9	-10	11
1	3	9	25	-15
1	4	9	25	24
1	5	9	61	51
1	6	9	21	16
1	7	9	-19	15
1	8	9	32	28
1	9	9	85	75
1	10	9	-23	9
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1	12	9	-25	12
1	13	9	73	73
2	1	9	13	-14
2	2	9	144	-158
2	3	9	-13	12
2	4	9	78	-83
2	5	9	-16	14
2	6	9	92	-94
2	7	9	29	29
2	8	9	-21	-31

7	11	9	61	60
8	1	9	-21	-8
8	2	9	28	-30
8	3	9	23	-15
8	4	9	50	-52
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8	6	9	-23	-1
8	7	9	-24	-3
8	8	9	-25	-18
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8	10	9	26	23
9	1	9	29	-31
9	2	9	28	31
9	3	9	44	-43
9	4	9	45	48
9	5	9	-24	8
9	6	9	31	36
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9	8	9	35	39
9	9	9	38	40
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11	2	9	36	35
11	3	9	-25	-19
11	4	9	33	31
11	5	9	31	-36
11	6	9	36	37
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12	1	9	-25	1
12	2	9	-26	16
12	3	9	-26	-4
12	4	9	-26	-4
12	5	9	-26	5
13	1	9	31	-37
13	2	9	-26	18
13	3	9	45	-50
0	0	10	0	-59
0	1	10	0	-5
0	2	10	21	-22
0	3	10	62	-58
0	4	10	59	-54
0	5	10	45	-46
0	6	10	-18	-10
0	7	10	87	-84
0	8	10	46	-37
0	9	10	49	-51
0	10	10	-23	2
0	11	10	53	-61
0	12	10	-25	-17
1	1	10	0	18
1	2	10	49	-52
1	3	10	29	-21
1	4	10	23	-26
1	5	10	21	24
1	6	10	71	-62
1	7	10	-19	-7

7	3	10	-20	6
7	4	10	100	-99
7	5	10	26	-15
7	6	10	75	-77
7	7	10	-23	17
7	8	10	78	-81
7	9	10	-25	-4
7	10	10	44	-47
8	1	10	45	41
8	2	10	-21	0
8	3	10	-22	4
8	4	10	37	-24
8	5	10	-23	11
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Table 3. *Interatomic distances and angles in* $Zr(IO_3)_4$

Within the iodate group

$I-O_1$	$1{\cdot}814 \pm 0{\cdot}022$ Å	$\angle O_1-I-O_2$	$98° 58' \pm 52'$
$I-O_2$	$1{\cdot}836 \pm 0{\cdot}022$	$\angle O_1-I-O_3$	$92° 47' \pm 56'$
$I-O_3$	$1{\cdot}846 \pm 0{\cdot}024$	$\angle O_2-I-O_3$	$92° 30' \pm 1°$
O_1-O_2	$2{\cdot}78 \pm 0{\cdot}03$	$\angle O_1-O_2-O_3$	$58° 6' \pm 50'$
O_1-O_3	$2{\cdot}64 \pm 0{\cdot}03$	$\angle O_2-O_3-O_1$	$58° 53' \pm 50'$
O_2-O_3	$2{\cdot}67 \pm 0{\cdot}03$	$\angle O_3-O_1-O_2$	$63° 1' \pm 50'$

Within the antiprism

$Zr-O_2$	$2{\cdot}197 \pm 0{\cdot}018$ Å	O_2-O_2	$2{\cdot}62 \pm 0{\cdot}03$ Å
$Zr-O_3$	$2{\cdot}216 \pm 0{\cdot}024$	O_3-O_3	$2{\cdot}68 \pm 0{\cdot}03$
		O_2-O_3	$2{\cdot}69 \pm 0{\cdot}03$
		O_2-O_3	$2{\cdot}77 \pm 0{\cdot}03$

Non-bonded I–O distances

$I-O_1$	$2{\cdot}94 \pm 0{\cdot}02$ Å	$I-O_3$	$2{\cdot}94 \pm 0{\cdot}02$ Å
$I-O_1$	$2{\cdot}55 \pm 0{\cdot}02$	$I-O_3$	$3{\cdot}11 \pm 0{\cdot}02$
$I-O_2$	$2{\cdot}83 \pm 0{\cdot}02$		

Distances across the $\bar{4}$ axis

O_1-O_1	$4{\cdot}46 \pm 0{\cdot}03$ Å
O_2-O_2	$5{\cdot}01 \pm 0{\cdot}03$
O_3-O_3	$5{\cdot}14 \pm 0{\cdot}03$

(1954), in a redetermination of the structure of HIO_3 by neutron diffraction, found this distance to be 2·50 Å. Other examples of a short non-bonded I–O distance are found in $Ce(IO_3)_4$ (2·68 Å) and for three of the four non-equivalent iodate groups in $Ce(IO_3)_4.H_2O$ (2·56 Å). In all cases this short distance is to an oxygen which is not part of the coordination polyhedron of the cation. It is interesting to note that in $NaIO_3$ (MacGillavry & Van Eck, 1943) the two non-equivalent oxygen atoms in the structure are both in the coordination sphere of the sodium and there are no short non-bonded I–O distances.

In $Zr(IO_3)_4$ the iodine has five non-bonded oxygen neighbors in addition to the three oxygen atoms in the iodate group. These eight neighbors form a rather crude antiprism. A somewhat similar arrangement of eight oxygen neighbors is found in $Ce(IO_3)_4$ and $NaIO_3$ while in HIO_3 and $Ce(IO_3)_4.H_2O$ all iodine atoms have a more or less distorted octahedral coordination of oxygen atoms.

An extremely interesting feature of this structure is the large amount of empty space. With the exception of O_1, all atoms are in the quadrants containing the fourfold axes, and the O_1 atoms are just outside these quadrants. Voids surrounding the fourfold inversion axes extend completely through the crystal. The closest approach of atoms across the $\bar{4}$ axis is an O_1-O_1 distance of 4·46 Å. In addition, there are two large holes between zirconium atoms along the fourfold axis. Four O_1 and four O_2 atoms at the corners of a slightly distorted antiprism surround one hole. Four O_1 and four O_3 atoms at the corners of a slightly distorted cube surround the other hole. These two holes are slightly larger than the hole in which zirconium is found.

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