Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1972). **B28**, 979

The crystal structure of $CsIOF_4$.†

By R. R. Ryan and L. B. Asprey, *Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico* 87544, *U.S.A.*

(*Received* 2 *June* 1971)

The colorless crystals of $CsIOF_4$ are orthorhombic with space group *Pmcn*, $Z=4$. Room-temperature cell constants are $a=6{\cdot}024$, $b=15{\cdot}488$, and $c=6{\cdot}214$ Å. Data were collected on an automated four-circle diffractometer. The structure contains IOF_4^- anions (idealized symmetry C_{4v}) with four fluorine atoms in the equatorial plane and the oxygen atom on the axial site. The cesium ion has a coordination number of 10.

Recrystallization of stoichiometric amounts of CsI and IF_5 from acetonitrile produced colorless single crystals with the proper unit-cell volume to contain four molecules of $CsIF_6$. The Raman spectrum of the substance showed, however, an intense peak at 888 wave numbers which is expected for an I=O stretching frequency. Since the only ion which contains an I=O bond and has the right molecular volume for IF_6^- is IOF_4^-, and since neither chemical nor structural information existed in the literature for this ion, an X-ray investigation was undertaken.

Several crystals were placed in glass capillaries in an inert atmosphere and examined by precession techniques. The crystal faces were of the prism {011} and of the pinacoid {100}. The photographs taken with Mo $K\alpha$ radiation showed orthorhombic symmetry with the systematic absences: $h0l$, l odd; $hk0$, $h+k$ odd. The systematic absences are consistent with the space groups *Pmcn* and $P2_1cn$. In all cases, the a^* axis was approximately along the axis of the glass capillary. ω scans of several reflections on an automated Picker diffractometer showed that all the crystals were fractured about the a^* axis so that the splitting of the peaks was most severe for large k and/or l values. The best crystal showed three peaks of approximately equal intensity for which the maxima of the 'satellite' peaks were separated from the central peak by about 0·1° in ω for the worst reflections investigated. This crystal was used for determing cell constants and for data collection.

Cell dimensions and their estimated standard errors obtained by least-squares refinement on the positions of 12 high-order reflections as determined on the diffractometer using Mo $K\alpha_1$ radiation ($\lambda=0{\cdot}70930$ Å) are $a=6{\cdot}024$ (2), $b=15{\cdot}488$ (6), and $c=6{\cdot}214$ (3) Å.

Intensities were collected using Mo $K\alpha$ radiation, a single-crystal graphite monochromator (002 plane), and a take-off angle of 5°. The count was taken using a θ–2θ scan over a 2θ range of 2° in 0·05° steps for two sec at each step; stationary-counter stationary-crystal background counts of 20 sec were taken at each end of the scan. Intensities were measured for all hkl planes in the positive octant and for their Friedel related reflections, resulting in 2315 measurements. The redundant (assuming *Pmcn*) reflections were averaged, resulting in 1003 reflections observed according to the criterion $I \geq 3\sigma(I)$ where $\sigma^2(I)=f^2(t)\,(T+B)+\sigma_s^2(T-B)^2$, T being the total count, B the estimated background, and $f(t)$ a time-dependent correction factor determined as described below. The quantity σ_s^2 was taken to be $2{\cdot}5\times10^{-4}$, a number which we feel to be a reasonable estimate of the normalized variance of a re-

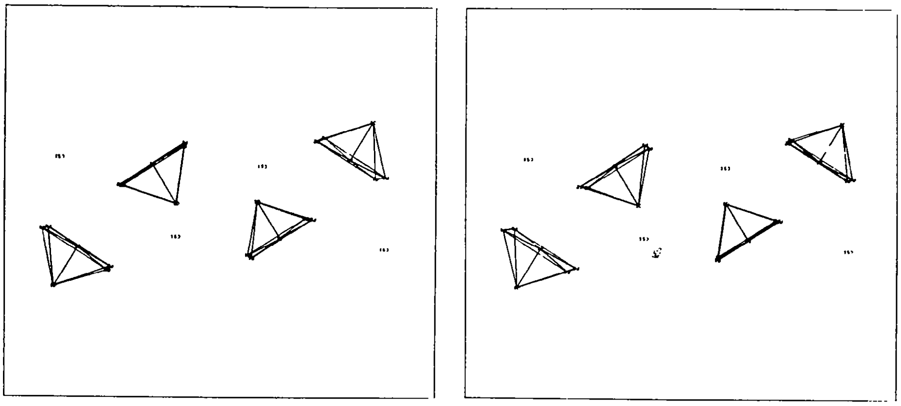

Fig. 1. Stereo view of the contents of the unit cell looking down the x axis with the y axis to the right. The four fluorine atoms near $y=\frac{1}{2}$ (and their symmetry equivalents) are F(1).

---

† This work was performed under the auspices of the United States Atomic Energy Commission.

Table 1. *Structure factors*

Column headings are l, F_o and F_c

H= 0 L= 0		
0	0	603
2	53	57
4	248	265
6	69	66
8	44	46
10	31	31
12	116	114
14	71	71
16	91	89
18	60	59
20	38	36
22	31	27
H= 0 L= 1		
1	37	41
2	32	36
3	50	50
4	166	194
5	5	5
6	71	83
7	-4	6
8	174	198
9	26	29
10	83	95
11	-4	1
12	117	120
13	-5	0
14	57	61
15	27	28
16	17	20
17	6	7
18	9	7
19	14	13
20	18	17
21	-6	1
22	32	30
23	-7	5
H= 0 L= 2		
0	288	298
1	23	25
2	7	10
3	125	141
4	183	213
5	10	11
6	38	43
7	55	64
8	8	7
9	54	60
10	12	12
11	46	52
12	69	79
13	10	12
14	45	50
15	6	6
16	68	72
17	-5	3
18	49	52
19	9	9
20	31	30
21	-6	2
22	29	25
H= 0 L= 3		
1	48	49
2	-5	3
3	72	76
4	128	140
5	6	9
6	23	25
7	29	34
8	149	177
9	-5	6
10	59	70
11	14	16
12	63	77
13	0	0
14	26	31
15	40	44
16	11	12
17	6	5
18	-6	2
19	27	28
20	21	21
21	-7	2
22	24	21
H= 0 L= 4		
0	140	143
1	15	15
2	6	5
3	62	60
4	133	132
5	58	60
6	51	53
7	97	103
8	-5	6
9	34	38
10	-5	3
11	54	60
12	39	43
13	14	17
14	29	32
15	13	15
16	44	47
17	-6	2
18	37	37
19	10	13
20	21	20
21	-7	3
H= 0 L= 5		
1	85	83
2	8	10
3	75	75
4	82	79
5	51	50
6	15	13
7	27	28
8	90	88
9	-5	0
10	31	32
11	39	39
12	43	42
13	-5	1
14	24	25
15	46	46
16	-6	1
17	-6	2
18	-7	5
19	35	32
H= 0 L= 6		
0	67	67
1	5	5
2	26	26
3	36	34
4	34	33
5	43	41
6	30	29
7	79	77
8	7	5
9	24	22
10	20	19
11	59	56
12	25	24
13	7	7
14	11	8
15	22	19
16	23	20
17	-7	1
18	19	16
H= 0 L= 7		
1	55	53
2	22	21
3	57	54
4	30	29
5	21	20
6	5	1
7	18	17
8	29	27
9	7	6
10	10	9
11	21	20
H= 0 L= 7		
12	17	15
13	10	10
14	17	15
15	37	33
H= 0 L= 8		
0	24	21
1	19	18
2	9	8
3	24	21
4	15	11
5	25	24
6	14	13
7	43	39
8	-6	1
9	10	17
10	13	10
11	41	36
12	13	10
H= 0 L= 9		
1	30	28
2	12	12
3	35	32
4	-6	4
5	8	7
6	7	5
H= 1 L= 0		
1	85	73
3	143	127
5	125	125
7	180	210
9	69	82
11	140	168
13	15	17
15	47	51
17	7	3
19	24	22
21	-6	3
23	46	36
H= 1 L= 1		
1	254	248
2	12	7
3	222	230
4	26	29
5	94	104
6	9	4
7	57	64
8	26	28
9	9	8
10	7	8
11	65	74
12	12	15
13	24	27
14	8	6
15	104	109
16	-6	1
17	7	4
18	-6	2
19	67	68
20	-7	3
21	14	8
22	-7	5
23	21	20
H= 1 L= 2		
0	111	102
1	32	26
2	13	11
3	136	131
4	60	62
5	105	112
6	7	1
7	195	206
8	15	15
9	60	76
10	22	14
11	127	148
12	21	23
13	10	21
14	22	26
15	34	46
16	21	23
17	-6	2
18	17	18
19	20	20
20	11	12
21	9	2
22	-7	7
H= 1 L= 3		
1	157	149
2	42	39
3	143	150
4	78	84
5	54	58
6	36	38
7	56	59
8	90	94
9	13	13
10	27	30
11	45	47
12	47	51
13	19	20
14	8	11
15	74	79
16	10	10
17	7	2
18	9	8
19	53	52
20	9	6
21	9	8
22	15	14
H= 1 L= 4		
0	134	128
1	40	38
2	12	4
3	44	46
4	87	93
5	70	77
6	-6	5
7	98	105
8	13	15
9	44	41
10	19	19
11	82	83
12	30	30
13	-6	2
14	32	33
15	24	20
16	33	33
17	12	11
18	20	27
19	14	12
20	17	15
21	-7	3
H= 1 L= 5		
1	71	66
2	-5	5
3	73	79
4	63	67
5	15	15
6	24	24
7	33	34
8	77	80
9	19	20
10	34	33
11	22	21
12	65	44
13	20	20
14	19	17
15	44	41
16	9	7
17	-7	6
18	-7	4
19	32	28
H= 1 L= 6		
0	103	99
H= 1 L= 6		
1	26	25
2	7	7
3	18	19
4	66	68
5	37	37
6	10	9
7	46	46
8	7	5
9	21	21
10	9	8
11	42	41
12	32	31
13	7	2
14	25	23
15	17	15
16	35	30
17	10	9
H= 1 L= 7		
1	23	22
2	-5	0
3	32	32
4	51	50
5	6	1
6	27	26
7	10	18
8	61	60
9	15	15
10	26	25
11	7	3
12	36	33
13	14	12
14	17	15
15	18	15
H= 1 L= 8		
0	64	60
1	18	16
2	8	8
3	-6	4
4	41	40
5	16	15
6	12	12
7	10	8
8	8	3
9	-6	4
10	-6	1
11	13	11
12	22	20
H= 1 L= 9		
1	-6	2
2	8	0
3	8	7
4	28	27
5	-6	5
6	7	5
H= 2 L= 0		
0	287	269
2	10	8
4	285	260
6	93	83
8	31	29
10	30	29
12	62	62
14	58	67
16	70	76
18	57	63
20	35	36
22	27	28
H= 2 L= 1		
1	80	72
2	57	59
3	31	30
4	219	207
5	70	67
6	55	53
7	10	6
8	231	236
9	-6	2
10	73	76
11	36	35
12	99	106
13	-8	5
14	33	33
15	16	17
16	16	16
17	-8	6
18	-7	3
19	13	13
20	24	23
21	-8	1
22	27	27
H= 2 L= 2		
0	266	250
1	25	24
2	49	46
3	18	18
4	155	154
5	42	41
6	45	44
7	70	72
8	24	25
9	-6	6
10	-7	1
11	44	43
12	63	67
13	12	8
14	50	50
15	20	20
16	62	64
17	8	5
18	50	51
19	-8	5
20	28	28
21	-7	5
22	26	24
H= 2 L= 3		
1	91	88
2	17	17
3	64	63
4	133	134
5	56	56
6	44	42
7	11	9
8	130	134
9	-7	1
10	47	49
11	39	39
12	80	83
13	9	7
14	42	41
15	30	30
16	15	5
17	-7	4
18	-7	2
19	25	23
20	16	16
21	8	2
H= 2 L= 4		
0	194	189
1	24	23
2	29	29
3	51	53
4	96	100
5	27	27
6	8	9
7	68	72
8	17	16
9	29	30
10	-6	1
11	60	64
12	52	53
13	11	9
14	31	30
15	20	19
16	49	46
17	-7	4
18	35	32
H= 2 L= 4		
19	10	11
20	20	18
H= 2 L= 5		
1	77	81
2	24	26
3	69	75
4	54	58
5	37	38
6	11	12
7	13	12
8	64	69
9	10	10
10	35	37
11	27	28
12	39	39
13	12	9
14	30	29
15	51	48
16	-7	4
17	-7	1
18	8	5
19	30	27
H= 2 L= 6		
0	55	57
1	14	15
2	7	0
3	44	46
4	45	46
5	29	30
6	27	28
7	63	65
8	-6	5
9	28	27
10	9	10
11	53	54
12	24	24
13	7	6
14	7	5
15	16	16
16	22	21
17	7	1
H= 2 L= 7		
1	43	45
2	19	20
3	47	49
4	21	20
5	15	16
6	10	5
7	21	20
8	28	28
9	8	7
10	15	15
11	18	17
12	11	10
13	6	7
14	13	12
H= 2 L= 8		
0	17	16
1	8	9
2	7	5
3	18	17
4	13	12
5	29	29
6	15	14
7	43	41
8	-6	2
9	16	15
10	9	9
11	34	31
H= 2 L= 9		
1	27	25
2	10	11
3	30	29
4	7	5
H= 3 L= 0		
1	22	21
3	110	99
5	138	123
7	210	186
9	77	69
11	130	125
13	21	18
15	45	41
17	10	7
19	20	20
21	-8	1
H= 3 L= 1		
1	183	166
2	16	12
3	189	173
4	11	10
5	77	72
6	6	4
7	69	63
8	23	21
9	9	5
10	18	16
11	69	59
12	14	12
13	17	16
14	9	5
15	96	93
16	-7	5
17	-8	3
18	-8	1
19	62	61
20	-8	2
21	11	7
22	-8	5
H= 3 L= 2		
0	87	81
1	31	28
2	17	15
3	111	103
4	72	66
5	92	86
6	6	4
7	163	160
8	7	4
9	67	65
10	19	18
11	120	122
12	22	21
13	14	15
14	16	15
15	38	38
16	25	21
17	-8	3
18	16	14
19	16	17
20	9	8
21	-8	2
H= 3 L= 3		
1	132	126
2	22	21
3	130	126
4	61	58
5	52	53
6	33	33
7	40	40
8	72	73
9	11	9
10	39	31
11	41	40
12	45	45
13	23	21
14	11	10
15	74	68
16	15	12
17	-8	2
18	9	8
19	40	44
20	-8	5
H= 3 L= 4		
0	115	111
1	42	41
2	9	8
3	37	35
4	71	71
5	54	53
6	7	1
7	81	81
8	14	13
9	34	33
10	15	13
11	78	76
12	31	28
13	-7	1
14	29	27
15	27	26
16	28	27
17	9	8
18	24	23
19	11	9
H= 3 L= 5		
1	61	60
2	9	7
3	64	65
4	59	60
5	18	16
6	23	22
7	26	25
8	67	68
9	19	19
10	27	26
11	21	19
12	30	30
13	19	19
14	16	15
15	35	34
16	8	4
17	7	4
18	9	4
H= 3 L= 6		
0	79	82
1	18	19
2	10	9
3	12	11
4	53	54
5	33	33
6	11	10
7	41	41
8	9	7
9	19	15
10	7	5
11	34	35
12	26	26
13	-7	1
14	22	21
15	15	14
16	26	25
H= 3 L= 7		
1	10	18
2	-6	2
3	27	27
4	45	44
5	-6	1
6	14	13
7	16	16
8	51	53
9	13	14
10	21	21
11	-6	3
12	29	28
13	10	10
H= 3 L= 8		
0	48	49
1	13	13
2	7	6
3	7	3
4	35	36
5	14	14
6	13	13
7	9	8
8	-6	2
9	6	4
H= 4 L= 0		
0	298	283
2	32	30
4	167	154
6	12	13
8	30	29
10	22	21
12	79	71
14	54	51
16	71	65
18	49	45
20	29	27
H= 4 L= 1		
1	31	28
2	11	9
3	32	30
4	136	126
5	16	9
6	53	48
7	-5	0
8	148	138
9	15	14
10	64	61
11	-5	3
12	92	87
13	-6	2
14	43	41
15	21	18
16	13	13
17	11	4
18	-7	4
19	10	9
20	14	13
H= 4 L= 2		
0	195	183
1	12	12
2	13	11
3	64	63
4	130	131
5	12	8
6	28	27
7	46	44
8	10	8
9	32	31
10	9	8
11	39	37
12	56	56
13	9	10
14	37	36
15	9	7
16	53	52
17	-7	3
18	40	38
19	-8	7
20	24	22
H= 4 L= 3		
1	46	42
2	7	3
3	52	49
4	92	90
5	15	14
6	21	20
7	20	18
8	116	117
9	-6	3
10	51	50
11	14	14
12	55	56
13	-6	2
14	25	24
15	29	31
16	12	9
17	8	3
18	-8	1
H= 4 L= 3		
19	24	20
H= 4 L= 4		
0	108	105
1	9	5
2	8	5
3	44	41
4	87	87
5	37	37
6	31	31
7	69	69
8	-6	3
9	27	27
10	-6	1
11	44	44
12	34	33
13	12	11
14	25	22
15	12	11
16	38	34
17	-8	2
18	30	27
H= 4 L= 5		
1	57	56
2	11	10
3	53	53
4	54	53
5	33	33
6	11	10
7	22	20
8	62	62
9	-7	1
10	26	25
11	29	27
12	34	31
13	-7	0
14	20	19
15	35	35
16	-7	1
17	8	1
H= 4 L= 6		
0	47	47
1	-6	4
2	18	17
3	27	27
4	28	25
5	29	30
6	22	21
7	54	55
8	7	2
9	18	17
10	14	14
11	40	41
12	17	17
13	-7	4
14	-7	6
H= 4 L= 7		
1	37	38
2	14	15
3	38	40
4	23	21
5	14	14
6	-7	1
7	15	14
8	21	20
9	-6	5
10	8	7
11	14	15
H= 4 L= 8		
0	15	15
1	13	13
2	7	7
3	16	15
4	10	8
5	18	19
6	10	10
H= 5 L= 0		
1	40	40
3	71	67
5	59	55
7	120	112
9	50	47
11	111	103
13	8	8
15	34	32
17	-6	0
19	15	14
H= 5 L= 1		
1	126	121
2	7	3
3	119	113
4	21	20
5	57	54
6	7	5
7	33	31
8	19	18
9	7	5
10	-5	2
11	46	43
12	12	10
13	21	19
14	7	4
15	71	66
16	-6	1
17	6	2
18	-7	2
19	46	42
H= 5 L= 2		
0	55	53
1	16	15
2	15	13
3	63	61
4	29	27
5	63	61
6	6	1
7	117	114
8	15	14
9	42	42
10	7	4
11	89	86
12	15	13
13	13	13
14	20	18
15	29	29
16	13	13
17	-7	2
18	12	12
H= 5 L= 3		
1	81	78
2	21	21
3	85	84
4	49	48
5	33	31
6	20	20
7	35	36
8	55	54
9	11	10
10	17	15
11	29	28
12	30	30
13	12	11
14	9	6
15	43	48
16	-7	5
17	-7	1
18	-8	4
H= 5 L= 4		
0	71	69
1	17	17
2	-5	1
3	29	27
4	53	55
5	47	48
H= 5 L= 4		
6	-6	6
7	65	64
8	10	8
9	24	25
10	13	13
11	49	49
12	18	17
13	-7	3
14	21	21
15	19	18
16	24	22
H= 5 L= 5		
1	37	37
2	8	3
3	46	47
4	40	40
5	8	7
6	14	14
7	22	22
8	48	49
9	13	12
10	23	22
11	12	12
12	28	26
13	12	12
14	13	11
15	30	27
H= 5 L= 6		
0	61	61
1	18	17
2	-6	3
3	13	13
4	44	43
5	23	22
6	9	6
7	28	27
8	-7	2
9	14	15
10	8	6
11	27	26
12	21	20
H= 5 L= 7		
1	15	14
2	-7	1
3	19	21
4	30	31
5	-7	1
6	10	10
7	11	12
8	36	37
H= 6 L= 0		
0	131	131
2	7	2
4	105	106
6	23	22
8	12	10
10	12	11
12	40	38
14	36	33
16	43	40
H= 6 L= 1		
1	20	20
2	11	10
3	15	14
4	86	84
5	18	19
6	27	26
7	8	6
8	107	105
9	6	2
10	43	40
11	14	13
12	55	55
13	-6	3
14	21	20
15	9	10
16	11	9
17	-6	2
H= 6 L= 2		
0	115	114
1	7	7
2	16	16
3	13	10
4	77	76
5	17	18
6	21	20
7	33	33
8	11	10
9	7	6
10	-5	1
11	22	21
12	35	34
13	-6	3
14	28	26
15	9	8
16	30	35
H= 6 L= 3		
1	37	36
2	8	5
3	32	31
4	65	65
5	22	22
6	20	19
7	9	8
8	69	70
9	6	1
10	26	25
11	18	18
12	42	42
13	-6	2
14	22	21
15	22	22
16	-7	2
H= 6 L= 4		
0	80	83
1	9	7
2	13	14
3	25	25
4	49	50
5	17	17
6	12	11
7	38	39
8	8	8
9	14	15
10	-6	0
11	33	33
12	25	26
13	8	5
14	19	17
H= 6 L= 5		
1	40	41
2	12	11
3	36	38
4	32	32
5	29	20
6	8	5
7	9	6
8	36	38
9	-7	4
10	17	18
11	16	16
12	22	21
H= 6 L= 6		
0	31	31
1	10	8
2	7	5
3	21	22
4	23	23
5	17	16
6	14	15
7	35	35
8	9	2
H= 6 L= 6		
9	14	14
H= 6 L= 7		
1	24	25
2	12	11
H= 7 L= 0		
1	8	7
3	37	37
5	46	49
7	76	79
9	27	28
11	56	55
13	9	9
15	21	19
H= 7 L= 1		
1	63	65
2	7	2
3	66	68
4	7	6
5	28	29
6	6	2
7	26	26
8	11	10
9	-5	4
10	7	7
11	26	26
12	6	5
13	7	7
14	-6	2
H= 7 L= 2		
0	30	30
1	12	13
2	7	6
3	38	40
4	26	28
5	36	36
6	-6	1
7	64	66
8	-6	2
9	27	28
10	10	9
11	53	54
12	9	9
13	9	6
14	9	6
H= 7 L= 3		
1	50	51
2	9	7
3	50	53
4	23	24
5	19	20
6	12	13
7	18	18
8	30	31
9	7	4
10	15	14
11	17	18
12	19	20
13	12	11
H= 7 L= 4		
0	47	49
1	17	19
2	-6	4
3	17	17
4	29	30
5	22	23
6	-6	1
7	34	35
8	-6	0
9	15	16
10	-7	5
11	35	30
H= 7 L= 5		
1	25	27
2	-6	2
3	28	29
4	26	27
5	11	8
6	11	11
7	12	12
8	30	31
H= 7 L= 6		
0	37	39
1	10	9
H= 8 L= 0		
0	78	87
2	9	9
4	52	56
6	6	5
8	9	9
10	7	7
H= 8 L= 1		
1	11	11
2	-5	0
3	9	10
4	44	48
5	7	6
6	16	16
7	-6	1
8	51	55
9	8	4
10	22	22
11	-6	3
H= 8 L= 2		
0	62	67
1	-6	3
2	7	6
3	17	19
4	43	47
5	7	5
6	10	11
7	17	17
8	-6	4
9	8	8
10	-6	2
H= 8 L= 3		
1	18	19
2	-6	3
3	18	19
4	31	34
5	9	8
6	8	8
7	6	5
8	40	45
H= 8 L= 4		
0	40	44
1	-6	1
2	-6	3
3	14	16
4	29	33
5	13	13
H= 9 L= 0		
1	11	13
3	20	23
H= 9 L= 1		
1	33	38
2	-6	0
3	32	38

flection due to random variations other than counting statistics. The R index, estimated by comparison of equivalent reflections, was 0·06.

The intensity of a standard reflection, measured after every 50 reflections was found to decrease by approximately 10% during the course of data collection. Multiplicative correction factors $[f(t)]$ for the data were determined by fitting a polynomial to the intensity measurements of the standard reflection. The order of the polynomial was determined from significance tests based on the sum-of-the-squares of the residuals (Hamilton, 1965). Corrections were made for Lorentz and polarization factors. The graphite crystal in the monochromator was assumed to be of perfect mosaicity giving the following form for the polarization factor: $(\cos^2 2\alpha+\cos^2 2\theta)/(1+\cos^2 2\alpha)$, where α is the angle the beam makes with the monochromator. The absorption corrections were made with the Busing & Levy (1957) method using Burnham's (1962) program as modified by Larson, Cromer & Roof (1964). The linear absorption correction for Mo $K\alpha$ radiation is 112 cm^{-1}, and the calculated transmission varied from 0·1 to 0·3.

Structure factors (Table 1) were calculated using the scattering factors of Doyle & Turner (1968) for the neutral atoms cesium, iodine, oxygen, and fluorine, and the dispersion terms of Cromer & Liberman (1970), *i.e.*, Cs: $\Delta f' = -0{\cdot}664$, $\Delta f'' = 2{\cdot}119$ and I: $\Delta f' = -0{\cdot}726$ and $\Delta f'' = 1{\cdot}812$.

The Patterson function could be interpreted in terms of two heavy atoms in the special position 4(c) in $Pmcn$, one with the coordinates $x \equiv 0{\cdot}25$, $y \simeq 0{\cdot}9$, $z \simeq 0{\cdot}25$, and one with the coordinates $x \equiv 0{\cdot}25$, $y \simeq 0{\cdot}16$, and $z \simeq 0{\cdot}25$. Refinement of this structure, using iodine scattering amplitudes for both atoms, converged to an R index $[R=\sum(||F_o|-|F_c||)/\sum|F_o|]$ of 0·15. A difference Fourier map showed three unique peaks. Two of these were about 2·0 Å from a heavy atom and consequently were assigned as fluorine atoms. The remaining peak was assigned as an oxygen atom. The heavy atom that was surrounded by four fluorine atoms and one oxygen atom was assigned as iodine. The remaining heavy atom was assigned as cesium.

All refinements were carried out using Larson's (1971) full-matrix least-squares program. The function minimized was $\sum w_i(|F_o|-|F_c|)^2$, where w_i is the weight defined as $1/\sigma^2(F_o)$.

The structure refined to a weighted R_w index, $R_w = \sum w_i^{1/2}||F_o|-|F_c^*||/\sum w_i^{1/2}|F_o|$ of 0·059 with all atoms anisotropic. The unweighted R index was 0·065. The R_w index with only the heavy atoms anisotropic was 0·070. The hypothesis that the light atoms vibrate isotropically can thus be rejected at the 0·05 confidence level. Parameter shifts in the last refinement were less than 0·001σ for all parameters. The standard deviation of an observation of unit weight is 4·7, indicating significant systematic errors in the data and/or model. The final difference Fourier map showed residuals near the heavy-atom position ranging in value from $-2{\cdot}0$ to 2·3 e.Å^{-3}; the largest residuals elsewhere were about 1·0 e.Å^{-3} with $\sigma(\varrho)=0{\cdot}4$ e.Å^{-3}. The final parameters are given in Table 2.

The structure of the IOF_4^- ion (see Fig. 1) has idealized symmetry C_{4v}, with the oxygen atom occupying the axial position as is expected from electron-pair repulsion theory (Gillespie & Nyholm, 1957). This geometry has been established by microwave spectroscopy for the isoelectronic $XeOF_4$ molecule (Martins & Wilson, 1968) with the parameters Xe–O = 1·703 (15), Xe–F = 1·900 (5) Å and angle O–Xe–F = 91·8 (5)°. These parameters may be compared

Table 2. *Fractional coordinates and thermal parameters* (× 10^4) *for* $CsIOF_4$

The thermal parameters are defined by the equation:

$$\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]\,.$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs	2500	8968 (1)	2185 (2)	136 (2)	27·3 (4)	207 (3)	0	0	−2 (2)
I	2500	1609 (1)	2284 (1)	126 (2)	24·1 (2)	136 (2)	0	0	−7 (1)
O	2500	1030 (10)	9920 (20)	153 (23)	44 (6)	231 (32)	0	0	−107 (22)
F(1)	230 (10)	840 (10)	3450 (20)	298 (21)	42 (4)	384 (27)	−87 (16)	283 (43)	8 (2)
F(2)	180 (10)	2360 (10)	1020 (10)	162 (14)	52 (4)	232 (18)	54 (12)	− 49 (29)	1 (2)

with the average distances and angles for IOF_4^- in the present study: I–F = 1·965 (2), I–O = 1·72 (1) Å and angle O–I–F = 88·5 (2)°. Distances and angles for IOF_4 are shown in Table 3. The trend to shorter distances, as one moves to the right in the periodic table, has been established in the isoelectronic series MF_5E (see Table 4), although the magnitude of the change in the present case is certainly more than would be expected by such an analogy. In addition, it is tempting to argue that the larger O–M–F angle in the xenon compound (and the shorter distances) is at least partially due to the decrease in lone-pair to fluorine bond repulsions relative to the oxygen bond to fluorine bond repulsions as one moves to the right in the periodic table. It should be noted, however, that no such increase in angle can be established in the isoelectronic series shown in Table 4.

Table 3. *Distances and angles*

I——O		1·72 (1) Å	Cs–F(1)	(2)	3·18 (1)
I——F(1)	(2)	1·95 (1)	Cs–F(1′)	(2)	3·30 (1)
I——F(2)	(2)	1·98 (1)	Cs–F(2)	(2)	3·29 (1)
O——F(1)	(2)	2·60 (1)	Cs–F(2′)	(2)	3·17 (1)
O——F(2)	(2)	2·58 (1)	Cs–O	(2)	3·28 (1)
F(1)–F(2)	(2)	2·80 (1)			
F(1)–F(1′)		2·73 (1)	O——I——F(1)	(2)	89·9 (4)°
F(2)–F(2′)		2·79 (1)	O——I——F(2)	(2)	88·1 (4)
			F(1)–I——F(2)	(2)	90·7 (3)
			F(1)–I——F(1′)		88·9 (5)
			F(2)–I——F(2′)		88·6 (4)

The anion is coordinated by two fluorine atoms (at an I–F distance of 3·14 Å) which lie on a line perpendicular to the presumed iodine lone-pair direction and by three Cs^+ ions which lie approximately above three of the triangular faces of the square pyramid. The intermolecular lone-pair to fluorine atom interactions apparently lengthen the F(2)–F(2′) distances, increase the F(2)–I–F(2′) angles, and may also be primarily responsible for the lengthening of the I–F(2) distance with respect to I–F(1). The Cs^+ ion is coordinated by eight fluorine atoms and two oxygen atoms at distances less than 3·5 Å.

The authors are indebted to Dr Don T. Cromer for assistance in the data collection process and to Dr Allen C. Larson for the use of his unpublished X-ray programs.

References

Bartlett, N., Einstein, F., Stewart, D. F. & Trotter, J. (1967). *J. Chem. Soc.* (*A*), 1190.

Burnham, C. W. (1962). *I.U.Cr. World List of Crystallographic Computer Programs.* Program 338.

Busing, W. R. & Levy, H. A. (1957). *Acta Cryst.* **10**, 180.

Cromer, D. T. & Lieberman, D. (1970). *J. Chem. Phys.* **53**, 1891.

Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* A**24**, 390.

Gillespie, R. J. & Nyholm, R. S. (1957). *Quart. Rev. Chem. Soc.* **11**, 339.

Hamilton, W. C. (1965). *Acta Cryst.* **4**, 689.

Jones, G. R., Burbank, R. D. & Bartlett, N. (1970). *Inorg. Chem.* **9**, 2264.

Larson, A. C. (1971). Unpublished programs.

Larson, A. C., Cromer, D. T. & Roof, R. B., Jr (1964). Report LA-3043, Los Alamos Scientific Laboratory, Los Alamos, NM.

Martins, J. & Wilson, E. B., Jr. (1968). *J. Mol. Spectry.* **26**, 410.

Mastin, S. H., Ryan, R. R. & Asprey, L. B. (1970). *Inorg. Chem.* **9**, 2100.

Table 4. *Distances and angles in the isoelectronic series* MF_5E

	SbF_5^{2-}*	TeF_5^-*	IF_5†	XeF_5^+‡
M–F (apical)	2·00 (9) Å	1·862 (4) Å	1·817 (10) Å	1·81 (8) Å
M–F (basal)	2·04 (9)	1·953 (3) 1·952 (3)	1·873 (5)	1·88 (8)
F_a–M–F_b	83 (2)°	79·4 (2)° 78·3 (2)	80·9 (2)°	79 (4)° 80 (4)

* Mastin, Ryan & Asprey (1970).
† Jones, Burbank & Bartlett (1970).
‡ Bartlett, Einstein, Stewart & Trotter (1967).