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The Crystal Srtucture of Calcium Diiodate(V) Hexahydrate

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The crystals of calcium diiodate(V) hexahydrate, $Ca(IO_3)_2 . 6H_2O$, are orthorhombic, space group Fdd2 *with 8 molecules in the unit cell. The structure consists of pyramidal anions joined to one another in chains by intermolecular I . . . O interactions. The chains are held together by calcium ions and by hydrogen bonds between water molecules and anions. The coordination polyhedron around calcium can be described as a square antiprism, with distances Ca–O = 2.43-2.57 Å. In the pyramidal anion the distances between oxygen and iodine atoms are I–O = 1.78, 1.90, 1.85 Å. The environment of the iodine atom is approximately octahedral: the coordination is completed by two water molecules and by one oxygen atom of another anion.*

Introduction

As part of researches on salts of oxyacids of heptavalent and pentavalent iodine, we have now determined the structure of the crystals of calcium diiodate(V) hexahydrate, $Ca(IO_3)_2 . 6H_2O$.

Experimental Section

Preparation. The crystals of the compound are obtained[1] in form of colorless prisms by concentrating solutions of calcium carbonate in periodic acid and concentrated hydrochloric acid.

Cristal Data. Compound: calcium diiodate(V) hexahydrate, $Ca(IO_3)_2 . 6H_2O$; F.W. 498.02

Crystal class: orthorhombic pyramidal

Unit cell: (from rotation and Weissenberg photographs around [010] and [001], CuKα radiation, $\lambda = 1.5418$ Å)

$a = 23.02(2)$, $b = 14.82(1)$, $c = 6.39(1)$ Å;

$V = 2180.0$ Å^3; $Z = 8$;

$D_x = 3.03$, $D_m = 2.97$ g.cm^{-3} (by picnometer method);

$\mu(CuK\alpha) = 497.0$ cm^{-1};

Space group: *Fdd2* ($C_{2v}(19)$ - No. 43) from systematic absences; the crystals are piezoelectric.

Intensity Data. Three-dimensional intensity data have been determined photometrically on integrated equi-inclination Weissenberg, photographs (multiple film technique) of layers $h0\ell, h1\ell, \ldots, h3\ell$ and $hk0$, $hk1, \ldots, hk5$ (626 independent reflections out of 685 possible).

Calculations. Usual Lorentz and polarisation corrections, but not anomalous dispersion corrections, have been applied. Absorption corrections have been applied as for cylindrical specimens with $\mu\bar{R}_{[010]} = 8.5$ (crystal section 0.28×0.40 mm); $\mu\bar{R}_{[001]} = 5.0$ (crystal section 0.19×0.25 mm). Interlayer scaling constants have been calculated by the method of Rollet and Sparks[2]. Atomic form factors from Cromer and Mann[3] have been used.

The structure has been solved by Patterson and Fourier methods and refined by differential syntheses. Anisotropic temperature factors have been introduced following the method of Nardelli and Fava[4], although their physical significance is doubious. The final conventional agreement index was $R = 11.8\%$. The computer programs prepared by Nardelli and coworkers[5-8] have been employed.

Table I. Fractional atomic coordinates (with e.s.d.'s $\times 10^4$).

	x	*y*	*z*
I	1393(1)	4853(1)	1833(4)
Ca	2500(4)	2500(4)	2500(15)
O(1)	0669(12)	5281(18)	1848(49)
O(2)	1785(11)	5826(7)	3166(38)
O(3)	1558(17)	5162(17)	−0915(40)
$H_2O(1)$	2442(13)	0858(18)	1613(50)
$H_2O(2)$	1537(21)	1974(12)	3443(113)
$H_2O(3)$	2747(14)	1525(15)	5562(59)

All the calculations have been performed on the computer Olivetti Elea 6001/S of Centro di Calcolo Elettronico of the University of Parma.

The results of the structure determination are reported in Tables I-VI.

(1) M. Biagini Cingi, F. Emiliani, and C. Guastini, *Acta Cryst.*, *23*, 1114 (1967).

(2) J.S. Rollett and R.A. Sparks, *Acta Cryst.*, *13*, 273 (1960).
(3) D.T. Cromer and J.B. Mann, *Acta Cryst.*, *A24*, 321 (1968).
(4) M. Nardelli and G. Fava, *Ric. Sci.*, *30*, 898 (1960).
(5) M. Nardelli, P. Domiano, A. Musatti, and G. Andreetti, *Ric. Sci.*, *34*, (II-A) 711 (1964).
(6) M. Nardelli, A. Musatti, P. Domiano, and G. Andreetti, *Ric. Sci.* *35*, (II-A) 469 (1965).
(7) M. Nardelli, G. Andreetti, P. Domiano, and P. Musatti, *Ric. Sci.*, *35*, (II-A) 477 (1965).
(8) M. Nardelli, A. Musatti, P. Domiano, and G. Andreetti, *Ric. Sci*, *35*, (II-A) 807 (1965).

Table II. Anisotropic thermal parameters ($Å^2$) *

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	1.669	0.918	2.787	—0.011	0.077	0.049
Ca	1.513	0.841	2.760	0.129	0.073	—0.001
O(1)	2.624	0.389	4.177	0.483	—0.019	—0.067
O(2)	3.001	1.528	4.083	—0.185	—0.572	—1.081
O(3)	2.659	2.965	1.966	0.514	—0.325	0.035
$H_2O(1)$	1.072	2.437	3.871	—0.683	0.191	—0.413
$H_2O(2)$	3.411	0.371	4.807	0.137	0.173	—0.240
$H_2O(3)$	2.137	2.420	4.098	—0.953	0.168	1.342

Shifts of the last cycle $|\Delta B_{ij}|_{av}=0.091$ $|\Delta B_{ij}|_{max}=0.293$ * $B_{ij}=8^2\pi^2U_{ij}$ referred to the base **a***, **b***, **c***.

Table III. Observed and calculated structure factors.
= after F_o indicates unobserved reflections.

h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$
0	0	4	6186	4506	3	5	7	990	939	6	6	0	3986	3785	9	5	7	584	460	12	12	0	601-	8	16	6	2	536	524	20	12	0	748	599
0	0	8	1079	1370	3	7	1	2919	3439	6	6	2	2718	2842	9	7	1	1633	1274	12	12	2	2696	2523	16	6	4	1326	1312	20	12	2	1892	2013
0	2	2	5879	5301	3	7	3	1869	2427	6	6	4	2005	2267	9	7	3	1580	1624	12	12	4	601	614	16	6	6	525	463	20	14	0	188-	2165
0	2	6	2383	2789	3	7	5	1751	1737	6	6	6	1138	1090	9	7	5	1532	1289	12	14	0	3514	2813	16	8	0	1303	784	21	1	1	1615	1710
0	4	0	8163	8318	3	7	7	1002	831	6	8	0	3438	2741	9	7	7	359-	698	12	14	2	796	740	16	8	2	2193	2026	21	1	3	1544	1733
0	4	4	4387	4732	3	9	1	2470	2723	6	8	2	1633	1745	9	9	1	2842	2597	12	14	4	1291	1406	16	8	4	341	353	21	1	5	990	942
0	4	8	919	1000	3	9	3	1162	1337	6	8	4	1981	2269	9	9	3	2393	2394	12	16	0	371-	143	16	8	6	182-	978	21	3	1	1763	1824
0	6	2	2937	3643	3	9	5	1627	1444	6	8	6	955	866	9	9	5	1734	1330	12	16	2	1957	2194	16	10	0	2753	2421	21	3	3	1633	1840
0	6	6	2181	2161	3	9	7	895	772	6	10	0	3538	3057	9	11	1	2541	2237	13	1	1	1279	1091	16	10	2	606	735	21	3	5	867	900
0	8	0	4075	4655	3	11	1	2429	2511	6	10	2	3220	3242	9	11	3	1722	1727	13	1	3	1326	1738	16	10	4	1892	1778	21	5	1	1651	1450
0	8	4	2654	3084	3	11	3	1509	1509	6	10	4	925	715	9	11	5	1627	1446	13	1	5	377	481	16	12	0	1097	888	21	5	3	1734	1809
0	10	2	1439	2113	3	11	5	1202	1036	6	10	6	1851	1374	9	13	1	3095	2824	13	1	7	617	583	16	12	2	2535	2496	21	5	5	984	971
0	10	6	2164	1537	3	13	1	1509	1561	6	12	0	3685	3427	9	13	3	2193	2218	13	3	1	1686	1507	16	12	4	230	245	21	7	1	2046	1756
0	12	0	3514	3037	3	13	3	624	621	6	12	2	412	407	9	13	5	1485	1380	13	3	3	1337	1598	16	14	0	2948	2719	21	7	3	1704	1744
0	12	4	1368	1213	3	13	5	963	887	6	12	4	2181	2153	9	15	1	2158	2002	13	3	5	448	410	16	14	2	218-	270	21	7	5	123-	814
0	14	2	406	458	3	15	1	1651	1607	6	12	6	595	597	9	15	3	1657	1808	13	3	7	624	584	16	16	0	188-	151	21	9	1	1568	1321
0	16	0	560-	295	3	15	3	907	818	6	14	0	1728	1305	9	17	1	2058	2225	13	5	1	1757	1570	17	1	1	1957	2086	21	9	3	1114	1208
0	16	4	289	332	3	15	5	117-	615	6	14	2	2818	2888	10	0	2	4487	4948	13	5	3	1621	1882	17	1	3	1220	1567	21	11	1	1462	1370
0	18	2	737	903	3	17	1	654	716	6	14	4	572	472	10	0	6	1079	1652	13	5	5	855	788	17	1	5	1184	1289	21	11	3	1043	1103
1	1	1	3497	3274	3	17	3	672	800	6	16	0	3408	2662	10	2	0	4758	4349	13	5	7	790	703	17	3	1	1886	2026	21	13	1	182-	592
1	1	3	3048	3645	4	0	0	6976	6036	6	16	2	329	404	10	2	2	513	448	13	7	1	2818	2420	17	3	3	873	1029	22	0	2	1869	2264
1	1	5	984	1469	4	0	4	3986	4265	6	16	4	1532	1915	10	2	4	3290	3657	13	7	3	1722	1677	17	3	5	1291	1291	22	2	0	2818	2962
1	1	7	1182	995	4	0	8	996	1363	6	18	0	295-	207	10	2	6	242-	319	13	7	5	814	672	17	5	1	2175	2028	22	2	2	333-	133
1	3	1	3030	3105	4	2	0	590-	192	6	18	2	1792	2136	10	4	0	1780	1567	13	9	1	2069	1631	17	5	3	1403	1384	22	2	4	1433	1658
1	3	3	3584	3946	4	2	2	5284	5943	7	1	1	3584	3827	10	4	2	3390	3824	13	9	3	2011	1935	17	5	5	972	892	22	4	0	612	438
1	3	5	1397	1651	4	2	4	460	565	7	1	3	3685	4016	10	4	4	578	918	13	9	5	1368	1189	17	7	1	2011	1881	22	4	2	1951	2243
1	3	7	1279	1130	4	2	6	1445	1826	7	1	5	1456	1728	10	4	6	1037	1287	13	11	1	2458	2035	17	7	3	802	833	22	4	4	248-	117
1	5	1	2872	3427	4	2	8	94-	84	7	1	7	1255	1266	10	6	0	3290	3078	13	11	3	1827	1793	17	7	5	1020	987	22	6	0	3042	2874
1	5	3	2494	2934	4	4	0	6716	6814	7	3	1	3313	3729	10	6	2	1892	1830	13	11	5	1138	1032	17	9	1	2098	1834	22	6	2	672	648
1	5	5	1031	1043	4	4	2	1026	1214	7	3	3	2594	3500	10	6	4	2005	2271	13	13	1	1509	1355	17	9	3	1255	1076	22	6	4	1439	1546
1	5	7	901	812	4	4	4	3485	3938	7	3	5	1190	1489	10	6	6	873	758	13	13	3	1433	1682	17	9	5	1031	930	22	8	0	990	763
1	7	1	2589	2972	4	4	6	377	468	7	3	7	1439	1329	10	8	0	3143	2708	13	15	1	1892	1790	17	11	1	1314	1158	22	8	2	1692	1568
1	7	3	2058	2365	4	4	8	52-	1346	7	5	1	3125	2962	10	8	2	2901	2779	13	15	3	1433	1563	17	11	3	1326	1286	22	8	4	477	588
1	7	5	1190	1451	4	6	0	1114	855	7	5	3	2925	3501	10	8	4	1556	1611	13	17	1	141-	1281	17	13	1	1934	1750	22	10	0	1651	1521
1	7	7	1173	1000	4	6	2	4522	5264	7	5	5	1468	1411	10	8	6	955	784	14	0	2	3190	3649	17	13	3	955	1158	22	10	2	873	835
1	9	1	1556	2111	4	6	4	1061	1117	7	5	7	1208	1057	10	10	0	2294	2062	14	0	6	1474	2092	17	15	1	937	1107	22	12	0	737	666
1	9	3	2093	2420	4	6	6	1686	1610	7	7	1	2806	2647	10	10	2	2411	2208	14	2	0	5076	5324	18	0	2	3886	4358	22	12	2	394	640
1	9	5	949	957	4	8	0	2959	2908	7	7	3	2240	2368	10	10	4	1663	1590	14	2	2	495	688	18	0	6	1079	1688	23	1	1	713	724
1	9	7	725	568	4	8	2	1757	1902	7	7	5	1380	1229	10	10	6	1220	955	14	2	4	2753	3379	18	2	0	3166	3396	23	1	3	624	563
1	11	1	1863	2232	4	8	4	2583	2920	7	7	7	1061	1027	10	12	0	2494	2203	14	2	6	283	195	18	2	2	618	418	23	1	5	347	380
1	11	3	1409	1768	4	8	6	737	757	7	9	1	2329	2072	10	12	2	1898	1685	14	4	0	1031	713	18	2	4	2122	2621	23	3	1	825	717
1	11	5	1338	1243	4	10	0	2393	2139	7	9	3	2512	2445	10	12	4	1769	1707	14	4	2	3290	3628	18	2	6	212	154	23	3	3	879	903
1	13	1	2405	2585	4	10	2	2535	2528	7	9	5	1031	966	10	14	0	612-	178	14	4	4	554	415	18	4	0	1085	943	23	3	5	117-	281
1	13	3	1657	1760	4	10	4	843	862	7	9	7	253-	831	10	14	2	1910	1888	14	4	6	1633	1995	18	4	2	2948	3469	23	5	1	531	479
1	13	5	1320	1043	4	10	6	1291	958	7	11	1	1391	045	10	14	4	618	639	14	6	0	5879	5660	18	4	4	341-	143	23	5	3	672	675
1	15	1	1526	1518	4	12	0	861	630	7	11	3	1934	1974	10	16	0	2636	2137	14	6	2	495-	236	18	4	6	1179	1306	23	7	1	1491	1376
1	15	3	1674	1765	4	12	2	1722	1709	7	11	5	990	813	10	16	2	624	524	14	6	4	2181	2363	18	6	0	2529	2012	23	7	3	1202	1282
1	15	5	1126	1258	4	12	4	1332	1257	7	13	1	1710	1524	10	18	0	159-	946	14	6	6	312	303	18	6	2	566	452	23	9	1	1138	1115
1	17	1	2075	2080	4	12	6	843	689	7	13	3	1179	1212	11	1	1	3608	4044	14	8	0	689	342	18	6	4	1869	2065	23	9	3	925	1065
1	17	3	1226	1393	4	14	0	1568	1421	7	13	5	448	499	11	1	3	2535	2979	14	8	2	2488	2341	18	6	6	123-	114	23	11	1	1550	1762
1	19	1	123-	1239	4	14	2	1439	1236	7	15	1	531	576	11	1	5	2044	2168	14	8	4	790	710	18	8	0	683-	106	24	0	0	1320	1367
2	0	2	1433	1830	4	14	4	919	898	7	15	3	849	840	11	1	7	1031	1004	14	8	6	1875	1440	18	8	2	2753	2524	24	0	4	772	986
2	0	6	200	295	4	16	0	531-	107	7	17	1	913	813	11	3	1	4075	4557	14	10	0	2948	2438	18	8	4	341-	198	24	2	0	737	733
2	2	0	590-	57	4	16	2	1285	1313	7	17	3	401	453	11	3	3	1415	2012	14	10	2	554	530	18	10	0	1963	1625	24	2	2	1592	1717
2	2	2	1592	1869	4	16	4	371	445	8	0	0	5596	5905	11	3	5	1686	1990	14	10	4	1609	1490	18	10	2	394	379	24	2	4	388	427
2	2	4	748	1265	4	18	0	1120	897	8	0	4	2688	3098	11	3	7	1085	1013	14	12	0	1809	2328	18	10	4	1285	1300	24	4	0	1391	1070
2	2	6	300	353	4	18	2	159-	214	8	2	0	1138	675	11	5	1	3956	3899	14	12	2	1092	903	18	12	0	442-	122	24	4	2	855	936
2	2	8	454	411	5	1	1	2523	2260	8	2	2	2748	3496	11	5	3	2252	2332	14	12	4	554	561	18	12	2	1674	1548	24	6	4	972	1210
2	4	0	2081	1725	5	1	3	719	795	8	2	4	768	1045	11	5	5	1916	1923	14	14	0	1356	987	18	12	4	111-	242	24	6	0	1532	1301
2	4	2	1196	1521	5	1	5	1138	1258	8	2	6	1439	1883	11	5	7	1214	1026	14	14	2	701	737	18	14	0	318-	283	24	6	2	1562	1510
2	4	4	701	1273	5	1	7	689	560	8	4	0	4399	4621	11	7	1	2948	2544	14	14	4	111-	536	18	14	2	377	385	24	6	4	790	884
2	4	6	289	289	5	3	1	1568	1702	8	4	2	1055	1570	11	7	3	1940	1786	14	16	0	1196	992	19	1	1	1792	1823	24	8	0	895	690
2	4	8	76-	354	5	3	3	1249	1722	8	4	4	1946	2255	11	7	5	1804	1626	14	16	2	141-	208	19	1	3	695	842	24	8	2	1184	1148
2	6	0	1014	683	5	3	5	1374	1585	8	4	6	578	689	11	7	7	248-	854	15	1	1	3160	3565	19	1	5	960	1064	24	10	0	1910	1674
2	6	2	2753	3152	5	3	7	365	296	8	6	0	2017	1441	11	9	1	2688	2368	15	1	3	2294	2655	19	3	1	1550	1790	24	10	2	873	927
2	6	4	595	572	5	5	1	2199	2145	8	6	2	2104	1901	11	9	3	1415	1269	15	1	5	1150	1334	19	3	3	895	1110	25	1	1	1910	1995
2	6	6	1120	1051	5	5	3	1374	1522	8	6	4	1184	1193	11	9	5	1728	1446	15	1	7	972	886	19	3	5	1261	1265	25	1	3	1338	1388
2	8	0	3732	3868	5	5	5	1568	1436	8	6	6	1615	1526	11	11	1	1273	1097	15	3	1	2441	2429	19	5	1	2282	2143	25	3	1	2005	1937
2	8	2	719	947	5	5	7	837	682	8	8	0	3885	3574	11	11	3	931	793	15	3	3	2535	2869	19	5	3	1108	1125	25	3	3	1108	1168
2	8	4	1184	1667	5	7	1	4393	4435	8	8	2	2535	2284	11	11	5	1255	1094	15	3	5	1097	1300	19	5	5	1214	1144	25	5	1	1780	1610
2	8	6	554-	326	5	7	3	1898	1934	8	8	4	1680	1664	11	13	1	1285	1058	15	3	7	100-	784	19	7	1	1639	1497	25	5	3	972	982
2	10	0	660-	93	5	7	5	1368	1357	8	8	6	1232	1053	11	13	3	955	841	15	5	1	2630	2343	19	7	3	1279	1291	25	7	1	1474	1338
2	10	2	2989	3393	5	7	7	754	647	8	10	0	2589	2390	11	13	5	907	797	15	5	3	1951	2143	19	7	5	1208	1176	25	7	3	819	925
2	10	4	849	919	5	9	1	3307	3016	8	10	2	1869	1719	12	15	1	630	511	15	5	5	1374	1244	19	9	1	2028	1733	25	9	3	1214	1261
2	10	6	2164	1646	5	9	3	1951	2166	8	10	4	1445	1345	11	15	3	242-	307	15	7	1	2630	2181	19	9	3	1338	1214	26	0	2	1827	2148
2	12	0	2648	2954	5	9	5	1745	1700	8	10	6	1550	1144	11	17	1	713	788	15	7	3	1880	1851	19	9	5	135-	1402	26	2	0	1657	1491
2	12	2	1079	1186	5	9	7	1190	974	8	12	0	2458	2190	12	0	0	265	40	15	7	5	1243	1043	19	11	1	1521	1348	26	2	2	471	429
2	12	4	2306	2437	5	11	1	3726	3612	8	12	2	2512	2524	12	0	4	861	1370	15	9	1	1680	1259	19	11	3	1049	1091	26	4	0	601	539
2	12	6	212-	111	5	11	3	2034	2084	8	12	4	1356	1275	12	2	0	1132	1023	15	9	3	2152	2038	19	13	1	1692	1745	26	4	2	1645	1784
2	14	0	689-	137	5	11	5	1804	1586	8	12	6	123-	1054	12	2	2	2393	2713	15	9	5	1291	1187	19	13	3	106-	1331	26	6	0	901	652
2	14	2	3054	3163	5	13	1	2017	1834	8	14	0	2931	2203	12	2	4	400-	179	15	11	1	2087	1756	20	0	0	1214	1368	26	6	2	584	616
2	14	4	412	416	5	13	3	1940	2119	8	14	2	766	771	12	2	6	666	740	15	11	3	1526	1423	20	0	4	525	903	26	8	0	1079	947
2	16	0	2889	2649	5	13	5	1804	1680	8	14	4	1431	1513	12	4	0	1385	1262	15	11	5	808	665	20	2	0	790	525	26	8	2	123-	1290
2	16	2	612	631	5	15	1	2488	2485	8	16	0	901	871	12	4	2	1073	1320	15	13	1	1202	1019	20	2	2	955	675	27	1	1	371	457
2	16	4	2005	2202	5	15	3	1804	1969	8	16	2	2005	2094	12	4	4	1031	1523	15	13	3	943	979	20	2	4	383	427	27	1	3	377	414
2	18	0	825	627	5	17	1	1833	1791	8	16	4	70-	442	12	4	6	654	707	15	15	1	1362	1236	20	2	6	70-	399	27	3	1	323	255
2	18	2	2098	2644	5	17	3	1208	1408	8	18	0	1757	1768	12	6	0	1645	1218	15	15	3	106-	836	20	4	0	1674	1551	27	3	3	141-	445
3	1	1	4906	4997	6	0	2	1479	1409	9	1	1	2854	2760	12	6	2	2771	2743	16	0	0	889	1224	20	4	2	966	1049	27	5	1	766	775
3	1	3	2506	2951	6	0	6	996	1337	9	1	3	713	704	12	6	4	1344	1409	16	0	4	602	848	20	4	4	454	442	27	7	1	212-	573
3	1	5	1509	1966	6	2	0	5106	4479	9	1	5	383-	248	12	6	6	831	658	16	2	0	1150	953	20	6	0	2335	2108	28	0	0	2317	2222
3	1	7	1439	1292	6	2	2	1314	1504	9	1	7	253-	219	12	8	0	1739	1277	16	2	2	683	870	20	6	2	737	213	28	2	0	177	8
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3	3	3	1657	2059	6	2	6	436	447	9	3	3	460	589	12	8	4	949	1077	16	2	6	737	796	20	8	0	1427	867	28	4	0	1987	1827
3	3	5	1857	2191	6	2	8	70-	481	9	3	5	642	795	12	8	6	1427	1098	16	4	0	1097	1012	20	8	2	2211	2045	28	4	2	111-	278
3	3	7	1184	1135	6	4	0	4128	3576	9	3	7	542	494	12	10	0	2494	2210	16	4	2	1079	1378	20	8	4	436	484	28	6	0	654	768
3	5	1	2919	3345	6	4	2	1380	1788	9	5	1	4039	3639	12	10	2	1786	1460	16	4	4	618	603	20	10	0	3048	2572	29	1	1	1320	1360
3	5	3	2753	3117	6	4	4	683	979	9	5	3	1544	1732	12	10	4	1928	1814	16	4	6	672	681	20	10	2	454	377	29	3	1	153-	1140
3	5	5	1951	2100	6	4	6	937	1289	9	5	5	873	762	12	10	6	460	294	16	6	0	2306	1939	20	10	4	1538	1700					

Table IV. Coordination around iodine.

I-O(1)	1.78(3) Å	O(1)-O(2)	2.82(4) Å
I-O(2)	1.90(2)	O(1)-O(3)	2.71(5)
I-O(3)	1.85(3)	O(2)-O(3)	2.84(4)
O(1)-I-O(2)	99.1(1.1)°	O(2)-O(1)-O(3)	61.7(1.0)°
O(1)-I-O(3)	96.2(1.5)	O(1)-O(2)-O(3)	57.2(1.1)
O(2)-I-O(3)	98.0(1.2)	O(1)-O(3)-O(2)	61.1(1.0)
I-H_2O(1'')	2.89(3) Å	I-O(2''')	2.85(2) Å
I-H_2O(2')	2.86(7)		
O(1)-I-O(2''')	76.8(1.0)°	H_2O(1'')-I-O(3)	81.6(1.3)°
O(1)-I-H_2O(2')	75.0(1.4)	H_2O(1'')-I-O(2''')	101.9(0.7)
O(3)-I-O(2''')	93.5(1.1)	H_2O(1'')-I-H_2O(2')	107.1(1.1)
O(2''')-I-H_2O(2')	84.0(0.9)	H_2O(1'')-I-O(1)	177.4(1.2)
O(2)-I-H_2O(2')	84.4(1.0)	O(2)-I-O(2''')	168.3(0.9)
H_2O(1'')-I-O(2)	81.8(0.9)	O(3)-I-H_2O(2')	171.2(1.5)

Asymmetric units:

'	¼−x	¼+y	¼+z	v	x	−½+y	−½+z
''	½−x	½−y	z	vi	x	−½+y	½+z
'''	¼−x	−¼+y	−¼+z	vii	¼−x	−¼+y	¾+z
iv	¼−x	¾−y	−¼+z	viii	¼+x	¾−y	¾+z

Table V. Coordination around calcium.

Ca-H_2O(1)	2.50(3) Å	O(1''')-H_2O(1'')	2.99(4) Å
Ca-H_2O(1'')	2.50(3)	H_2O(1'')-H_2O(3'')	2.80(5)
Ca-H_2O(2)	2.43(5)	H_2O(3'')-H_2O(2)	3.08(5)
Ca-H_2O(2'')	2.43(5)	H_2O(2)-O(1''')	2.96(7)
Ca-H_2O(3)	2.50(3)	O(1''')-O(1^{iv})	3.19(4)
Ca-H_2O(3'')	2.50(3)	O(1''')-H_2O(1)	3.49(4)
Ca-O(1''')	2.57(3)	H_2O(1)-H_2O(2)	2.91(5)
Ca-O(1^{iv})	2.57(3)	H_2O(2)-H_2O(3)	3.17(6)
		H_2O(3)-H_2O(3'')	3.11(3)
O(1''')-Ca-H_2O(2)	72.5(1.7)°	H_2O(3'')-H_2O(2)-O(1''')	88.5(1.3)°
H_2O(2)-Ca-H_2O(3'')	77.5(1.5)	H_2O(1'')-O(1''')-O(1^{iv})	68.7(0.9)
H_2O(3'')-Ca-H_2O(1'')	68.1(1.0)	O(1^{iv})-O(1''')-H_2O(1)	53.0(0.8)
H_2O(1'')-Ca-O(1''')	72.4(0.9)	H_2O(1)-O(1''')-H_2O(2)	52.8(1.0)
O(1''')-Ca-O(1^{iv})	76.8(0.9)	O(1''')-H_2O(1'')-O(1^{iv})	58.3(0.8)
O(1''')-Ca-H_2O(1)	87.0(1.0)	O(1^{iv})-H_2O(1'')-H_2O(2'')	54.1(1.3)
H_2O(1)-Ca-H_2O(2)	72.2(1.0)	H_2O(2'')-H_2O(1'')-H_2O(3'')	67.4(1.6)
H_2O(2)-Ca-H_2O(3)	80.1(1.6)	H_2O(1'')-H_2O(3'')-H_2O(2'')	57.9(1.4)
H_2O(3)-Ca-H_2O(3'')	76.9(1.0)	H_2O(2'')-H_2O(3'')-H_2O(3)	58.8(0.9)
H_2O(2)-O(1''')-H_2O(1'')	88.4(1.3)	H_2O(3)-H_2O(3'')-H_2O(2)	61.6(1.1)
O(1''')-H_2O(1'')-H_2O(3'')	93.3(1.2)	H_2O(3'')-H_2O(2)-H_2O(3)	59.6(1.2)
H_2O(1'')-H_2O(3'')-H_2O(2)	89.6(1.7)	H_2O(3)-H_2O(2)-H_2O(1)	54.7(1.2)
		H_2O(1)-H_2O(2)-O(1''')	73.1(1.7)

Asymmetric units: see Table IV.

Table VI. Hydrogen bonds.

H_2O(1)-O(2^{v})	2.67(4) Å	H_2O(2)-O(3^{vi})	2.72(3) Å
H_2O(1)-O(3^{vi})	2.78(4)	H_2O(3)-O(1^{viii})	2.80(5)
H_2O(2)-O(3^{vii})	2.64(7)	H_2O(3)-O(2^{vi})	2.96(4)

Asymmetric units: see Table IV.

Description of the Structure and Discussion

The clinographic projection of the structure is shown in Figure 1. The structure consists of chains of pyramidal anions IO_3^- joined to one another by intermolecular I . . . O interactions. The chains are held together by bridging Ca^{2+} ions and by hydrogen bonds of water molecules.

The coordination polyhedron around calcium (Figure 2) can be described as a square antiprism whose corners are occupied by six water molecules and two oxygen atoms belonging to different anions. The bonds around Ca^{2+} are in the range Ca–O = 2.43-2.57 Å, the longest ones being those with the oxygen atoms of the anions. The angles in the polyhedron are fairly close to those of the regular antiprism. This type of coordination has been found also in calcium bromide tetra(diacetamide), $CaBr_2 . 4(CH_3CO)_2NH$[9] with distances Ca–O = 2.37-2.46 Å. Coordination numbers from six to nine are rather common for calcium. Coordination number 8 gives rise to different kinds of polyhedra with distances Ca–O = 2.41-2.54 [10], Ca–O = 2.37-2.57 Å and Ca–N = 2.49 Å [11], Ca–O = 2.37-2.50

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Table VII. Environment of iodine atom in iodate(V) crystals.

Compound	Coordination number	I–O(1)	I–O(2)	I–O(3)	I...O	I...O	I...O	I...O	I...O	I...OH_2	I...OH_2	I...Cl
$Ca(IO_3)_2 \cdot 6H_2O$	6	1.78(3)	1.90(2)	1.85(3)	2.85(2)					2.86(7)	2.89(3)	
$Sr(IO_3)_2 \cdot H_2O$[16]	7	1.786(8)	1.806(9)	1.825(6)	2.853(11)	2.846(11)	3.168(6)	3.219(8)				
$K_2H(IO_3)_2Cl$[17]	6	1.89(3)	1.83(2)	1.94(1)	2.61(1)	2.95(2)						3.07(1)
	6	1.94(3)	1.81(3)	1.96(2)	2.47(4)	2.59(2)						3.03(1)
$Ce(IO_3)_4 \cdot H_2O$[18]	6	1.81	1.83	1.84	2.93	2.99	3.00					
	6	1.82	1.82	1.83	2.56	2.78	2.99					
	6	1.83	1.82	1.86	2.51	2.73				3.10		
	6	1.77	1.82	1.82	2.55	2.66				3.00		
$Ce(IO_3)_4$[19]	8	1.78(9)	1.84(9)	1.83(9)	2.68(9)	2.90(9)	3.07(9)	3.25(9)	3.28(9)			
$Zr(IO_3)_4$[20]	8	1.81(2)	1.84(2)	1.85(2)	2.55(2)	2.83(2)	2.94(2)	2.94(2)	3.11(2)			
HI_3O_8[21]	6	1.80	1.78	1.97	2.58	2.62	2.71					
	6	1.78	1.79	1.95	2.38	2.56	2.83					
	7	1.90	1.79	1.81	2.54	2.59	3.11	3.17				
$LiIO_3$[22]	6	1.81(1)	1.81(1)	1.81(1)	2.89(1)	2.89(1)	2.89(1)					
α-HIO_3[23]	6	1.82	1.90	1.78	2.50	2.77	2.88					

and Ca–N = 2.59 [12], in some cases one or two of the bonds are much longer (~2.9 Å) than the others [13-15].

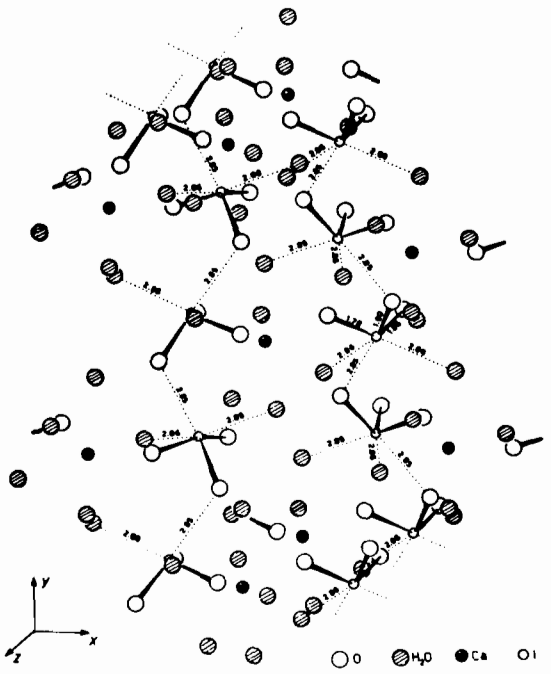

Figure 1. Clinographic projection of the structure.

The iodate anion is pyramidal with bonds between iodine and oxygen I–O(1) = 1.78, I–O(2) = 1.90, I–O(3) = 1.85 Å.

These can be compared with values found in other iodates (Table VII). The environment of each iodine atom of the anion (Figure 3) is approximately octahedral; three corners of the octahedron are occupied by the oxygen atoms of the anion, one corner by one oxygen atom of a different anion, I...O = 2.85 Å and two corners by water molecules, I...OH_2 (1) = 2.89 and I...OH_2(2) = 2.86 Å. The intermolecular distances between iodine and oxygen atoms do not present here any particular short values (2.5 Å) as those found in other iodates.

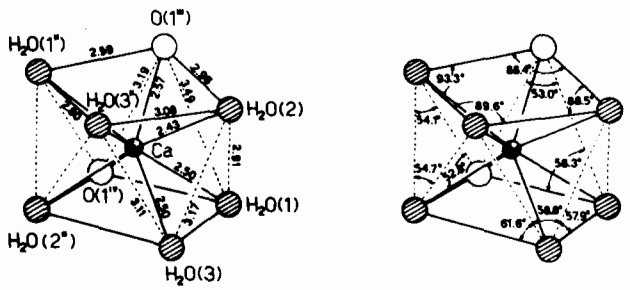

Figure 2. Coordination polyhedron around calcium ion.

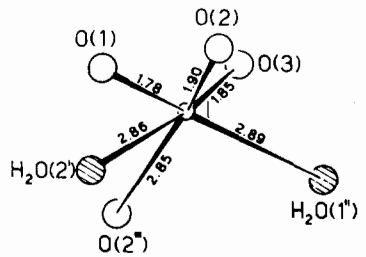

Figure 3. Environment of iodine atom. Distances between iodine and $H_2O(2')$, $H_2O(1'')$, O(2''') correspond to dotted lines of Fig. 1.

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Each water molecule forms two hydrogen bonds with oxygen atoms of the anion: $H_2O(1)\ldots O(2)=2.67$ and $H_2O(1)\ldots O(3)=2.78$ Å, $H_2O(2)\ldots O(3)=2.64$ and $H_2O(2)\ldots O(3)=2.72$ Å, $H_2O(3)\ldots O(1)=2.80$ and $H_2O(3)\ldots O(2)=2.96$ Å. Some of them are particularly strong: they determine the packing of the chains in the crystal structure.

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