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Refinement of the Structure of $NaIO_4$

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$NaIO_4$ has been re-examined. It crystallizes in space group $I4_1/a$ with $a=b=5{\cdot}337$, $c=11{\cdot}947$ Å; $Z=4$. Anisotropic refinement reduced R to 8·94% for 740 observed reflexions. The vibrationally corrected I–O length is $1{\cdot}775 \pm 7$ Å. The structure consists of IO_4^- anions, slightly compressed in the **c** direction, and Na^+ cations, each surrounded by eight oxygen atoms at distances of 2·54 or 2·60 Å.

Introduction

Sodium periodate together with other periodates *e.g.* KIO_4 (Hylleraas, 1926), crystallizes with the lattice type of scheelite ($CaWO_4$) (Hiorthdahl, 1887). The lattice parameters and the space group C_{4h}^6–$I4_1/a$ were determined by Kirkpatrick & Dickinson (1926) who assigned the iodine and sodium atoms to the two fourfold positions (4*a* and 4*b*). The oxygen atom parameters were later determined approximately by Hazlewood (1938).

The present reinvestigation was undertaken to provide the more precise dimensions now needed for discussions of the bonding in tetrahedral oxyanions.

Experimental

Tetragonal bipyramidal crystals of $NaIO_4$ were obtained from an aqueous solution of a Hopkins & Williams Ltd. product, held slightly above 40°C. A small well-developed crystal was placed in a drop of distilled water and was rotated in the water by a fine needle slowly but continuously. The progress of the etching of the surface was observed through a binocular stereomicroscope. In this way a small almost spherical specimen was prepared with an average diameter of 0·1 mm. The specimen was then mounted at random on a special goniometer head (Kálmán, 1967) by means of which one of the *a* axes was properly oriented. Equi-inclination multiple-film photographs were taken with Mo $K\alpha$ radiation for the layers: $h0l \rightarrow h4l$. The intensities were estimated visually using standard scales, made from one good reflexion on each layer. After the data reduction 927 independent[†] $|F_o|$ values were obtained, of which 187 were too weak for observation, mainly due to the absence of the iodine and sodium contributions from *hkl* reflexions with $2k+l=2n+2$. Owing to the small diameter of the specimen ($\mu R=0{\cdot}47$) absorption corrections were ignored. The lattice parameters measured from the Weissenberg diagrams were in good agreement with those obtained by extrapolation to 19°C from the data of Deshpande, Suryanarayana & Pawar (1968).

Crystal data

$NaIO_4$, $M=213{\cdot}89$. Tetragonal; $a=b=5{\cdot}337\pm0{\cdot}001$, $c=11{\cdot}947\pm0{\cdot}002$ Å; $V=340{\cdot}29$ Å^3, $Z=4$, $D_c=4{\cdot}174$ g.cm^{-3}, $D_x=4{\cdot}12$ g.cm^{-3} (Kirkpatrick & Dickinson, 1926), $F(000)=384$; space group $I4_1/a$ (no. 88), μ for Mo $K\alpha$ ($\lambda=0{\cdot}7107$ Å) 94·8 cm^{-1}.

Refinement

Following Hazlewood (1938), the space group representation with the iodine atom at the origin at $\bar{4}$ was used. His oxygen parameters were taken as the starting point for a full-matrix least-squares refinement with a program written by Dr J. S. Stephens for the ATLAS computer. Five independent scale factors were used and all atoms were treated with anisotropic vibrations. In order to correct for anomalous dispersion, complex scattering factors were used for iodine [$\Delta f'=-0{\cdot}64$, $\Delta f''=2{\cdot}15$, Cromer (1965)]. Form factors for neutral atoms were taken from a recent table supplied by Ibers (1968). The final weighting scheme was

$$w=(7{\cdot}0+0{\cdot}15|F_o|+0{\cdot}008|F_o|^2)^{-1}\,.$$

The refinement reduced the unweighted residual R to 8·94% and $R'=[\sum w\Delta^2)/(\sum w|kF_o|^2)]^{1/2}$ to 11·60% for the 740 observed reflexions. The final parameters are shown in Table 1 and the structure factors in Table 2.

Table 1. *Positional and vibrational* (Å^2) *parameters with their estimated standard deviations*

	I	Na	O
x/a	0	0	−0·2341 (13)
y/b	0	0	0·1501 (13)
z/c	0	$\frac{1}{2}$	0·0806 (6)
U_{11}	0·0127 (2)	0·0412 (46)	0·0180 (24)
U_{22}	0·0127 (2)	0·0412 (46)	0·0219 (27)
U_{33}	0·0128 (2)	0·0322 (49)	0·0262 (22)
$2U_{12}$	0	0	0·0046 (24)
$2U_{13}$	0	0	0·0006 (21)
$2U_{23}$	0	0	0·0013 (22)

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[†] Strictly speaking 190 reflexions were measured twice in the consequence of the symmetry relation $|F(h,k,l)|=|F(-k,h,l)|$. These reflexions, however, were collected from different layer-photographs around the same axis, and independent scale factors were used in the refinement.

Table 2. *Structure factors for* $NaIO_4$

The columns are h, l, $10|F_o|$, $10|F_c|$, $10A_c$ and $10B_c$. Unobserved values are indicated by asterisks.

h	l	$10\lvert F_o\rvert$	$10\lvert F_c\rvert$	$10A_c$	$10B_c$
K = 0					
0	4	1705	1629	1627	85
0	8	1126	1138	1135	77
0	12	1190	1159	1157	66
0	14	579	579	577	52
0	20	290	345	345	38
0	24	257	270	269	27
1	3	1287	1179	875	-790
1	5	611	659	423	506
1	7	611	619	475	-597
1	9	708	719	470	544
1	11	515	594	455	-384
1	13	515	521	336	398
1	15	450	457	335	-280
1	17	257	310	194	242
1	19	225	260	205	-162
1	21	225	230	141	179
1	23	161	185	143	-114
2	0	1416	1380	1378	84
2	2	322	257	0	-257
2	4	1995	1903	1901	82
2	6	45	21	0	-21*
2	8	1448	1413	1411	74
2	10	64	87	0	87*
2	12	708	739	736	63
2	14	45	33	0	-33
2	16	611	583	581	50
2	18	55	9	0	-9*
2	20	450	393	391	37
2	22	55	13	0	13*
2	24	257	218	217	255
3	1	676	645	415	495
3	3	708	644	493	-414
3	5	997	944	628	705
3	7	857	826	620	-547
3	9	579	558	345	415
3	11	547	467	360	-297
3	13	386	379	238	295
3	15	257	328	256	-205
3	17	354	341	218	262
3	19	257	278	215	-177
3	21	193	203	127	159
3	23	161	164	129	-102
4	0	1138	1313	1311	75
4	2	418	292	0	292
4	4	1093	1164	1162	73
4	6	32	29	0	29*
4	8	997	925	923	66
4	10	161	151	0	-151
4	12	644	687	685	56
4	14	64	67	0	67*
4	16	483	464	462	44
4	18	55	17	0	17*
4	20	354	310	309	32
4	22	55	26	0	-26*
4	24	193	203	202	23
5	1	611	654	427	496
5	3	450	525	404	-336
5	5	450	528	339	404
5	7	450	476	367	-304
5	9	418	416	263	321
5	11	418	428	328	-275
5	13	322	361	230	278
5	15	257	280	218	-176
5	17	193	247	155	192
5	19	193	200	156	-125
5	21	145	164	102	129
6	0	708	786	784	61
6	2	129	157	0	-157
6	4	708	749	747	59
6	6	32	13	0	-13*
6	8	676	632	629	54
6	10	64	89	0	89*
6	12	514	478	476	45
6	14	55	45	0	-45*
6	16	428	349	347	36
6	18	55	10	0	-10*
6	20	290	244	243	26
6	22	55	18	0	18*
7	1	354	366	231	284
7	3	418	466	354	-302
7	5	290	321	200	251
7	7	290	311	243	-194
7	9	418	366	235	280
7	11	257	256	200	-159
7	13	225	242	152	189
7	15	257	246	190	-157
7	17	161	167	103	132
7	19	161	150	118	-93
7	21	161	140	87	109
8	0	611	542	540	46
8	2	64	22	0	22*
8	4	450	440	439	44
8	6	64	1	0	1*
8	8	386	375	375	40
8	10	64	15	0	-15*
8	12	354	353	351	34
8	14	64	9	0	9*
8	16	257	242	241	27
8	18	64	1	0	1*
8	20	161	164	165	20
9	1	257	285	180	218
9	3	225	214	168	-131
9	5	290	255	160	196
9	7	257	232	181	-146
9	9	161	180	110	142
9	11	161	208	161	-131
9	13	161	181	114	140
9	15	161	155	106	-82
9	17	129	134	83	105
10	0	290	253	251	31
10	2	64	6	0	6*
10	4	386	301	299	30
10	6	64	0	0	0*
10	8	553	272	271	27
10	10	64	4	0	-4*
10	12	225	184	183	24
10	14	64	3	0	3*
11	1	161	134	82	107
11	3	193	161	126	-101
11	5	161	161	101	126
11	7	161	154	120	-97
11	9	145	139	87	109
12	0	257	183	182	21
12	2	64	2	0	2*
12	4	225	163	162	199
12	6	64	1	0	1*
12	8	193	145	143	18
K = 1					
0	3	1206	1179	790	875
0	5	698	659	506	-423
0	7	666	619	397	475
0	9	761	719	544	-470
0	11	539	594	384	455
0	13	476	521	398	-336
0	15	444	457	280	355
0	17	349	310	242	-194
0	19	254	260	162	203
0	21	222	230	179	-144
0	23	190	183	114	143
1	4	730	573	0	573
1	6	1555	1562	1560	80
1	8	317	266	0	-266
1	10	984	1112	1110	71
1	12	48	33	0	-33*
1	14	698	733	731	58
1	16	63	84	0	84*
1	18	508	467	464	44
1	20	63	29	0	-29
1	22	317	302	300	31
1	24	63	8	0	-8*
2	1	571	484	382	-299
-2	1	1174	1173	870	-787
2	3	1301	986	655	737
-2	3	444	455	277	360
2	5	952	955	712	-633
-2	5	1015	955	714	-634
2	7	761	866	573	649
-2	7	761	783	514	590
2	9	730	710	536	-456
-2	9	412	444	348	-276
2	11	412	428	268	334
-2	11	539	632	415	479
2	13	381	371	290	-231
-2	13	476	493	377	-318
2	15	444	392	249	302
-2	15	317	320	198	251
2	17	381	336	259	-213
-2	17	349	353	272	-226
2	19	286	291	185	225
-2	19	286	267	168	208
2	21	254	232	180	-147
-2	21	190	191	151	-117
2	23	190	161	99	127
-2	23	159	190	120	147
3	2	1332	1306	1304	79
-3	2	1491	1622	1620	79
3	4	127	113	0	-113
-3	4	127	87	0	87
3	6	1323	1499	1497	74
-3	6	1047	1091	1088	74
3	8	63	65	0	65*
-3	8	63	49	0	-49*
3	10	857	864	861	65
-3	10	888	941	939	65
3	12	54	7	0	7*
-3	12	54	5	0	-5*
3	14	571	568	566	55
-3	14	571	663	661	55
3	16	54	23	0	-23*
-3	16	54	18	0	18*
3	18	476	460	458	40
-3	18	349	392	390	40
3	20	63	9	0	9*
-3	20	63	7	0	-7*
3	22	286	269	268	29
-3	22	286	273	271	29
3	24	63	2	0	2*
-3	24	63	1	0	-1*
4	1	761	790	595	-521
-4	1	571	611	467	-393
4	3	698	629	407	480
-4	3	730	859	570	642
4	5	476	570	437	-366
-4	5	412	503	389	-318
4	7	539	519	332	399
-4	7	444	489	311	378
4	9	508	478	368	-304
-4	9	539	611	462	-399
4	11	508	482	311	369
-4	11	412	399	251	309
4	13	412	418	321	-268
-4	13	381	372	288	-235
4	15	381	321	203	249
-4	15	381	377	242	288
4	17	254	265	206	-166
-4	17	286	243	191	-151
4	19	222	217	135	170
-4	19	190	217	135	170
4	21	190	180	141	-112
-4	21	222	204	158	-129
4	23	159	158	98	123
-4	23	222	142	88	113
5	2	1206	1113	1111	68
-5	2	793	875	873	68
5	4	54	2	0	-2*
-5	4	54	52	0	52*
5	6	666	638	635	63
-5	6	888	992	990	63
5	8	54	2	0	2*
-5	8	54	34	0	-34*
5	10	666	709	707	55
-5	10	507	626	624	55
5	12	64	0	0	0*
-5	12	64	5	0	-5*
5	14	539	541	539	45
-5	14	444	437	434	45
5	16	63	0	0	0*
-5	16	63	16	0	16*
5	18	286	286	284	34
-5	18	349	367	366	34
5	20	127	0	0	0*
-5	20	127	6	0	-6*
5	22	254	227	226	25
-5	22	254	221	219	25
6	1	539	539	410	-349
-6	1	381	408	317	-257
6	3	444	423	268	328
-6	3	412	423	268	328
6	5	412	436	336	-278
-6	5	476	532	404	-346
6	7	381	391	248	303
-6	7	444	494	321	376
6	9	349	338	263	-211
-6	9	349	358	278	-227
6	11	381	366	234	281
-6	11	286	303	190	236
6	13	349	311	240	-198
-6	13	254	255	200	-158
6	15	254	240	150	187
-6	15	222	228	141	179
6	17	254	216	168	-135
-6	17	254	236	183	-150
6	19	222	172	106	135
-6	19	222	200	127	155
6	21	159	141	111	-87
-6	21	159	149	117	-92
7	2	508	558	555	53
-7	2	539	626	623	53
7	4	54	49	0	-49*
-7	4	54	5	0	-5*
7	6	571	615	612	49
-7	6	508	504	502	49
7	8	54	52	0	52*
-7	8	54	6	0	6*
7	10	476	424	422	45
-7	10	476	456	454	45
7	12	63	8	0	8*
-7	12	63	3	0	-3*
7	14	349	317	315	35
-7	14	349	352	351	35
7	16	63	18	0	-18*
-7	16	63	2	0	-2*
7	18	286	266	265	27
-7	18	254	235	233	27
7	20	63	5	0	5*
-7	20	63	2	0	2*
8	1	286	268	211	-166
-8	1	349	375	287	-242
8	3	349	333	212	256
-8	3	286	322	205	249
8	5	349	311	240	-198
-8	5	190	236	187	-144
8	7	317	298	189	230
-8	7	190	219	134	174
8	9	317	276	213	-175
-8	9	222	254	198	-160
8	11	222	201	124	159
-8	11	222	259	165	200
8	13	222	183	144	-113
-8	13	254	237	183	-151
8	15	190	185	115	144
-8	15	190	188	119	147
8	17	159	156	122	-97
-8	17	127	136	108	-83
9	2	381	374	372	37
-9	2	381	382	380	37
9	4	63	60	0	60*
-9	4	63	23	0	-23*
9	6	349	333	331	35
-9	6	317	321	319	35
9	8	63	42	0	-42*
-9	8	63	15	0	15*
9	10	317	290	289	31
-9	10	286	293	291	31
9	12	63	9	0	-9*
-9	12	63	5	0	5*
9	14	254	229	228	25
-9	14	255	234	233	25
9	16	63	24	0	24*
-9	16	63	9	0	-9*
10	1	222	200	156	-125
-10	1	190	188	147	-117
10	3	254	205	129	159
-10	3	190	175	107	137
10	5	222	178	140	-111
-10	5	254	220	169	-140
10	7	222	171	106	134
-10	7	254	203	129	157
10	9	222	172	134	-108
-10	9	254	151	119	-93
10	11	222	150	93	117
-10	11	159	147	91	115
10	13	159	135	106	-84
-10	13	143	124	98	-76
11	2	254	219	218	25
-11	2	254	214	212	25
11	4	63	28	0	-28*
-11	4	63	8	0	8*
11	6	254	211	210	24
-11	6	222	222	220	24
11	8	63	20	0	20*
-11	8	63	6	0	-6*
11	10	190	177	176	21
-11	10	159	172	171	21
K = 2					
0	2	120	237	0	237
0	4	2538	1903	1901	82
0	6	30	21	0	21*
0	8	1480	1413	1411	74
0	10	60	87	0	-87*
0	12	634	739	736	63
0	14	51	33	0	33*
0	16	574	583	581	50
0	18	51	9	0	9*
0	20	363	393	391	37
0	22	60	13	0	-13*
0	24	242	219	217	26
1	3	574	455	360	-278
-1	3	1359	986	737	-655
1	5	1178	955	634	714
-1	5	1208	953	633	712
1	7	785	783	590	-514
-1	7	937	866	649	-575
1	9	453	444	276	348
-1	9	634	710	465	536
1	11	634	632	478	413
-1	11	363	428	334	-268
1	13	453	493	318	377
-1	13	393	371	231	290
1	15	363	320	251	-198
-1	15	393	392	302	-249
1	17	332	353	226	272
-1	17	363	335	213	259
1	19	272	267	208	-168
-1	19	272	291	225	-185
1	21	181	191	117	151
-1	21	212	232	147	180
1	23	212	190	147	-120
-1	23	151	161	127	-100
2	0	2054	1848	1846	81
2	2	151	96	0	96
2	4	1631	1412	1410	79
2	6	30	7	0	7*
2	8	1057	1080	1078	71
2	10	121	40	0	-40
2	12	785	843	841	61
2	14	51	18	0	18*
2	16	514	520	518	48
2	18	51	3	0	3*
2	20	393	337	335	35
2	22	60	6	0	-6*
2	24	242	229	228	25
3	1	574	617	396	473
-3	1	937	1043	698	775
3	3	1027	975	726	-650
-3	3	634	716	543	-467
3	5	634	530	336	410
-3	5	453	463	289	362
3	7	483	531	409	-339
-3	7	362	421	331	-261
3	9	604	677	445	511
-3	9	423	509	325	392
3	11	393	409	318	-258
-3	11	544	570	432	-371
3	13	423	386	244	299
-3	13	483	495	322	377
3	15	453	400	306	-258
-3	15	393	358	276	-228
3	17	242	253	156	198
-3	17	242	251	157	199
3	19	242	231	180	-144
-3	19	212	202	160	-123
3	21	212	218	138	169
-3	21	181	186	115	146
4	0	1269	1203	1201	72
4	2	242	223	0	-223
-4	2	91	76	0	-76
4	4	997	1044	1042	70
-4	4	937	1017	1014	70
4	6	30	20	0	-20*
-4	6	30	9	0	-9*
4	8	876	834	831	65
-4	8	725	807	805	65
4	10	151	123	0	123
-4	10	51	43	0	43*
4	12	695	648	646	54
-4	12	755	674	672	54
4	14	51	57	0	-57*
-4	14	51	18	0	-18*
4	16	483	438	436	42
-4	16	423	434	432	42
4	18	60	13	0	-13*
-4	18	60	6	0	-6*
4	20	242	291	289	31
-4	20	242	284	283	31
4	22	60	22	0	22*
-4	22	60	8	0	8*
4	24	181	195	194	22
-4	24	181	198	197	22
5	1	604	633	413	479
-5	1	363	425	259	337
5	3	544	500	384	-319
-5	3	604	601	456	-391
5	5	483	471	300	363
-5	5	544	541	350	413
5	7	393	424	328	-269
-5	7	514	516	393	-334
5	9	393	385	243	299
-5	9	483	473	305	361
5	11	483	409	313	-262
-5	11	272	302	238	-187
5	13	423	356	228	274
-5	13	273	276	171	217
5	15	272	273	213	-172
-5	15	303	292	226	-185
5	17	242	231	145	180
-5	17	242	239	151	186
5	19	151	186	146	-115
-5	19	212	213	165	-135
5	21	151	154	95	121
-5	21	151	175	110	136
6	0	816	741	738	59
6	2	151	111	0	111
-6	2	51	37	0	37*
6	4	693	690	687	57
-6	4	695	732	731	57
6	6	51	9	0	9*
-6	6	51	3	0	3*
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6	18	60	7	0	7*
-6	18	60	3	0	3*
6	20	272	230	228	25
-6	20	242	243	241	25
7	1	363	322	201	252
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7	3	393	338	263	-212
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9	9	212	199	124	155
-9	9	242	231	147	178
9	11	212	191	148	-120
-9	11	212	160	126	-98
9	13	151	169	106	131
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9	15	151	144	115	-89
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0	13	572	379	295	-238
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6	15	270	260	166	200
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6	17	169	173	137	-107
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6	19	169	160	99	125
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7	14	338	311	309	32
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7	16	68	6	0	6*
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7	18	169	217	215	25
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8	13	169	194	151	-122
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0	18	59	17	0	-17*
0	20	277	310	309	32
0	22	69	26	0	26*
0	24	208	205	202	23
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-1	5	657	570	366	437
1	7	519	489	378	-311
-1	7	622	519	399	-332
1	9	726	611	399	462
-1	9	450	478	305	368
1	11	484	399	309	-251
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1	13	415	372	235	288
-1	13	415	418	268	321
1	15	415	377	288	-242
-1	15	311	321	249	-205
1	17	242	243	151	191
-1	17	277	265	166	206
1	19	208	217	170	-135
-1	19	208	217	170	-135
1	21	208	204	129	158
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1	23	173	143	113	-88
-1	23	173	158	123	-98
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2	2	104	76	0	76
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-2	6	35	20	0	20*
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2	10	58	43	0	-43*
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2	18	69	6	0	6*
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2	20	277	284	283	31
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2	22	69	8	0	-8*
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3	11	415	436	354	-281
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3	13	380	356	226	274
-3	13	311	302	188	236
3	15	277	248	195	-153
-3	15	208	267	210	-167
3	17	311	271	172	209
-3	17	242	276	176	213
3	19	242	214	166	-134
-3	19	208	227	176	-144
3	21	173	155	96	122
-3	21	158	169	105	132
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4	4	934	877	873	62
4	6	35	4	0	4*
4	8	899	747	745	56
4	10	59	36	0	-36*
4	12	415	458	455	47
4	14	59	19	0	19*
4	16	346	379	378	37
4	18	69	3	0	3*
4	20	208	275	274	27
4	22	69	7	0	-7*
5	1	311	370	231	289
-5	1	519	469	301	359
5	3	484	455	349	-292
-5	3	415	449	345	-287
5	5	484	460	296	352
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5	7	415	432	330	-278
-5	7	311	361	280	-228
5	9	311	374	259	288
-5	9	511	358	227	276
5	11	242	275	215	-171
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5	15	242	239	186	-150
-5	15	242	243	189	-153
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5	19	208	184	143	-116
-5	19	208	165	129	-102
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6	8	519	453	451	45
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6	12	484	412	410	38
-6	12	415	450	449	38
6	14	69	8	0	-8*
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6	16	277	280	278	30
-6	16	242	273	271	30
6	18	69	1	0	1*
-6	18	69	2	0	2*
6	20	208	191	190	23
-6	20	208	181	180	23
7	1	277	375	242	287
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7	3	277	322	249	-205
-7	3	277	329	254	-209
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7	7	242	219	174	-133
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7	9	277	254	160	198
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7	11	242	259	200	-164
-7	11	242	233	181	-146
7	13	242	237	151	182
-7	13	208	214	135	166
7	15	208	189	147	-119
-7	15	208	189	147	-119
7	17	173	136	83	108
-7	17	173	144	89	114
8	0	346	410	408	38
8	2	52	29	0	-29*
-8	2	52	41	0	-41*
8	4	380	378	376	37
-8	4	371	391	390	37
8	6	69	5	0	-5*
-8	6	69	6	0	-6*
8	8	276	312	311	34
-8	8	311	348	346	34
8	10	69	23	0	23*
-8	10	69	31	0	31*
8	12	277	278	276	28
-8	12	242	235	233	28
8	14	69	10	0	-10*
-8	14	69	15	0	-15*
8	16	208	199	198	23
-8	16	208	208	206	23
9	1	173	183	112	144
-9	1	208	194	120	152
9	3	208	217	168	-137
-9	3	208	199	156	-124
9	5	208	209	131	162
-9	5	173	216	137	167
9	7	173	201	136	-127
-9	7	173	204	158	-129
9	9	173	183	115	142
-9	9	173	171	106	133
10	0	208	217	216	27
10	2	69	19	0	19*
-10	2	69	36	0	36*
10	4	242	243	242	26
-10	4	242	226	225	26
10	6	69	2	0	2*
-10	6	69	4	0	4*
10	8	208	218	217	24
-10	8	208	200	199	24

Table 3. *Interatomic distances and bond angles with their e.s.d.'s*

I–O		1·769 Å (uncorrected)
		1·775 ± 7 Å (corrected)
$O(x,y,z)$–I–$O(-x,-y,\ z)$		114·05 ± 0·40° (twice)
$O(x,y,z)$–I–$O(\ y,-x,-z)$		107·33 ± 0·36° (four times)
Intra-tetrahedral		
$O(x,y,z)\cdots O(\ y,-x,-z)$		2·85 ± 0·01 Å
$O(-y,\ x,-z)$		2·85
$O(-x,-y,\ z)$		2·97
Inter-tetrahedral		
$O(x,y,z)\cdots O(\ x,\frac{1}{2}+y,\frac{1}{4}-z)$	—	2·87
$O(x,-\frac{1}{2}+y,\frac{1}{4}-z)$	▨	2·87
$O(-x,\frac{1}{2}-y,\frac{1}{4}-z)$	⋯	2·92

Though the iodine vibrations are practically isotropic, the oxygen vibrations are decidedly anisotropic and it was therefore necessary to determine coordinate corrections for rigid-body librations of the periodate tetrahedron by the method of Cruickshank (1965, 1961*a*). This increased the I–O length by 0·006 Å. Tables 3 and 4 give the various distances and angles in the crystal structure.

Table 4. *Sodium* $(0,0,\frac{1}{2})$*-oxygen distances*

Oxygen atoms from layer of iodate tetrahedra, with the iodine atom at $z=\frac{1}{2}$

O(i)	$[-\frac{1}{2}+y,\ -\frac{1}{2}-x,\ \frac{1}{2}-z]\cdots$Na	2·54 Å
O(ii)	$[-\frac{1}{2}-x,\ \ \frac{1}{2}-y,\ \frac{1}{2}+z]\cdots$Na	2·54
O(iii)	$[\ \ \frac{1}{2}+x,\ -\frac{1}{2}+y,\ \frac{1}{2}+z]\cdots$Na	2·54
O(iv)	$[\ \ \frac{1}{2}-y,\ \ \frac{1}{2}+x,\ \frac{1}{2}-z]\cdots$Na	2·54

Table 4 (*cont.*)

Oxygen atoms from adjacent layers of iodate tetrahedra, with the iodine atom at $z=\frac{1}{4}$ or $\frac{3}{4}$

O(v)	$[-\frac{1}{2}-x,\ -y,\ \frac{3}{4}-z]\cdots$Na	2·60 Å
O(vi)	$[y,\ -\frac{1}{2}-x,\ \frac{1}{4}+z]\cdots$Na	2·60
O(vii)	$[-y,\ \frac{1}{2}+x,\ \frac{1}{4}+z]\cdots$Na	2·60
O(viii)	$[\frac{1}{2}+x,\ y,\ \frac{3}{4}-z]\cdots$Na	2·60

Discussion

The corrected I–O bond of 1·775 ± 7 Å is similar in length to the short bonds ranging from 1·78 to 1·81 Å found in different iodates and periodates [$LiIO_3$ (De Boer, van Bolhuis, Olthof-Hazekamp & Vos, 1966), $K_4H_2I_2O_{10}$ (Ferrari, Braibanti & Tiripicchio, 1965), H_5IO_6 (Feikema, 1966), α-HIO_3 and HI_3O_8 (Feikema & Vos, 1966)]. Such bonds evidently have an appreciable multiple-bond character in comparison with the distances of 1·96 to 2·02 Å for bridging bonds in $K_4H_2I_2O_{10}$ and HI_3O_8. The periodate ion is isoelectronic with xenon tetroxide XeO_4, for which a bond length of 1·736 ± 3 Å has been determined with gas-phase electron diffraction by Gundersen & Hedberg (1969). The difference of 0·039 ± 10 Å (say) between I–O and Xe–O is comparable to the trend predicted by Cruickshank (1961*b*) for Cl–O and Ar–O in his discussion of the isoelectronic series SiO_4^{4-} to ArO_4.

Our final I–O bond length of 1·775 Å is close to Hazlewood's (1938) value of 1·792 Å, but the iodate tetrahedron is now more compressed in the **c** direction than in Hazlewood's description. This may be explicable on the basis of the packing of the tetrahedra (Fig. 1). Besides its three partners in the same tetrahedron (and two sodium neighbours), each oxygen atom has three other oxygen neighbours at distances of 2·87–2·92 Å. These distances are almost the same as the intra-tetrahedral O···O distances of 2·85–2·97 Å (Table 3). In the less distorted model of Hazlewood, the inter-tetrahedral distances (2·68–2·84 Å) are less than the intra-tetrahedral distances (2·90–2·95 Å). Thus the angular distortions may have relieved some inter-tetrahedral repulsions.

The environment of a sodium cation is shown in Fig. 2. Eight oxygen atoms form two rather irregular tetrahedra enclosing the sodium ion. The four oxygen atoms, which belong to the layer of iodate tetrahedra at the same level of z as the sodium ion, are significantly nearer (2·54 Å) to the cation than those which are on the upper and lower layers of iodate tetrahedra (2·60 Å).

We defer discussion of the differences in the thermal expansions of the sodium and potassium salts until we have completed a parallel analysis of KIO_4.

Note added in proof: - The structure of XeO_4 has now been reported in full by Gundersen, Hedberg & Huston (1970). Huston & Claasen (1970) have shown the similarity of the force constants in IO_4^- and XeO_4, and have contrasted their values of F, the principal non-bonded repulsion constant, with that in OsO_4. This difference may arise from the same cause as the differing distortions of selenate and chromate tetrahedra discussed by Stephens & Cruickshank (1970).

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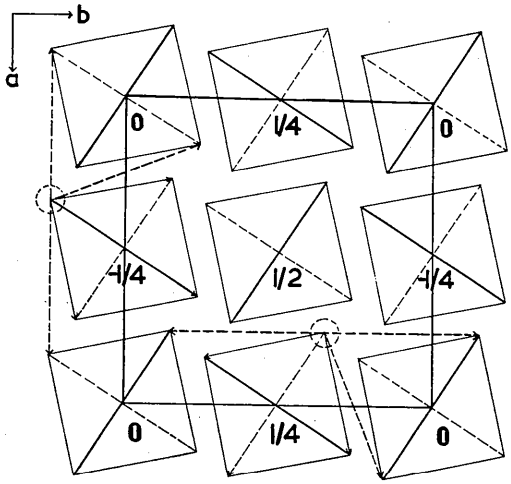

Fig. 1. Periodate tetrahedra viewed down the c axis. Inter-tetrahedral O···O contacts are also indicated by dashed lines. The z coordinates of iodine atoms are also shown.

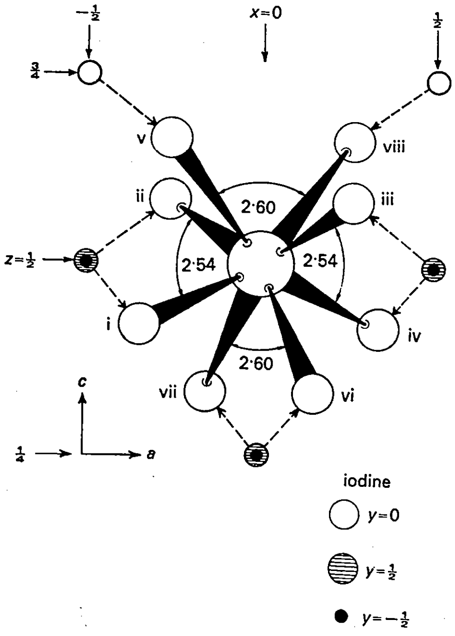

Fig. 2. Oxygen environment of the sodium cation at $(0,0,\frac{1}{2})$. See Table 4 for identification of oxygen atoms.

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Crystal Structures of Four New Polytypes of Cadmium Iodide

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Crystal structures of four new polytypes of cadmium iodide, two rhombohedral and two hexagonal, have been determined. The structures of the rhombohedral polytypes, *viz.* $24R$ and $36R$, have been found to be $(2213)_3$ and $(22112121)_3$, in Zhdanov notation. The two hexagonal polytypes, *viz.* $18H_g$ and $30H_d$, have been found to possess the structures $(22)\,(11)_7$ and $(2211)_4\,1122$ respectively. All four polytypes were found to have grown in syntactic coalescence with other polytypes, showing a transformation of structure during growth. The polytype $30H_d$ is the largest hexagonal cadmium iodide polytype for which the atomic structure is known. The growth of these polytypes is discussed.

Introduction

Hitherto, over 80 cadmium iodide polytypes have been reported with cell heights ranging from 6·84 ($2H$) to 218·88 Å ($64H$). Of these, the crystal structures of only 20 polytypes, 17 hexagonal and 3 rhombohedral, have been determined(Mitchell, 1956; Srivastava & Verma, 1962, 1964, 1965; Chadha & Trigunayat, 1967*a*,*b*; 1968; Agrawal & Trigunayat, 1968). During the course of a study of one-dimensional disorder in cadmium iodide crystals, 46 hexagonal and 7 rhombohedral polytypes have been discovered (Jain, 1968), from which it has been possible to work out the complete crystal structures of two rhombohedral and two hexagonal polytypes, *viz.* $24R, 36R, 18H_g$ and $30H_d$. The crystals show significant structure-transformations during growth and provide information regarding the origin of polytypism in crystals.

Experimental

c and *a* axis oscillation photographs of cadmium iodide crystals were used for the identification of the polytypes. In the case of the *c* axis photographs the identity of the polytype could be established by direct measurement of the *c* parameter, which could also be calculated from the *a* and *b* dimensions, which are the same for all polytypes, from the *a* axis photographs (Trigunayat, 1959). The *c* axis oscillation photographs were taken over a 15° range (from the position where the *a* axis made an angle of 31·5° with the incident X-ray beam to the position $(31{\cdot}5+15)=46{\cdot}5°$). This range of oscillation was found to be the most suitable for all cadmium iodide polytypes as it includes all the reflexions from 10.0 to 10.*X* for an *X*H polytype. In the case of the *a*-axis photographs, the usual range of oscillation, *viz.* 25 to 40°, which covers the surface reflexion spots (Chadha & Trigunayat, 1967*a*), was chosen. In the structures determinations the intensities of the reflexions were compared on both the oscillation and Weissenberg photographs, because the crystals were too thick to give transmission diffraction spots. As has already been shown by Ramsdell (1944) and Mitchell (1955), it is sufficient to compare the observed and calculated intensities of only the 10.*l* or 01.*l* reflexions in order to determine a crystal structure. Zero-layer *a* axis Weissenberg photographs were therefore used for the structure determination.