Acta Cryst. (1970). B**26**, 1075

Crystal and Molecular Structure of Hexaquomagnesium Trihydrogenhexaoxoiodate(VII)

BY F. BIGOLI, A. M. MANOTTI LANFREDI, A. TIRIPICCHIO AND M. TIRIPICCHIO CAMELLINI

Istituto di Chimica Generale, University of Parma, Parma, Italy

(*Received* 8 *July* 1969)

Crystals of hexaquomagnesium trihydrogenhexaoxoiodate(VII), $[Mg(OH_2)_6][H_3IO_6]$, are monoclinic, space group *Pc*. The unit-cell constants are $a = 5{\cdot}180$ (6), $b = 9{\cdot}886$ (13), $c = 10{\cdot}625$ (7) Å, $\beta = 116{\cdot}90$ (15)°, $Z = 2$. The structure was solved from three-dimensional data ($R = 8{\cdot}8\%$). The structure consists of octahedral cations $[Mg(OH_2)_6]^{2+}$ and octahedral anions $[H_3IO_6]^{2-}$. The iodine–oxygen bond lengths range from 2·01 to 1·78 Å, and the magnesium–water bond lengths from 2·15 to 2·06 Å. The hexaquocations and the trihydrogenhexaoxoiodato(VII) anions are held together by a dense network of hydrogen bonds. There are fourteen independent possible hydrogen bonds O···O, shorter than 2·86 Å, the shortest being 2·56 Å.

Introduction

As part of a programme of research on compounds of oxygenated acids of iodine(VII) and iodine(V) (Ferrari, Braibanti & Tiripicchio, 1965; Ferrari, Cingi & Guastini, 1967; Biagini Cingi, Emiliani & Guastini, 1967; Braibanti, Tiripicchio & Manotti Lanfredi, 1967) a hydrated magnesium periodate has been examined. The compound could be represented, assuming the existence of hexaquomagnesium cations, either as an enneaoxodiiodate(VII), $[Mg(OH_2)_6]_2[I_2O_9].3H_2O$, or as a dihydrogendecaoxodiiodate(VII), $[Mg(OH_2)_6]_2[H_2I_2O_{10}].2H_2O$, or as a trihydrogenhexaoxoiodate(VII), $[Mg(OH_2)_6][H_3IO_6]$. According to Siebert (1967) the compound should be considered as a dihydrogendecaoxodiiodate(VII), an assignment based on an analysis of the infrared spectrum of the compound. On the other hand, Ferrari, Cingi & Guastini (1967) concluded, on the grounds of chromatographic tests, that the compound is very likely a trihydrogenhexaoxoiodate(VII). Therefore, the study of the crystal structure of this compound has been undertaken in order to solve the problem.

Table 1. *Fractional atomic coordinates (with e.s.d.'s)* × 10^4

	x	*y*	*z*
I	0000	2206 (2)	2500
Mg	−0295 (37)	2869 (22)	7516 (20)
O(1)	−1025 (97)	1054 (17)	0780 (37)
O(2)	−2034 (92)	1064 (26)	3005 (46)
O(3)	1085 (89)	3319 (14)	4080 (39)
O(4)	2067 (102)	3304 (32)	1759 (47)
O(5)	−3447 (76)	3252 (32)	1337 (44)
O(6)	3463 (70)	1086 (32)	3543 (41)
O(7)	2528 (97)	1541 (24)	9173 (47)
O(8)	−3411 (102)	1485 (30)	7398 (61)
O(9)	−3292 (90)	3993 (26)	5875 (40)
O(10)	2976 (91)	4168 (32)	7725 (50)
O(11)	−0851 (86)	4095 (22)	9021 (41)
O(12)	0633 (78)	1672 (26)	6129 (45)

Experimental

Preparation

Crystals of the compound were obtained by evaporation of aqueous solutions, obtained from equivalent amounts of magnesium carbonate and periodic acid.

Table 2. *Anisotropic thermal parameters* (Å²)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	2·402	2·641	2·696	−0·020	1·239	−0·008
Mg	1·776	2·272	2·328	−0·231	1·119	0·132
O(1)	3·614	3·497	3·941	−0·045	1·634	−0·344
O(2)	3·815	2·994	3·736	0·244	1·291	−0·147
O(3)	3·635	2·728	3·812	0·362	1·607	0·288
O(4)	3·101	2·694	3·312	−0·253	1·610	−0·048
O(5)	3·089	3·221	3·361	0·259	1·358	0·363
O(6)	3·132	3·339	3·683	0·377	1·607	0·596
O(7)	3·335	3·055	3·713	−0·151	1·624	0·051
O(8)	3·169	3·847	5·010	−0·005	1·986	0·041
O(9)	3·948	4·301	4·182	0·035	1·698	0·140
O(10)	3·484	3·856	3·800	0·163	1·738	0·073
O(11)	2·914	3·309	3·287	−0·099	1·456	−0·018
O(12)	3·484	3·569	3·626	0·161	1·692	0·020

Shifts in the last cycle

$|\Delta B_{ij}|_{av} = 0{\cdot}064$, $|\Delta B_{ij}|_{max} = 0{\cdot}177$.

Table 3. *Observed and calculated structure factors*

The $10F_o$ followed by = were unobserved.

h	k	l	$10F_o$	$10F_c$	α	h	k	l	$10F_o$	$10F_c$	α	h	k	l	$10F_o$	$10F_c$	α	h	k	l	$10F_o$	$10F_c$	α	h	k	l	$10F_o$	$10F_c$	α
1	0	0	1205	1349	359	4	1	3	260	235	8	1	2	1	386	383	163	-3	2	10	392	343	3	-3	3	7	302	284	185	3	4	5	239	228	351
2	0	0	611	570	3	-4	1	3	534	580	351	-1	2	1	465	407	194	-4	2	10	338	293	15	-4	3	7	293	287	168	-3	4	5	312	330	350
3	0	0	836	823	349	5	1	3	194	181	8	2	2	1	502	463	134	-5	2	10	256	239	14	-5	3	7	211	196	155	4	4	5	127	149	353
4	0	0	420	387	349	-5	1	3	349	301	345	-2	2	1	550	560	245	-6	2	10	185	207	9	-6	3	7	178	177	171	-4	4	5	229	253	14
5	0	0	289	244	1	-6	1	3	203	176	341	3	2	1	204	190	179	0	2	11	107	95	26	0	3	8	161	172	159	-5	4	5	223	234	11
0	0	2	1184	1335	179	0	1	4	205	205	49	-3	2	1	309	296	198	1	2	11	27=	67	353	1	3	8	123	136	185	-6	4	5	159	162	359
1	0	2	462	540	181	1	1	4	120	146	338	4	2	1	152	129	190	-1	2	11	134	121	347	-1	3	8	188	196	149	0	4	6	269	276	179
-1	0	2	1146	1265	183	-1	1	4	429	492	84	-4	2	1	228	197	167	-2	2	11	191	165	355	2	3	8	127	115	184	1	4	6	237	268	183
2	0	2	742	833	175	2	1	4	145	175	40	5	2	1	122	103	156	-3	2	11	173	148	22	-2	3	8	172	162	143	-1	4	6	384	425	174
-2	0	2	272	363	175	-2	1	4	152	123	263	-5	2	1	135	128	231	-4	2	11	129	100	345	-3	3	8	158	153	152	2	4	6	249	264	179
3	0	2	594	581	172	3	1	4	67	53	312	-6	2	1	83	85	203	-5	2	11	110	90	351	-4	3	8	164	156	187	-2	4	6	436	411	191
-3	0	2	702	782	172	-3	1	4	136	148	302	0	2	2	971	973	352	0	2	12	32=	173	189	-5	3	8	146	139	173	3	4	6	182	179	185
4	0	2	357	323	179	4	1	4	77	56	290	1	2	2	703	825	353	-1	2	12	237	208	181	-6	3	8	103	111	152	-3	4	6	315	306	177
-4	0	2	679	642	184	-4	1	4	82	48	61	-1	2	2	958	997	7	-2	2	12	246	217	185	0	3	9	177	200	5	-4	4	6	281	300	172
5	0	2	365	301	173	-5	1	4	63=	34	311	2	2	2	613	674	0	-3	2	12	251	219	182	1	3	9	153	154	357	-5	4	6	253	273	192
-5	0	2	363	309	185	-6	1	4	78	57	345	-2	2	2	684	847	7	-4	2	12	251	229	187	-1	3	9	260	295	3	-6	4	6	180	194	184
-6	0	2	275	232	187	0	1	5	248	299	176	3	2	2	486	472	351	-5	2	12	193	202	191	2	3	9	140	136	3	0	4	7	214	244	165
0	0	4	440	536	3	1	1	5	541	635	178	-3	2	2	591	654	4	-2	2	13	90	82	186	-2	3	9	216	212	355	1	4	7	222	262	195
1	0	4	742	818	353	-1	1	5	415	512	176	4	2	2	344	318	349	-3	2	13	113	98	204	-3	3	9	187	179	355	-1	4	7	244	290	176
-1	0	4	438	697	3	2	1	5	415	485	177	-4	2	2	479	467	14	-4	2	13	70	72	201	-4	3	9	269	258	349	2	4	7	197	199	178
2	0	4	556	641	365	-2	1	5	511	531	177	5	2	2	234	221	353	0	3	0	334	427	180	-5	3	9	212	201	341	-2	4	7	303	313	200
-2	0	4	631	605	13	3	1	5	259	243	191	-5	2	2	351	317	5	1	3	0	357	325	201	-6	3	9	128	145	351	3	4	7	105	116	173
3	0	4	367	349	347	-3	1	5	248	260	144	-6	2	2	215	201	4	2	3	0	328	294	156	0	3	10	97	98	348	-3	4	7	265	278	189
-3	0	4	717	786	12	4	1	5	218	185	192	0	2	3	582	584	50	3	3	0	281	264	188	1	3	10	107	98	0	-4	4	7	296	302	187
4	0	4	336	272	355	-4	1	5	303	365	164	1	2	3	357	420	41	4	3	0	219	205	207	-1	3	10	101	74	339	-5	4	7	254	260	196
-4	0	4	644	705	5	-5	1	5	305	287	176	-1	2	3	621	610	322	5	3	0	134	112	202	-2	3	10	125	111	1	-6	4	7	164	179	188
-5	0	4	417	399	7	-6	1	5	191	174	163	2	2	3	182	204	350	0	3	1	738	661	2	-3	3	10	166	151	353	0	4	8	263	290	358
-6	0	4	338	282	19	0	1	6	75	38	169	-2	2	3	264	315	308	1	3	1	537	544	28	-4	3	10	125	111	331	1	4	8	226	263	354
0	0	6	848	901	184	1	1	6	126	132	217	3	2	3	170	163	25	-1	3	1	570	536	14	-5	3	10	96	75	340	-1	4	8	271	320	359
1	0	6	577	667	176	-1	1	6	122	120	243	-3	2	3	162	176	349	2	3	1	529	553	20	-6	3	10	19=	81	354	2	4	8	160	158	359
-1	0	6	723	780	187	2	1	6	83	63	223	4	2	3	195	159	17	-2	3	1	299	328	353	0	3	11	140	130	176	-2	4	8	299	318	12
2	0	6	371	389	176	-2	1	6	101	87	172	-4	2	3	341	337	334	3	3	1	481	481	351	-1	3	11	175	158	175	-3	4	8	288	290	19
-2	0	6	825	818	178	3	1	6	59	44	98	5	2	3	80	78	2	-3	3	1	349	358	356	-2	3	11	229	196	163	-4	4	8	281	281	341
3	0	6	354	291	174	-3	1	6	121	98	132	-5	2	3	173	155	5	4	3	1	262	263	356	-3	3	11	208	194	170	-5	4	8	225	225	6
-3	0	6	825	802	193	4	1	6	16=	31	183	-6	2	3	104	93	39	-4	3	1	285	267	359	-4	3	11	225	212	177	-6	4	8	135	163	15
4	0	6	49=	159	174	-4	1	6	131	112	203	0	2	4	681	705	167	5	3	1	150	144	10	-5	3	11	193	187	171	0	4	9	233	257	358
-4	0	6	544	541	194	-5	1	6	101	89	156	1	2	4	596	697	174	-5	3	1	190	184	334	-1	3	12	70	62	190	1	4	9	206	226	0
-5	0	6	347	310	194	-6	1	6	91	66	122	-1	2	4	624	743	190	-6	3	1	16=	142	343	-2	3	12	102	84	186	-1	4	9	257	279	357
-6	0	6	246	212	200	0	1	7	215	240	358	2	2	4	455	546	179	0	3	2	432	370	18	-3	3	12	153	134	190	2	4	9	40	118	357
0	0	8	446	482	7	1	1	7	307	356	357	-2	2	4	813	798	199	1	3	2	421	410	303	-4	3	12	118	113	169	-2	4	9	275	299	13
1	0	8	297	306	3	-1	1	7	213	263	353	3	2	4	374	350	174	-1	3	2	290	283	339	-5	3	12	80	91	147	-3	4	9	263	262	18
-1	0	8	467	568	9	2	1	7	211	195	7	-3	2	4	563	653	188	2	3	2	259	278	335	-2	3	13	24=	106	356	-4	4	9	250	254	7
2	0	8	354	297	358	-2	1	7	572	641	357	4	2	4	269	242	171	-2	3	2	430	456	307	-3	3	13	113	122	351	-5	4	9	207	195	12
-2	0	8	637	603	353	3	1	7	159	142	12	-4	2	4	447	483	191	3	3	2	298	308	20	-4	3	13	20=	128	351	-6	4	9	76	112	16
3	0	8	56=	243	355	-3	1	7	475	456	347	-5	2	4	362	336	192	-3	3	2	176	164	336	0	4	0	147	110	180	0	4	10	198	210	179
-3	0	8	573	585	354	-4	1	7	317	293	338	-6	2	4	265	221	186	4	3	2	174	146	22	1	4	0	689	547	2	1	4	10	157	169	176
-4	0	8	433	391	12	-5	1	7	290	287	0	0	2	5	369	399	213	-4	3	2	82	63	356	2	4	0	734	667	358	-1	4	10	260	261	185
-5	0	8	331	297	5	-6	1	7	201	194	0	1	2	5	211	262	169	5	3	2	81	79	31	3	4	0	323	323	3	-2	4	10	273	267	184
-6	0	8	276	235	4	0	1	8	94	89	295	-1	2	5	361	422	185	-5	3	2	133	134	4	4	4	0	322	322	358	-3	4	10	233	219	186
0	0	10	259	265	181	1	1	8	72	63	0	2	2	5	166	190	148	-6	3	2	107	112	7	5	4	0	215	218	350	-4	4	10	228	233	187
1	0	10	227	190	181	-1	1	8	91	89	268	-2	2	5	468	412	143	0	3	3	528	490	167	0	4	1	132	62	14	-5	4	10	179	184	185
-1	0	10	305	309	180	2	1	8	47=	24	31	3	2	5	154	133	157	1	3	3	371	415	205	1	4	1	700	655	350	0	4	11	146	148	184
-2	0	10	387	319	181	-2	1	8	187	169	325	-3	2	5	181	168	192	-1	3	3	543	554	163	-1	4	1	498	430	4	-1	4	11	182	168	189
-3	0	10	404	393	183	3	1	8	21=	19	14	-4	2	5	97	82	172	2	3	3	286	320	185	2	4	1	549	504	351	-2	4	11	237	225	186
-4	0	10	328	317	190	-3	1	8	172	147	329	-4	2	5	192	217	203	-2	3	3	506	519	191	-2	4	1	795	763	9	-3	4	11	204	194	181
-5	0	10	315	268	191	-4	1	8	100	66	50	-5	2	5	159	147	182	3	3	3	298	300	181	3	4	1	285	286	6	-4	4	11	176	161	178
-6	0	10	294	270	189	-5	1	8	110	87	20	-6	2	5	84	66	200	-3	3	3	299	368	176	-3	4	1	363	351	7	-5	4	11	134	146	185
0	0	12	260	217	1	-6	1	8	74	52	357	0	2	6	525	572	2	4	3	3	228	202	195	4	4	1	294	280	354	-1	4	12	107	115	9
-1	0	12	373	292	357	0	1	9	231	255	186	1	2	6	454	510	1	-4	3	3	271	282	165	-4	4	1	285	284	5	-2	4	12	165	171	6
-2	0	12	299	240	3	1	1	9	168	165	189	-1	2	6	519	614	1	5	3	3	14=	115	182	5	4	1	156	156	347	-3	4	12	159	155	352
-3	0	12	328	276	17	-1	1	9	231	259	182	2	2	6	344	362	2	-5	3	3	230	227	167	-5	4	1	256	250	16	-4	4	12	144	145	355
-4	0	12	355	287	18	2	1	9	135	124	183	-2	2	6	697	683	4	-6	3	3	172	170	166	0	4	2	647	549	175	-3	4	13	30=	141	0
-5	0	12	221	196	10	-2	1	9	368	360	177	3	2	6	285	256	2	0	3	4	384	375	202	1	4	2	793	747	181	0	5	0	221	291	0
0	1	0	152	146	0	-3	1	9	452	411	175	-3	2	6	605	570	2	1	3	4	123	139	171	-1	4	2	592	545	179	1	5	0	438	381	6
1	1	0	175	157	344	-4	1	9	336	289	174	-4	2	6	416	438	359	-1	3	4	357	362	232	2	4	2	402	403	181	2	5	0	427	391	10
2	1	0	197	166	310	-5	1	9	284	263	171	-5	2	6	342	346	6	2	3	4	143	164	222	-2	4	2	750	781	187	3	5	0	339	321	2
3	1	0	102	88	54	-6	1	9	237	218	168	-6	2	6	257	238	11	-2	3	4	301	279	140	3	4	2	317	312	174	4	5	0	241	232	6
4	1	0	122	98	48	0	1	10	68	55	158	0	2	7	192	204	332	3	3	4	134	127	172	-3	4	2	405	411	190	5	5	0	123	126	19
5	1	0	94	67	11	1	1	10	56	48	193	1	2	7	164	188	3	-3	3	4	284	321	162	4	4	2	264	257	171	0	5	1	339	276	179
0	1	1	780	836	178	-1	1	10	63=	5	233	-1	2	7	178	185	3	4	3	4	88	77	157	-4	4	2	248	261	189	1	5	1	379	319	155
1	1	1	587	687	186	-2	1	10	67	52	226	2	2	7	146	142	345	-4	3	4	115	124	180	5	4	2	103	114	171	-1	5	1	367	318	176
-1	1	1	747	810	178	-3	1	10	112	88	170	-2	2	7	216	211	37	-5	3	4	126	125	158	-5	4	2	233	235	186	2	5	1	314	313	173
2	1	1	371	393	194	-4	1	10	59=	16	76	3	2	7	109	93	321	-6	3	4	146	140	178	-6	4	2	35=	139	187	-2	5	1	371	349	154
-2	1	1	614	685	186	-5	1	10	45=	6	322	-3	2	7	237	213	24	0	3	5	477	503	351	0	4	3	865	783	184	3	5	1	306	307	184
3	1	1	203	191	211	-6	1	10	56	45	157	-4	2	7	284	264	36	1	3	5	198	215	352	1	4	3	589	604	178	-3	5	1	200	191	172
-3	1	1	542	576	174	0	1	11	195	172	0	-5	2	7	152	135	39	-1	3	5	471	512	329	-1	4	3	789	737	183	4	5	1	190	191	193
4	1	1	229	222	185	1	1	11	20=	129	8	-6	2	7	66	58	0	2	3	5	142	160	356	2	4	3	287	329	181	-4	5	1	159	153	185
-4	1	1	426	411	169	-1	1	11	270	242	355	0	2	8	390	430	182	-2	3	5	507	470	353	-2	4	3	766	747	177	5	5	1	91	94	203
5	1	1	275	243	182	-2	1	11	257	211	354	1	2	8	287	324	173	3	3	5	234	221	15	3	4	3	280	290	175	-5	5	1	144	139	173
-5	1	1	311	268	176	-3	1	11	232	190	344	-1	2	8	405	491	188	-3	3	5	498	523	5	-3	4	3	351	402	187	0	5	2	365	322	179
-6	1	1	183	176	171	-4	1	11	221	188	353	2	2	8	263	238	179	4	3	5	141	134	13	4	4	3	212	192	169	1	5	2	435	417	200
0	1	2	229	179	203	-5	1	11	197	178	357	-2	2	8	547	549	179	-4	3	5	266	323	348	-4	4	3	208	219	199	-1	5	2	386	344	172
1	1	2	465	511	98	-6	1	11	8=	185	341	3	2	8	23=	177	179	-5	3	5	228	236	333	-5	4	3	219	216	190	2	5	2	379	362	185
-1	1	2	163	131	156	0	1	12	21=	16	3	-3	2	8	544	489	181	-6	3	5	211	186	2	-6	4	3	115=	131	190	-2	5	2	322	325	181
2	1	2	151	123	111	-1	1	12	41	20	5	-4	2	8	373	343	186	0	3	6	269	289	1	0	4	4	664	656	355	3	5	2	359	337	179
-2	1	2	377	435	120	-2	1	12	71	38	45	-5	2	8	320	298	186	1	3	6	133	148	40	1	4	4	351	392	6	-3	5	2	177	165	159
3	1	2	147	131	245	-3	1	12	86	54	210	-6	2	8	239	232	191	-1	3	6	265	285	13	-1	4	4	755	745	358	4	5	2	218	213	190
-3	1	2	131	130	164	-4	1	12	45	40	324	0	2	9	110	113	201	2	3	6	106	99	25	2	4	4	268	307	356	-4	5	2	155	160	157
4	1	2	63=	32	218	-5	1	12	43	26	302	1	2	9	169	163	221	-2	3	6	163	139	345	-2	4	4	696	634	6	5	5	2	12=	93	190
-4	1	2	74=	47	240	-1	1	13	13=	137	163	-1	2	9	171	174	133	3	3	6	113	95	330	3	4	4	282	281	354	-5	5	2	152	160	163
5	1	2	57	45	225	-2	1	13	180	157	173	2	2	9	95	84	181	-3	3	6	278	271	358	-3	4	4	382	401	2	0	5	3	382	324	343
-5	1	2	102	83	207	-3	1	13	147	134	172	-2	2	9	158	132	199	-4	3	6	258	274	9	4	4	4	174	171	357	1	5	3	272	282	333
-6	1	2	68	55	212	-4	1	13	153	154	164	-3	2	9	151	131	201	-5	3	6	183	181	331	-4	4	4	242	267	14	-1	5	3	343	313	21
0	1	3	546	622	328	0	2	0	1116	1204	180	-4	2	9	237	206	168	-6	3	6	141	134	327	-5	4	4	233	229	11	2	5	3	202	213	5
1	1	3	549	648	7	1	2	0	1000	1014	184	-5	2	9	170	144	185	0	3	7	350	396	188	-6	4	4	144	148	357	-2	5	3	419	405	341
-1	1	3	682	740	358	2	2	0	839	791	194	-6	2	9	58	53	181	1	3	7	158	190	178	0	4	5	431	447	3	3	5	3	200	198	4
2	1	3	411	486	5	3	2	0	601	573	179	0	2	10	262	276	356	-1	3	7	367	425	184	1	4	5	247	298	5	-3	5	3	225	230	343
-2	1	3	430	489	7	4	2	0	451	409	172	1	2	10	221	209	354	2	3	7	204	212	181	-1	4	5	554	581	7	4	5	3	98	100	354
3	1	3	241	239	8	5	2	0	308	281	179	-1	2	10	312	325	9	-2	3	7	195	187	179	2	4	5	255	288	7	-4	5	3	82	74	40
-3	1	3	516	564	357	0	2	1	537	456	183	-2	2	10	361	333	6	3	3	7	180	169	185	-2	4	5	510	471	353	-5	5	3	122	132	7

Crystal data

Compound: hexaquomagnesium trihydrogenhexaoxoiodate(VII), $[Mg(OH_2)_6]$ $[H_3IO_6]$, F.W. 358·35.

Crystal class: monoclinic, domatic.

Unit cell (Cu $K\alpha$, $\bar{\lambda}=1{\cdot}5418$ Å; from rotation and Weissenberg photographs around [100] and [010]):

$a = 5{\cdot}180(6)$, $b = 9{\cdot}886(13)$, $c = 10{\cdot}625(7)$ Å

β 116·90(15)°, $V = 485{\cdot}4$ Å^3, $Z = 2$

$D_x = 2{\cdot}45$, $D_m = 2{\cdot}45$ g.cm^{-3}

Space group: Pc (C_s^2, No. 7) from systematic absences and positive piezoelectric responce.

μ(Cu $K\alpha$) = 276·9 cm^{-1}.

Table 3 (*cont.*)

h	k	l	$10F_o$	$10F_c$	α	h	k	l	$10F_o$	$10F_c$	α	h	k	l	$10F_o$	$10F_c$	α	h	k	l	$10F_o$	$10F_c$	α	h	k	l	$10F_o$	$10F_c$	α
-6	5	3	15=	121	1	2	5	8	167	158	2	5	6	1	25	157	172	-2	6	6	181	171	358	4	7	0	190	194	188	2	7	5	89	84	24
0	5	4	404	377	355	-2	5	8	126	114	8	-5	6	1	201	224	182	3	6	6	80	94	330	5	7	0	11=	160	182	-2	7	5	76	62	4
1	5	4	158	163	13	-3	5	8	113	105	356	0	6	2	357	295	21	-3	6	6	165	171	15	0	7	1	173	129	4	3	7	5	53	65	299
-1	5	4	446	413	332	-4	5	8	228	228	343	1	6	2	306	276	20	-4	6	6	168	181	31	1	7	1	263	215	313	-3	7	5	93	84	346
2	5	4	103	98	359	-5	5	8	163	152	335	-1	6	2	297	272	339	-5	6	6	94	103	14	-1	7	1	209	177	325	-4	7	5	96	103	23
-2	5	4	471	451	354	-6	5	8	18	124	339	2	6	2	231	193	347	0	6	7	339	352	4	2	7	1	234	195	300	-5	7	5	49	57	339
3	5	4	183	188	12	0	5	9	126	142	160	-2	6	2	217	193	16	1	6	7	228	256	359	-2	7	1	182	162	356	0	7	6	194	173	357
-3	5	4	348	360	1	1	5	9	126	140	172	3	6	2	159	158	15	-1	6	7	364	410	1	3	7	1	116	105	37	1	7	6	221	241	357
4	5	4	122	128	18	-1	5	9	141	153	174	-3	6	2	188	183	3	2	6	7	204	219	357	-3	7	1	96	79	5	-1	7	6	238	243	357
-4	5	4	174	210	344	-2	5	9	161	161	174	4	6	2	127	131	17	-2	6	7	323	333	4	4	7	1	93	88	34	2	7	6	187	194	4
-5	5	4	206	206	351	-3	5	9	144	137	166	-4	6	2	203	192	337	-3	6	7	308	330	9	-4	7	1	63	63	341	-2	7	6	295	313	357
-6	5	4	24=	151	355	-4	5	9	125	114	166	-5	6	2	91	102	15	-4	6	7	283	302	3	-5	7	1	64	76	32	-3	7	6	224	227	339
0	5	5	321	322	184	-5	5	9	101	103	182	0	6	3	715	651	355	-5	6	7	154	229	3	0	7	2	421	331	353	-4	7	6	182	193	340
1	5	5	137	147	200	0	5	10	102	111	178	1	6	3	506	492	352	0	6	8	112	114	167	1	7	2	412	380	4	-5	7	6	158	182	358
-1	5	5	271	270	204	1	5	10	97	115	172	-1	6	3	626	577	9	1	6	8	123	133	203	-1	7	2	431	361	356	0	7	7	75	72	149
2	5	5	127	126	215	-1	5	10	149	152	166	2	6	3	372	377	351	-1	6	8	132	133	152	2	7	2	276	246	10	1	7	7	79	87	199
-2	5	5	252	236	181	-2	5	10	179	182	166	-2	6	3	642	608	4	2	6	8	74	90	152	-2	7	2	381	396	3	-1	7	7	85	87	151
3	5	5	118	115	168	-3	5	10	141	137	174	3	6	3	343	340	354	-2	6	8	103	103	216	3	7	2	160	151	9	2	7	7	38	43	180
-3	5	5	310	333	178	-4	5	10	196	195	164	-3	6	3	427	474	7	-3	6	8	125	120	204	-3	7	2	295	310	355	-2	7	7	110	111	169
-4	5	5	163	186	182	-5	5	10	156	169	165	4	6	3	168	191	349	-4	6	8	176	180	186	4	7	2	138	159	3	-3	7	7	86	87	173
-5	5	5	137	147	163	0	5	11	80	88	355	-4	6	3	254	272	19	-5	6	8	98	108	190	-4	7	2	251	261	351	-4	7	7	110	115	209
-6	5	5	28=	136	169	-1	5	11	74	67	12	-5	6	3	208	225	7	0	6	9	221=	254	170	-5	7	2	156	177	352	-5	7	7	76	85	190
0	5	6	342	353	181	-2	5	11	112	113	12	0	6	4	398	353	213	1	6	9	174	204	170	0	7	3	215	184	213	0	7	8	154	161	176
1	5	6	102	110	188	-3	5	11	141	146	1	1	6	4	199	186	202	-1	6	9	272	306	188	1	7	3	177	162	131	1	7	8	150	160	184
-1	5	6	343	363	173	-4	5	11	105	113	348	-1	6	4	394	352	162	-2	6	9	283	296	184	-1	7	3	160	124	215	-1	7	8	172	186	176
2	5	6	117	137	185	-5	5	11	67	90	344	2	6	4	120	118	166	-3	6	9	265	273	188	2	7	3	89	92	175	-2	7	8	245	265	180
-2	5	6	224	208	172	-1	5	12	19=	82	8	-2	6	4	332	319	137	-4	6	9	228	246	191	-2	7	3	202	180	123	-3	7	8	236	241	174
3	5	6	145	146	187	-2	5	12	107	122	349	3	6	4	130	126	185	-5	6	9	158	189	187	3	7	3	89	81	192	-4	7	8	189	200	165
-3	5	6	347	332	182	-3	5	12	141	146	352	-3	6	4	170	163	167	0	6	10	78	89	24	-3	7	3	106	95	167	-5	7	8	132	166	174
-4	5	6	263	270	172	-4	5	12	110	135	355	4	6	4	74	93	191	-1	6	10	112	117	333	4	7	3	36	45	150	0	7	9	58	65	334
-5	5	6	185	190	160	0	6	0	159	211	180	-4	6	4	186	181	167	-2	6	10	130	130	353	-4	7	3	54	46	220	1	7	9	18=	70	6
-6	5	6	134	166	169	1	6	0	375	272	153	-5	6	4	129	134	172	-3	6	10	105	105	9	-5	7	3	45	57	211	-1	7	9	56	55	298
0	5	7	198	226	354	2	6	0	398	350	134	0	6	5	513	504	173	-4	6	10	121	135	340	0	7	4	331	293	179	-2	7	9	77	69	353
1	5	7	111	132	7	3	6	0	221	196	167	1	6	5	299	320	182	-5	6	10	72	113	347	1	7	4	295	314	182	-3	7	9	83	78	352
-1	5	7	236	254	357	4	6	0	127	124	184	-1	6	5	513	503	179	-1	6	11	152	181	7	-1	7	4	356	346	176	-4	7	9	40	35	16
2	5	7	120	127	9	5	6	0	75	85	147	2	6	5	267	291	182	-2	6	11	186	200	4	2	7	4	246	262	176	-5	7	9	32	45	37
-2	5	7	144	144	342	0	6	1	650	529	184	-2	6	5	466	440	189	-3	6	11	188	206	1	-2	7	4	325	317	176	0	7	10	98	135	37
3	5	7	20=	92	358	1	6	1	642	587	181	3	6	5	221	235	177	-4	6	11	154=	197	7	3	7	4	164	178	186	-1	7	10	132	157	359
-3	5	7	193	185	356	-1	6	1	635	557	181	-3	6	5	416	462	184	-2	6	12	23=	103	178	-3	7	4	190	228	172	-2	7	10	165	176	357
-4	5	7	203	210	8	2	6	1	528	472	181	-4	6	5	279	319	187	-3	6	12	27=	106	192	-4	7	4	202	236	173	-3	7	10	156	157	354
-5	5	7	158	161	347	-2	6	1	604	581	176	-5	6	5	203	229	189	0	7	0	158	243	180	-5	7	4	176	192	171	-4	7	10	123	150	354
-6	5	7	96	128	339	3	6	1	421	405	174	0	6	6	201	192	357	1	7	0	469	374	182	0	7	5	143	138	34	-1	7	11	12	30	195
0	5	8	201	216	1	-3	6	1	416	394	187	1	6	6	143	142	343	2	7	0	379	350	188	1	7	5	105	108	30	-2	7	11	46	58	222
1	5	8	150	166	3	4	6	1	278	290	172	-1	6	6	226	226	7	3	7	0	239	214	200	-1	7	5	229	209	53	-3	7	11	58	72	207
-1	5	8	264	294	358	-4	6	1	296	301	190	2	6	6	127	130	337																		

Intensity measurement

Integrated reflexions (831 observed out of 867 possible reflexions) *h*0*l*, *h*1*l*···*h*7*l* and 0*kl* were obtained by a Weissenberg camera and their intensities measured by a microdensitometer. The crystal used was a pseudo-hexagonal elongated prism and absorption corrections were applied as for cylindrical specimens ($\mu\bar{R}[010] = 5{\cdot}3$). The scattering factors were used in analytical form (Moore, 1963). No correction for anomalous dispersion was introduced because the iodine atoms were considered to be centrosymmetric with respect to each other and therefore their contributions to $\Delta f''$ cancelled one another out.

The calculations were performed on the computer Olivetti Elea 6001/S of the Centro di Calcolo elettronico of the University of Parma.

Determination and refinement of the structure

The structure was solved by Patterson and Fourier methods. The Fourier syntheses showed unequivocally that the structure of this compound is derived from hexaoxoiodic(VII) acid (orthoperiodic acid) and any

Table 4. *Main interatomic distances and angles* (*with e.s.d.'s* × 10^2)

I–O(1)	2·01 (3) Å	Mg–O(7)	2·15 (4) Å
I–O(2)	1·78 (5)	Mg–O(8)	2·08 (6)
I–O(3)	1·87 (3)	Mg–O(9)	2·06 (4)
I–O(4)	1·93 (5)	Mg–O(10)	2·06 (5)
I–O(5)	1·95 (4)	Mg–O(11)	2·13 (4)
I–O(6)	1·97 (4)	Mg–O(12)	2·11 (4)
O(1)–I–O(2)	88·0 (1·7)°	O(7)—Mg–O(8)	82·5 (2·0)°
O(1)–I–O(3)	177·1 (1·8)	O(7)—Mg–O(9)	174·4 (1·9)
O(1)–I–O(4)	85·1 (1·7)	O(7)—Mg–O(10)	94·1 (1·9)
O(1)–I–O(5)	86·2 (1·6)	O(7)—Mg–O(11)	90·3 (1·6)
O(1)–I–O(6)	89·5 (1·6)	O(7)—Mg–O(12)	86·8 (1·8)
O(2)–I–O(3)	94·6 (1·8)	O(8)—Mg–O(9)	92·1 (2·0)
O(2)–I–O(4)	173·1 (1·7)	O(8)—Mg–O(10)	176·4 (2·1)
O(2)–I–O(5)	91·7 (1·8)	O(8)—Mg–O(11)	93·1 (2·0)
O(2)–I–O(6)	89·2 (1·8)	O(8)—Mg–O(12)	90·3 (1·9)
O(3)–I–O(4)	92·2 (1·7)	O(9)—Mg–O(10)	91·3 (1·9)
O(3)–I–O(5)	94·3 (1·6)	O(9)—Mg–O(11)	91·3 (1·7)
O(3)–I–O(6)	89·9 (1·6)	O(9)—Mg–O(12)	91·9 (1·7)
O(4)–I–O(5)	87·8 (1·9)	O(10)–Mg–O(11)	87·0 (1·9)
O(4)–I–O(6)	90·8 (1·8)	O(10)–Mg–O(12)	89·3 (1·8)
O(5)–I–O(6)	175·6 (1·6)	O(11)–Mg–O(12)	175·1 (2·0)

other possible hypothesis can be excluded. The refinement was carried out by differential syntheses; anisotropic thermal parameters were refined by the method of Nardelli & Fava (1960) ($R=8{\cdot}8\%$, observed reflexions only). No definite physical significance can be attributed to the thermal parameters since their accuracy was highly affected by the systematic errors in the experimental data. The final results are quoted in Tables 1–5.

Table 5. *Possible hydrogen bonds* ($\leq 2{\cdot}86$ Å)

O(2)—O(6^{i})	2·64 (8) Å
O(5)—O(4^{i})	2·56 (8)
O(7)—O(5^{ii})	2·86 (6)
O(7)—O(6^{iii})	2·78 (4)
O(8)—O(2^{iii})	2·62 (4)
O(8)—O(12^{i})	2·76 (8)
O(9)—O(3^{i})	2·75 (7)
O(9)—O(5^{iv})	2·78 (4)
O(10)–O(4^{iv})	2·66 (5)
O(10)–O(11^{v})	2·85 (8)
O(11)–O(3^{iv})	2·74 (4)
O(11)–O(4^{vi})	2·72 (6)
O(12)–O(3)	2·81 (5)
O(12)–O(1^{iii})	2·80 (4)

Asymmetric units

i	$x-1$	y	z
ii	$1+x$	y	$1+z$
iii	x	$-y$	$\frac{1}{2}+z$
iv	x	$1-y$	$\frac{1}{2}+z$
v	$1+x$	y	z
vi	x	y	$1+z$

Discussion

The whole structure (Fig. 1) appears to be built up from anions $[H_3IO_6]^{2-}$ and hexaquocations, in approximate octahedra, held together by a dense network of hydrogen bonds. The iodine–oxygen bonds are not equal, ranging from 1·78 to 2·01 Å (Fig. 2). Oxygen atoms shared between I and H correspond generally to the longest iodine–oxygen bonds and unshared oxygen atoms to the shortest ones (Ferrari, Braibanti & Tiripicchio, 1965). Therefore I–O(2) = 1·78 and I–O(3) = 1·87 Å can be classified as I–O bonds and I–O(1) = 2·01 Å and I–O(6) = 1·97 Å as I–OH while I–O(5) = 1·95 and I–O(4) = 1·93 Å could share one hydrogen atom because they form a very strong hydrogen bond with one another [O(5)···O(4^{i}) = 2·56 Å]. In principle the assignment of H to O(5) seems more likely because this were so the anion would be *trans*-octahedrally coordinated (Jones, 1964) and consequently the hydrogen atoms should be as far as possible from one another.

Unfortunately the standard deviations are rather high. The angles between iodine–oxygen bonds show an average deviation ±2·3° from 90° with maximum deviation −4·9°, which suggests that the deviation from the octahedral configuration is not too high. The metal–water distances in the hexaquomagnesium cation range from 2·06 to 2·15 Å (Fig. 2). Distances quoted in the literature for this aquo cation are: Mg–OH_2 = 2·115, 2·068, 2·068 (Nardelli, Fava & Giraldi, 1962), 2·054, 2·099, 2·045, 2·046, 2·092, 2·055 (Baur, 1964), 2·054,

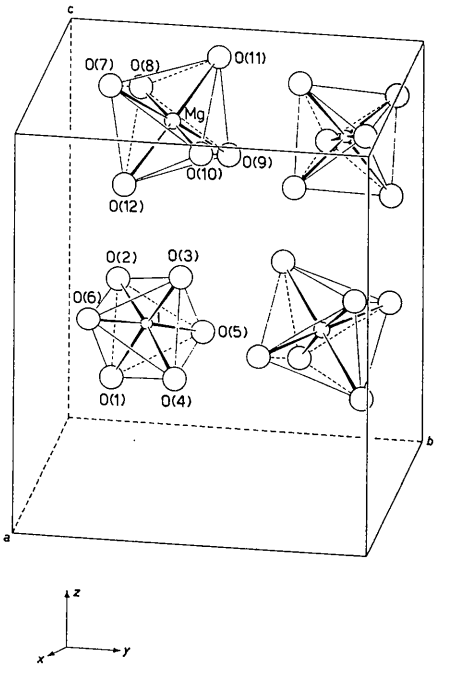

Fig. 1. Clinographic view of the structure.

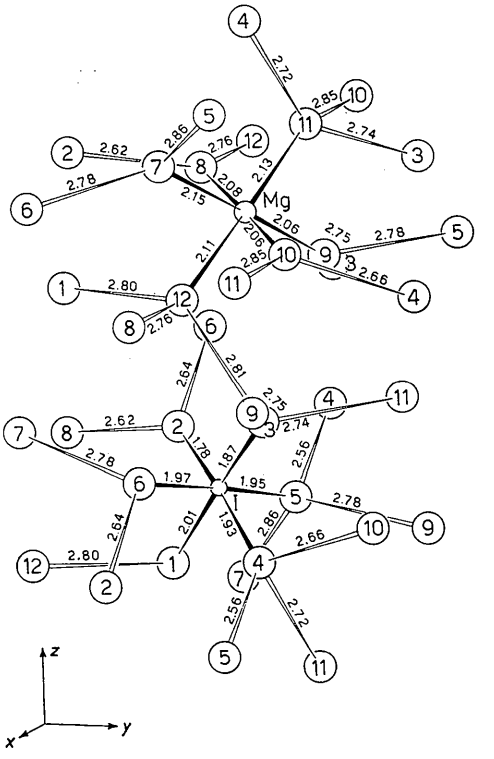

Fig. 2. Hydrogen bonds radiating from the octahedral groups $[Mg(OH_2)_6]^{2+}$ and $[H_3IO_6]^{2-}$.

2·059, 2·083 and 2·044, 2·046, 2·080 (Zalkin, Ruben & Templeton, 1964), 2·081, 2·080, 2·061 (Johnson, 1965), 2·059, 2·061, 2·065 (Sasvari & Jeffrey, 1966), 2·083, 2·073, 2·051 (Margulis & Templeton, 1962), and 2·053, 2·061, 2·063 Å (Braibanti, Tiripicchio, Manotti Lanfredi & Bigoli, 1969). The angles around the magnesium atom are again approximately octahedral. The hydrogen bonds (Table 5) play an important role in the crystal structure. They are numerous and strong. There are fourteen independent possible hydrogen bonds $O\cdots O \leq 2{\cdot}86$ Å (Fig. 2). An attempt has been made to distinguish between donor (of hydrogen) and acceptor atoms and a reasonable scheme consistent with the assignment of hydrogen atoms in the anion has been obtained. According to this tentative scheme two hydrogen bonds are assigned to each water molecule on the assumption that the water molecules contribute to the bond as hydrogen donors. The corresponding angles with the oxygen atoms bound through hydrogen bridges are: $O(6^{iii})\cdots O(7)\cdots O(5^{ii}) = 127{\cdot}2$, $O(2^{iii})\cdots O(8)\cdots O(12^{i}) = 107{\cdot}7$, $O(3^{i})\cdots O(9)\cdots O(5^{iv}) = 104{\cdot}7$, $O(4^{iv})\cdots O(10)\cdots O(11^{v}) = 100{\cdot}0$, $O(3^{iv})\cdots O(11)\cdots O(4^{vi}) = 102{\cdot}9$ and $O(1^{iii})\cdots O(12)\cdots O(3) = 125{\cdot}6°$, which are reasonable values (Hamilton & Ibers, 1968). These bonds connect water molecules either with anions or with other molecules. Two more strong hydrogen bonds occur between anions $O(2)\cdots O(6^{i}) = 2{\cdot}64$ Å, with O(6) as donor, and $O(5)\cdots O(4^{i}) = 2{\cdot}56$ Å, possibly with the hydrogen atom shared between the two. Even if limited by uncertainties due to the experimental errors, these conclusions seem acceptable.

The authors wish to thank the Consiglio Nazionale delle Ricerche, Rome, for financial support.

References

BAUR, W. H. (1964). *Acta Cryst.* **17**, 1361.

BIAGINI CINGI, M., EMILIANI, F. & GUASTINI, C. (1967). *Acta Cryst.* **23**, 1114.

BRAIBANTI, A., TIRIPICCHIO, A. & MANOTTI LANFREDI, A. M. (1967). *Chem. Comm.* p. 1128.

BRAIBANTI, A., TIRIPICCHIO, A., MANOTTI LANFREDI, A. M. & BIGOLI, F. (1969). *Acta Cryst.* B**25**, 354.

FERRARI, A., BRAIBANTI, A. & TIRIPICCHIO, A. (1965). *Acta Cryst.* **19**, 629.

FERRARI, A., CINGI, M. & GUASTINI, C. (1967). *Gazz. Chim. Ital.* **97**, 509.

HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*. New York: Benjamin.

JOHNSON, C. K. (1965). *Acta Cryst.* **18**, 1004.

JONES, M. M. (1964). *Elementary Coordination Chemistry*, p. 51. Englewood Cliffs, New Jersey: Prentice-Hall.

MARGULIS, T. N. & TEMPLETON, D. H. (1962). *Z. Kristallogr.* **117**, 344.

MOORE, F. H. (1963). *Acta Cryst.* **11**, 1169.

NARDELLI, M. & FAVA, G. (1960). *Ric. Sci.* **30**, 898.

NARDELLI, M., FAVA, G. & GIRALDI, G. (1962). *Acta Cryst.*

SASVARI, K. & JEFFREY, G. A. (1966). *Acta Cryst.* **20**, 875.

SIEBERT, H. (1967). *Fortschr. chem. Forsch.* **8**, 470.

ZALKIN, A., RUBEN, H. & TEMPLETON, D. H. (1964). *Acta Cryst.* **17**, 235.

Acta Cryst. (1970). B**26**, 1079

The Crystal Structure of Thiepin 1,1-Dioxide and the Question of π-Electron Delocalization in the Molecule

BY HERMAN L. AMMON

Division of Natural Sciences, University of California, Santa Cruz, California, and Department of Chemistry, University of Maryland, College Park, Maryland, U.S.A.

AND PLATO H. WATTS AND JAMES M. STEWART

Department of Chemistry, University of Maryland, College Park, Maryland, U.S.A.

(*Received* 28 *April* 1969 *and in revised form* 2 *October* 1969)

Thiepin 1,1-dioxide, $C_6H_6SO_2$, crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions of $a = 6{\cdot}788$, $b = 13{\cdot}173$, $c = 7{\cdot}596$ Å, $\beta = 109{\cdot}10°$, and four molecules per unit cell. Three-dimensional X-ray diffraction data were initially collected using a Weissenberg camera and Cu $K\alpha$ radiation; a second set was subsequently measured with Mo $K\alpha$ radiation on an automatic diffractometer. The structure was readily solved by location of the intermolecular S–S vectors in the Patterson function. Refinement was carried out by full matrix least-squares with anisotropic temperature factors to an R of 0·055 (weighted $R = 0{\cdot}024$). Hydrogen atoms were included with isotropic temperature factors. Only the counter data were used in the final refinement cycles. There is substantial evidence for double-bond character in the two C–S bonds; no firm conclusions can be drawn regarding delocalization in the carbon atom portion of the molecule.

Introduction

Sulfur may expand its valence shell beyond the Lewis octet by accepting ligand electrons of π symmetry into its unfilled 3*d* orbitals. The formation of a new chemical bond between the acceptor (sulfur) and donor (ligand) will occur if (*a*) the necessary donor and acceptor orbitals overlap appreciably with each other and