In due time an example of this technique will be given.

The use of anomalous scattering in the Patterson technique has been outlined by Pepinsky (Okaya, Saito & Pepinsky, 1955).

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

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The crystal structure of $Ce(IO_3)_4$ has been determined by single-crystal methods. Refinement of the structure was made by the method of least squares. $Ce(IO_3)_4$ is tetragonal, space group $P4_2/n$, with $a = 9{\cdot}90$ and $c = 5{\cdot}32$ Å. The cerium atoms are surrounded by eight oxygens at the corners of a distorted Archimedes antiprism. Two of the three oxygens in each iodate group are coordinated to cerium while the third oxygen is isolated. The three I–O bond lengths are 1·78, 1·84 and 1·83 Å, all ±0·09 Å. The average Ce–O distance is 2·33 Å. Within the limits of error, the iodate group has trigonal symmetry. Each iodine atom has five oxygen neighbors in addition to the three in the iodate group.

Introduction

In connection with some work being done in this laboratory by Dr Burton Lewis on magnetic properties of plutonium compounds it was desirable to know the crystal structure of $Pu(IO_3)_4$, particularly the coordination of the oxygen atoms about the plutonium. Instead of studying $Pu(IO_3)_4$ itself, the structure determination of the isomorphous $Ce(IO_3)_4$ was undertaken, primarily because Ce has a lower scattering power than Pu and also because of the health hazard of working with Pu compounds.

Experimental

The preparation of $Ce(IO_3)_4$, its morphology, optical properties and X-ray diffraction data have already been published (Staritzky & Cromer, 1956).

Weissenberg and precession photographs with Cu and Mo radiations showed $Ce(IO_3)_4$ to be tetragonal with

$$a = 9{\cdot}90 \pm 0{\cdot}02,\ c = 5{\cdot}32 \pm 0{\cdot}01\ \text{Å}\,.$$

Reflections of the type $hk0$ were observed only with $h+k = 2n$, and of the type $00l$ only with $l = 2n$. The space group is thus uniquely established as C_{4h}^4–$P4_2/n$. The calculated density with two formula units per cell is 5·35 g.cm.$^{-3}$. The observed density is 5·4 g.cm.$^{-3}$. Most of the crystals gave streaked diffraction spots, although the crystals were externally well developed.

A small crystal that gave a good diffraction pattern was ultimately found. This crystal showed the forms {001}, {111}, {100} and {110}. The distance across the crystal was 0·073 mm. and the distance between {001} faces was 0·032 mm. The cross-section normal to the c axis was an octagon, a favorable shape for minimizing absorption errors. As a rough approximation, the over-all shape of the crystal was that of an oblate spheroid. This crystal was mounted on the c axis and hkl data for $l = 0$–3 were obtained with a Geiger-counter attachment on the Weissenberg camera (Evans, 1953), using Mo $K\alpha$ radiation. Intensities were corrected for the Lp factors and converted to structure factors on a relative scale. No absorption corrections were made.

Determination of the structure

There were two Ce atoms and eight iodate groups to be located in the unit cell. In $P4_2/n$ there are two equivalent sets of twofold positions. The Ce atoms were therefore placed in 2(*a*) at 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. (The origin at $\bar{4}$ is used throughout this paper.) This special position contributes only to reflections with $h+k+l = 2n$ and it was observed that these reflections were in

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* Work done under the auspices of the Atomic Energy Commission.

general stronger than the others. The iodate ions were presumed to be in the general position 8(*g*). A Patterson projection in the *xy* plane was then computed. With the aid of this projection the iodine was found to be at $x \approx 0{\cdot}275$ and $y \approx 0{\cdot}002$. The Patterson projection also verified that the cerium atoms were in 2(*a*).

All reflections of the type *hhl* with *l* odd were absent with the exception of 331, which was weak. This pseudo-extinction can be accounted for by placing the iodine at $z \approx \frac{1}{2}$. Rough structure-factor calculations showed agreement was best with $z \approx 0{\cdot}46$.

An *hk*0 Fourier (Fig. 1) was next calculated, using phases determined by the Ce and I. There are numerous spurious peaks, particularly around the heavy atoms. In addition, there are two larger peaks which were interpreted as oxygen atoms, the plane of the three oxygen atoms of the iodate group being approximately normal to the *xy* plane and one I–O bond being nearly parallel with the *xy* plane. Two oxygen atoms therefore partially overlap in projection. The orientation of the iodate groups, as finally determined, is indicated in Fig. 1.

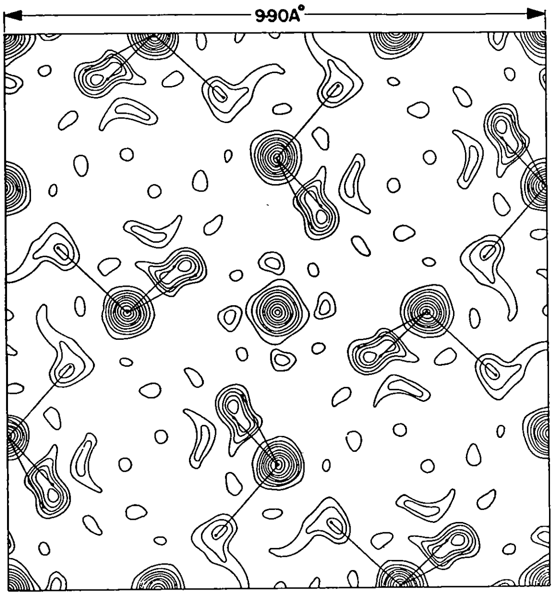

Fig. 1. Fourier projection of $Ce(IO_3)_4$ down the *c* axis. Contours are at equal arbitrary intervals, except that around the Ce and I the contours are at five times the interval elsewhere.

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

Variable	Initial value	Final value
K_0*	0·581	0·5282±0·0091
K_1	0·752	0·7183±0·0121
K_2	0·752	0·7125±0·0133
K_3	0·752	0·6735±0·0151
B(Ce)	1·00	0·903±0·112 × 10^{-16} cm.^{2}
B(I)	1·00	0·771±0·068 × 10^{-16} cm.^{2}
B(O)	1·50	1·53±0·48 × 10^{-16} cm.^{2}
x(I)	0·276	0·2769±0·0003
x(O_1)	0·410	0·4140±0·0039
x(O_2)	0·200	0·1900±0·0046
x(O_3)	0·170	0·1504±0·0045
y(I)	0·002	0·0014±0·0003
y(O_1)	0·125	0·1173±0·0039
y(O_2)	0·060	0·0826±0·0044
y(O_3)	0·080	0·0670±0·0044
z(I)	0·460	0·4633±0·0009
z(O_1)	0·475	0·4816±0·0125
z(O_2)	0·186	0·1984±0·0118
z(O_3)	0·709	0·6827±0·0117

* The K_i are defined by $F_o = KF_c$ and are reciprocal to the scale factor usually used.

Table 2. *Interatomic distances and angles in* $Ce(IO_3)_4$

The Roman numerals i–viii are used to identify crystallographically related atoms in the order given in the *Internationale Tabellen* for $P4_2/n$. If an atom is not in the unit cell whose origin is at 0, 0, 0, the cell in which it is located is indicated in parentheses

Within the iodate group

Ii—O$_1$i	1·78±0·09 Å	O$_1$–I–O$_2$	96·5±3·9°
–O$_2$i	1·84±0·09	O$_1$–I–O$_3$	104·8±3·9
–O$_3$i	1·83±0·09	O$_2$–I–O$_3$	90·6±3·9
O$_1$i–O$_2$i	2·70±0·13	O$_1$–O$_2$–O$_3$	65·2±3·1
O$_1$i–O$_3$i	2·86±0·13	O$_1$–O$_3$–O$_2$	58·9±3·1
O$_2$i–O$_3$i	2·61±0·13	O$_2$–O$_1$–O$_3$	55·9±3·1

Distance from I to the plane O$_1$–O$_2$–O$_3$ = 0·88.

Ce–O < 3·0 Å

Ceii–O$_3$iii	2·31±0·09 Å	Ceii–O$_2$iii	2·35±0·09 Å
–O$_3$iv	2·31±0·09	–O$_2$iv	2·35±0·09
–O$_3$vii	2·31±0·09	–O$_2$vii	2·35±0·09
–O$_3$viii	2·31±0·09	–O$_2$viii	2·35±0·09

Ce–I < 4·0 Å

Ceii–Iiii	3·69±0·01 Å	Ceii–Iiii (001)	3·96±0·01 Å
–Iiv	3·69±0·01	–Iiv (001)	3·96±0·01
–Ivii	3·69±0·01	–Ivii (00$\bar{1}$)	3·96±0·01
–Iviii	3·69±0·01	–Iviii (00$\bar{1}$)	3·96±0·01

I–I < 4·4 Å

Ii–Iviii	4·10±0·01 Å	Ii–Ivii (0$\bar{1}\bar{1}$)	4·10±0·01 Å
–Iviii (00$\bar{1}$)	4·10±0·01	–Iv ($\bar{1}$00)	3·90±0·01
–Ivii (0$\bar{1}$0)	4·10±0·01	–Ivi (0$\bar{1}$0)	3·90±0·01

Inter-iodate O–O < 3·0 Å

O$_1$i–O$_2$viii	2·78±0·13 Å	O$_2$i–O$_3$vi (0$\bar{1}$0)	2·68±0·13 Å
–O$_1$ii (0$\bar{1}$0)	2·88±0·13	–O$_3$v ($\bar{1}$00)	2·71±0·13

Inter-iodate I–O < 3·3 Å

Iviii–O$_1$i	2·90±0·09 Å	Iviii–O$_1$i (001)	3·07±0·09 Å
–O$_2$iv (001)	3·25±0·09	–O$_1$vii (0$\bar{1}$0)	3·28±0·09
–O$_3$iv	2·68±0·09		

Assuming the iodate group to be a trigonal pyramid with an I–O distance of 1·8 Å, and with the aid of the Fourier projection, it was possible to assign approximate *x*, *y*, *z* coordinates to all atoms. These coordinates (Table 1) were used as a starting point for a least-squares refinement.

The parameters in the refinement were the twelve coordinates of the iodate group, isotropic temperature factors for each chemical species of atom, and separate scale factors for each layer. Separate scale factors were necessary because data had been obtained for rotation

Table 3. *Observed and calculated structure factors for* $Ce(IO_3)_4$

Reflections marked with a single prime occur at too small an angle to be observed.

Reflections marked with a double prime were initially unobserved because they are rather weak or in a few cases because of arithmetic errors in computing the angular settings of the counter. They were thus omitted from the least-squares treatment. They were reinvestigated after it was found that the calculated values were equal to or greater than the estimated minimum.

k	F_o	F_c
1k0		
1	0'	54
3	86	76
5	51"	-49
7	151	151
9	86	-78
11	102	98
13	<48	-29
15	<53	44
2k0		
0	133	132
2	258	-272
4	27	-21
6	108	107
8	16	10
10	<40	-9
12	35	-53
14	<50	10
16	43	-59
3k0		
1	166	163
3	229	220
5	57	49
7	243	246
9	<38	3
11	153	146
13	<48	18
4k0		
0	286	305
2	122	112
4	299	300
6	96	95
8	150	151
10	93	97
12	29	51
14	103	99
5k0		
1	<26	4
3	40	48
5	168	-145
7	66	68
9	92	-98
11	29	44
13	84	-63
6k0		
0	119	108
2	91	-78
4	109	115
6	100	-67
8	<39	23
10	<44	5
12	<48	-16
14	<53	43
7k0		
1	139	144
3	205	210
5	51	55
7	213	204
9	48	53
11	149	154
13	<52	29
8k0		
0	174	168
2	35	-35
4	156	156
6	<39	1
8	100	71
10	<47	48
12	<51	14
14	58"	60
9k0		
1	70	-70
3	<38	12
5	77	-86
7	19	22
9	84	-91
11	<51	29
13	60	-63
10,k,0		
0	152	147
2	36	-40
4	126	122
6	<44	7
8	55	66
10	<50	49
12	<53	16
11,k,0		
1	98	107
3	142	146
5	49	67
7	135	138
9	<51	21
11	112	119
12,k,0		
0	102	83
2	57	-71
4	46	57
6	<48	-27
8	<51	19
10	<53	3
13,k,0		
1	<47	-19
3	<48	1
5	67	-46
7	<52	33
9	63"	-63
14,k,0		
0	135	130
2	<50	20
4	116	111
6	<53	34
8	86	66
15,k,0		
1	58	55
1k1		
0	0'	-55
1	0'	-10
2	277	293
3	29"	-28
4	<17	8
5	<19	3
6	156	163
7	<24	-12
8	59	57
9	<27	25
10	70	59
11	<31	-29
12	94	79
13	<35	9
14	<37	1
15	<39	-13
2k1		
0	80	-85
1	233	233
2	<14	10
3	133	129
4	42	-47
5	292	305
6	<22	-11
7	74	72
8	<26	-12
9	213	216
10	59	-26
11	35"	36
12	<33	-17
13	129	131
14	<37	-18
15	46	38
3k1		
0	130	-135
1	25	27
2	195	202
3	23	24
4	90	-84
5	32	40
6	46	52
7	<24	-12
8	32"	-39
9	33	33
10	<30	-8
11	<32	-20
12	<34	32
13	<35	18
14	<37	-39
4k1		
0	<17	-16
1	29"	-27
2	69	77
3	106	-106
4	<21	8
5	73	72
6	<24	11
7	93	-94
8	<27	2
9	59	64
10	<30	13
11	92	85
12	<34	14
13	<36	37
5k1		
0	45	46
1	<19	-7
2	340	297
3	40	-42
4	57	55
5	<23	-15
6	187	182
7	47	-53
8	87	87
9	<30	11
10	94	97
11	<33	-22
12	114	117
13	<37	0
6k1		
0	54	-44
1	156	153
2	<22	-4
3	71	69
4	37	-43
5	173	173
6	<26	-3
7	<27	15
8	<29	-11
9	152	153
10	<32	6
11	<34	0
12	<35	0
13	92	95
7k1		
0	169	-167
1	40	17
2	41	40
3	<24	5
4	118	-117
5	46	44
6	56"	30
7	<29	5
8	50"	-44
9	32"	39
10	<33	-34
11	<35	4
12	<37	-3
8k1		
0	39	-33
1	64	59
2	28"	28
3	<26	3
4	<27	-2
5	83	87
6	<29	27
7	53"	-44
8	<32	5
9	90	95
10	<34	-1
11	<36	-30
9k1		
0	52	48
1	<27	-11
2	212	218
3	<28	-16
4	67	66
5	<30	1
6	163	171
7	32"	-36
8	92	85
9	<34	-10
10	74	-78
10,k,1		
0	<29	-12
1	54	46
2	62	30
3	<30	1
4	<30	-12
5	72	73
6	<32	9
7	42"	-40
8	<35	-10
9	83	78
10	<37	-1
11,k,1		
0	98	-95
1	<31	17
2	49"	44
3	<32	6
4	91	-90
5	<33	18
6	<34	9
7	<35	-1
8	<36	-39
12,k,1		
0	<33	-26
1	65	63
2	<33	1
3	45"	37
4	<34	-25
5	106	106
6	<36	1
7	<37	11
13,k,1		
0	<35	25
1	<35	-20
2	132	140
3	<35	-18
4	<36	23
5	<36	2
6	61	97
14,k,1		
0	<37	-6
1	<37	-10
2	<37	20
3	<37	-28
15,k,1		
0	74	-51
1	<39	9
2	49	48
1k2		
0	0'	79
1	0'	-14
2	50	-59
3	183	176
4	48	49
5	<19	2
6	42	-41
7	127	122
8	<26	22
9	64	-61
10	<29	22
11	76	73
12	<33	-2
2k2		
0	90	103
1	<13	1
2	151	-149
3	81	84
4	74	71
5	<20	16
6	111	-108
7	79	82
8	<26	-9
9	<28	3
10	<30	-8
3k2		
0	<15	2
1	125	126
2	111	-120
3	198	195
4	38	37
5	39"	45
6	42	-45
7	168	165
8	<27	-10
9	<28	6
10	<30	-11
4k2		
0	276	283
1	64	-67
2	33"	22
3	<19	-13
4	247	243
5	58	-52
6	73	73
7	<26	4
8	125	119
9	59	-65
10	108"	100
5k2		
0	114	113
1	43	-38
2	<20	-13
3	<21	-7
4	80	93
5	83	-85
6	<25	16
7	66	62
8	<28	28
9	74	-76
10	<32	26
6k2		
0	106	101
1	31	34
2	97	-96
3	31"	31
4	107	105
5	<25	-9
6	<27	-20
7	42	51
8	<29	16
9	<30	-21
7k2		
0	<23	18
1	147	145
2	93	-93
3	169	163
4	<26	-14
5	71	70
6	44	-53
7	184	184
8	<31	-27
9	29"	36
8k2		
0	175	173
1	<26	-9
2	<26	-9
3	<27	-2
4	119	120
5	31"	-34
6	<29	18
7	31"	31
8	65	60
9	30"	35
9k2		
0	78	80
1	31"	-28
2	<28	2
3	<28	3
4	56	57
5	87"	-78
6	<31	18
7	36"	34
8	43"	40
9	67	-79
10,k,2		
0	130	128
1	<29	-2
2	<30	-18
3	<30	11
11,k,2		
0	<31	0
1	103	99
1k3		
0	0'	-3
1	0'	0
2	206	204
3	50	-56
4	<19	8
5	49	44
6	122	106
7	78	-74
8	57	52
9	36	34
10	48	39
2k3		
0	142	-153
1	163	165
2	<16	12
3	105	91
4	129	-126
5	205	182
6	22"	-27
7	68	56
8	71	-71
9	180	166
10	37"	-47
3k3		
0	76	-65
1	47	47
2	136	125
3	<19	-10
4	61	-53
5	84	81
6	34	33
7	<26	-16
8	<29	-2
9	61	76
10	<33	11
4k3		
0	21"	-21
1	<19	-14
2	121	127
3	42	-56
4	<22	-8
5	53	59
6	83	79
7	57	-49
8	<30	26
9	75	69
10	<33	29
5k3		
0	37	33
1	46	-49
2	227	204
3	79	-79
4	71	64
5	<25	0
6	153	138
7	112	-81
8	76	72
9	<32	7
10	92	76
6k3		
0	111	-105
1	140	123
2	34	31
3	85	73
4	76	-74
5	153	136
6	<29	6
7	<30	8
8	35"	-35
9	130	110
7k3		
0	101	-89
1	66	70
2	53	51
3	29"	36
4	72	-68
5	86	83
6	<30	19
7	<31	-2
8	46"	-37
8k3		
0	44"	-43
1	52	55
2	64	60
3	<29	5
4	38	-35
5	65	60
6	<32	33
7	<33	-33
8	<34	-4
9k3		
0	43	33
1	51	-48
2	163	150
3	79	-73
4	35	46
5	<32	-18
6	140	128
10,k,3		
0	41	-43
1	<32	27
2	48"	46
3	<33	5
4	<33	-28
5	79	64

about the *c* axis only. Internal correlation of the data was therefore not possible. Absorption errors would have been quite serious if the crystal had been mounted on any other axis. A desirable feature of the separate scale factors was that anisotropy in thermal motion could be partially accounted for. In so far as the anisotropy is the same for all atoms it can be represented by a constant multiplying factor for each layer. The shape of the crystal was such that the absorption error was primarily dependent on the diffraction angle and not greatly influenced by the angle about the rotation axis. The absorption error is, in effect, combined with the apparent thermal parameters. The complete 19 × 19 normal equations were used, no terms being neglected. The computing was done on the Maniac. The problem was allowed to go through seven cycles, although three cycles were sufficient to reduce all changes in variables below their standard deviation. About 35 min. were required per cycle. The results, with their standard deviations, are given in

Table 1. The standard deviations have been computed in the usual way, using the diagonals of the inverse matrix. The $\sigma(Z_i)$ are relatively large because of the limitation $l \leq 3$.

All observations were weighted equally. Form factors for Ce and I were taken from the *Internationale Tabellen* (1935) and were each reduced by 1·3 electrons to correct for anomalous dispersion (James, 1948). The McWeeny (1951) form factors for oxygen were used. The final set of observed and calculated structure factors is given in Table 3. $R = 7{\cdot}9\%$, where values of $F_o = 0$ have been omitted. If the oxygen contribution to the structure factors is omitted $R = 13{\cdot}1\%$, a substantial increase.

Inspection of Table 3 shows that the lower limit of observed reflections is rather high. The small size of the crystal and the low efficiency of a Geiger tube with Mo $K\alpha$ radiation are responsible for this. Had the structure determination been made entirely by Fourier methods, series-termination effects could have been large. The least-square method does not suffer from this restriction on the quantity of experimental data.

Discussion of the structure

A perspective drawing of the structure is given in Fig. 2. The various interatomic distances and angles are given in Table 2.

Ibers (1956) has reported the structure of $Ce(IO_3)_4.H_2O$. Our results agree fairly well and the structures are similar in some respects. In both compounds, the cerium atoms are surrounded by eight oxygens at the corners of a distorted Archimedes antiprism. However, because of the higher crystallographic symmetry of $Ce(IO_3)_4$, its antiprism is not as distorted. The antiprism coordination can be seen best by viewing in a direction approximately normal to the 110 planes. In both compounds two of the three oxygens in each iodate group are coordinated to cerium atoms while the third I–O bond is isolated. The average value of the three O–I–O angles is 97·3°. If Cruickshank's (1949) criteria are applied it is found that the differences in these angles are not significant. Likewise, the differences in the O–O–O angles from 60° are not significant.

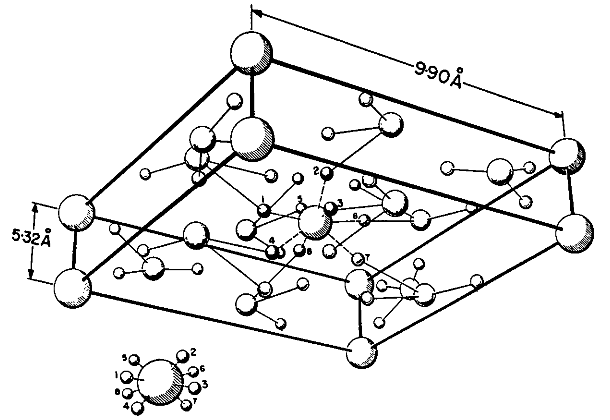

Fig. 2. Perspective drawing of the unit cell of $Ce(IO_3)_4$. The offset is a view of the Ce atom at the center of the cell as one looks along the [110] axis. The relative sizes of the atoms are distorted for the sake of clarity. In decreasing order of size the atoms are Ce, I and O.

One of the three I–O bonds appears shorter than the other two. Although this bond contraction is less than the standard deviation in the I–O bonds, it is what one might intuitively expect. It is an isolated bond, the oxygen atom not being a neighbor of a cerium atom.

In the anhydrous compound the iodine has five oxygen neighbors at distances ranging from 2·68 to 3·28 Å in addition to the three oxygens in the iodate ion. In the hydrated compound each iodine has only three extra oxygen neighbors.

There are no unusual distances and all compare well with those in other structures. Ibers (1956) has tabulated the interatomic distances observed in other iodates and in other cerium compounds. This tabulation is convenient for comparison with the present work.

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