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Direct Determination of the Crystal Structure of Bis(dichlorophosphate)bis(phosphoryl chloride) Magnesium: $Mg(PO_2Cl_2)_2(POCl_3)_2$

JENS NYBORG and JACOB DANIELSEN

Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

The crystal structure of $Mg(PO_2Cl_2)_2(POCl_3)_2$ has been determined by X-ray crystallographic methods. The space group is $P\bar{1}$ and the dimensions of the unit cell are: $a=11.21$ Å, $b=10.97$ Å, $c=9.75$ Å, $\alpha=116°44'$, $\beta=83°51'$, $\gamma=114°05'$. There are two formula units per unit cell. The structure was determined by the symbolic addition procedure, the geometrical parameters and the anisotropical temperature parameters were refined by the full matrix least squares method. The final R-value is 10 %. The magnesium ion is octahedrally coordinated to six oxygen atoms, four of which belong to dichlorophosphate ions forming bridges between the magnesium ions. The two remaining oxygen atoms in the octahedron belong to two phosphoryl chloride molecules.

This work continues the investigation of reaction products between metal oxides and phosphoryl chloride. These compounds were first prepared by Bassett and Taylor [1,2] in 1911. The structure of $Mn(PO_2Cl_2)_2(CH_3COOC_2H_5)_2$ has been solved previously.[3] The present compound was prepared by the method of Bassett and Taylor who suggested the formulae $MgO,2POCl_3$ or $MgO,3POCl_3$. We find, however, the reaction product to be $Mg(PO_2Cl_2)_2(POCl_3)_2$ and the structure is similar to the structure of $Mn(PO_2Cl_2)_2(CH_3COOC_2H_5)_2$. The reaction may be formulated as:

$$2MgO + 4POCl_3 = Mg(PO_2Cl_2)_2(POCl_3)_2 + MgCl_2$$

EXPERIMENTAL

Preparation. The compound was prepared according to Refs. 1, 2 except that the mixture of MgO and $POCl_3$ was heated to 131°C instead of 110°C. The MgO was prepared by heating $MgCO_3$ to 845°C for 2 h. The crystals of the reaction product are very sensitive to humidity and were dried in a desiccator with KOH and H_2SO_4. Some of the reaction product was dissolved in water and the solution was analyzed for Cl, HCl, and H_3PO_4.

None of the calculated values for $MgO,2POCl_3$, $MgO,3POCl_3$ or $Mg(PO_2Cl_2)_2(POCl_3)_2$ fit well with the experimental values. This is probably due to the presence of $MgCl_2$ and unreacted MgO in the sample.

X-Ray technique. A crystal of dimensions $2.5 \times 0.3 \times 0.3$ mm^3 was sealed in a Lindemann glass tube. The unit cell dimensions were determined from an oscillation diagram (Cu$K\alpha$), Weissenberg diagrams of two layers (Cu$K\alpha$), precession diagrams of two layers (Mo$K\alpha$), and Rimsky retigraph diagrams (Mo$K\alpha$) of six layers. The dimensions are: $a=11.21$ Å, $b=10.97$ Å, $c=9.75$ Å, $\alpha=116°44'$, $\beta=83°51'$, $\gamma=114°05'$. The space group must be $P1$ or $P\bar{1}$.

The crystal was now transferred to an Arndt-Phillips linear diffractometer, where the intensities from $hk0$ to $hk12$ were recorded using Mo$K\alpha$ radiation and balanced filters. There were many false reflections due to crystallites on the main crystal. Therefore the background for a peak was estimated as the smallest of the two background measurements at each side of the peak. For this reason and because it was very difficult to align the crystal accurately, the data material is thought to be of mediocre accuracy. Totally 4379 independent reflections were recorded. For 2108 reflections the intensity was less than two times the estimated standard deviation, these reflections were therefore considered insignificant. The data material was reduced and corrected for Lorentz-polarization effects by the GIER algol program G4, written by R. G. Hazell.[4] No correction was made for absorption or extinction.

STRUCTURE DETERMINATION

The 4379 normalized structure factors:

$$|E(h)| = F(h)/(\sum_{j=1}^{N} (f_j(h))^2)^{\frac{1}{2}}$$

were calculated by the method described by Karle and Karle.[5] For this calculation the content of the unit cell was supposed to be $2(MgO,2POCl_3)$, as this would give a reasonable density. Simple statistics were calculated to see if there was a centre of symmetry or not. The results are shown in Table 1

Table 1. Calculated and theoretical statistics of the normalized structure factors.

	$2(Mg(PO_2Cl_2)_2(POCl_3)_2)$	centrosymmetry	noncentrosymmetry
$\langle\|E\|^2\rangle$	1.0059	1.000	1.000
$\langle\|E\|\rangle$	0.8071	0.798	0.886
$\langle\|E^2-1\|\rangle$	0.9014	0.968	0.736
$\%\|E\|>1$	34.5	32	37
$\%\|E\|>2$	3.8	5	1.8
$\%\|E\|>3$	0.2	0.3	0.01

together with the theoretical values for a noncentrosymmetric and a centrosymmetric structure with infinetely many equal atoms per unit cell. Later the statistics were recalculated using the unit cell content: $2(Mg(PO_2Cl_2)_2(POCl_3)_2)$. The results did not differ significantly from the first calculated ones. The values in Table 1 indicate centrosymmetry and we tried to solve the structure by symbolic addition [5] for the space group $P\bar{1}$.

After a series of unsuccessful attempts, symbolic addition was tried for the space group $P1$. It was decided to apply the equation:

$$\phi(h)-(\phi(k)+\phi(h-k)) = n2\pi$$

where $\phi(h)$ is the phase for reflection h and n is an integer.

The probability for this equation being true is to a first approximation increasing monotonically with

$$p = |E(h)\cdot E(k)\cdot E(h-k)|$$

Table 2. The basic set of symbols.

h	k	l	E	Symbol	h	k	l	E	Symbol
−1	1	5	4.02	a	−6	4	5	3.00	l
−4	1	10	3.94	b	0	−4	5	2.90	m
1	−8	9	3.34	c	−6	−1	2	2.85	n
2	−7	6	3.61	d	7	−3	5	2.83	o
−1	2	7	3.40	f	0	1	10	2.78	p
6	−5	2	3.24	g	3	−8	1	2.76	r
−6	2	5	3.20	h	−4	2	6	2.72	s
−3	−7	5	2.99	j	2	−9	4	2.75	t
−12	5	5	3.03	k	5	−2	6	2.73	u

The 2271 significant reflections were now used and the 18 reflections with the greatest E-values were selected and were assigned symbols as shown in Table 2. Using equations of the type:

$$\phi(h_1)-(\mathrm{sy}(k_1)+\mathrm{sy}(h_1-k_1)) = n_1\cdot 2\pi$$
$$\phi(h_1)-(\mathrm{sy}(k_2)+\mathrm{sy}(h_1-k_2)) = n_2\cdot 2\pi$$

where $\mathrm{sy}(k_1)$, $\mathrm{sy}(h_1-k_1)$, $\mathrm{sy}(k_2)$, $\mathrm{sy}(h_1-k_2)$ are four of the 18 symbols, the number of unknown symbols could be reduced to 6: a,b,d,g,h,k.

As the reflection with the symbol b appeared seldom in combination with other reflections, it was removed from the basic set. The origin of the unit cell was chosen by setting a, g, and h to 0°, as the indices of these reflections are linearly independent. For the symbols d and k the following relations were found:

$$4k = n_1 2\pi$$
$$2d+3k = n_2 2\pi$$

where n_1 and n_2 are integers. This gives 8 possibilities for d and k. The 8 possibilities can be reduced to 4, as the possibilities two and two correspond to mutually enantiomorphic structures. For each of the 4 possibilities 193

Table 3. The four sets of phases.

Set	k	d	R_E in %
1	0	0	22.85
2	$\pi/2$	$-3\pi/4$	20.34
3	$\pi/2$	$\pi/4$	22.14
4	π	$-\pi/2$	21.39

Table 4. Fractional coordinates and temperature parameters. The temperature factor is $T(h)=\exp 2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)$.

Atom	x/a	$\sigma\times10^4$	y/b	$\sigma\times10^4$	z/c	$\sigma\times10^4$	U_{11} Å^2	$\sigma\times10^3$	U_{22} Å^2	$\sigma\times10^3$	U_{33} Å^2	$\sigma\times10^3$	U_{12} Å^2	$\sigma\times10^3$	U_{13} Å^2	$\sigma\times10^3$	U_{23} Å^2	$\sigma\times10^3$
Mg	0.0586	4	0.9926	5	0.2322	4	0.031	3	0.030	3	0.027	2	0.014	2	0.002	2	0.017	2
O_1	0.2155	11	0.1602	13	0.1864	11	0.047	7	0.060	8	0.060	7	0.016	7	0.018	6	0.035	7
O_2	0.1058	11	0.1431	12	0.4542	10	0.057	8	0.049	7	0.032	5	0.024	7	0.002	5	0.011	5
O_3	0.0804	10	0.1658	12	0.7229	10	0.050	7	0.039	7	0.045	6	−0.004	6	0.004	5	0.027	6
O_4	0.2063	12	0.9278	14	0.2566	12	0.067	9	0.072	9	0.063	7	0.047	8	−0.007	6	0.029	7
O_5	0.0438	10	0.8512	12	0.0064	9	0.043	7	0.048	7	0.029	5	0.023	6	0.009	5	0.020	5
O_6	0.0693	10	0.9335	12	0.7975	10	0.041	6	0.051	7	0.045	5	0.030	6	0.011	5	0.032	6
P_1	0.3281	4	0.2839	6	0.1918	5	0.028	3	0.060	3	0.057	3	0.003	2	0.007	2	0.040	2
P_2	0.2490	5	0.8261	6	0.2679	5	0.152	3	0.066	4	0.040	2	0.036	3	0.014	2	0.027	2
P_3	0.1521	4	0.2176	4	0.6151	4	0.029	2	0.027	2	0.025	2	0.006	2	0.004	1	0.011	2
P_4	0.0840	4	0.8418	5	0.8579	4	0.033	2	0.036	2	0.028	2	0.021	2	0.004	1	0.013	2
Cl_1	0.3540	6	0.4713	6	0.3751	6	0.089	4	0.060	4	0.089	4	−0.003	3	−0.006	3	0.011	3
Cl_2	0.3288	8	0.3215	8	0.0200	7	0.151	7	0.137	6	0.102	4	0.016	5	0.006	4	0.096	5
Cl_3	0.4906	6	0.2605	9	0.1964	10	0.040	3	0.153	7	0.194	7	0.038	4	−0.005	4	0.066	6
Cl_4	0.4385	6	0.8913	10	0.2693	9	0.056	4	0.218	9	0.162	6	0.079	5	0.040	4	0.115	6
Cl_5	0.1770	8	0.6265	7	0.0975	6	0.190	8	0.073	5	0.076	3	0.065	5	0.012	4	0.009	3
Cl_6	0.2054	7	0.7998	7	0.4511	6	0.124	5	0.114	5	0.066	3	0.046	4	0.021	3	0.061	4
Cl_7	0.3366	5	0.2374	8	0.6309	6	0.044	3	0.128	6	0.083	4	0.036	3	−0.006	3	0.035	4
Cl_8	0.1816	6	0.4312	5	0.6971	6	0.124	5	0.032	3	0.070	3	0.024	3	0.019	3	0.019	2
Cl_9	0.2735	5	0.8719	7	0.8511	6	0.042	3	0.129	5	0.094	4	0.058	3	0.025	3	0.062	4
Cl_{10}	0.0023	6	0.3710	6	0.2993	5	0.113	5	0.043	3	0.051	2	0.038	3	0.003	3	0.001	2

Table 5. Observed and calculated structure factors. Columns are: index h, $|F_{obs}|$ and F_{calc} on arbitrary scale.

	H,0,0		9	110	10		H,11,0		1	272	368	-2	720	-688	5	153	-160			
			10	131	-134				2	79	65	-1	53	-6	6	129	-62			
1	614	605				-4	203	217	3	109	99	0	138	136						
2	606	-572		H,5,0		-3	149	164	4	122	-99	1	338	303		H,7,1				
3	62	90				-2	119	14	5	611	-605	2	139	-103						
4	120	115	-14	104	-65				7	192	188	3	354	401	-11	147	-137			
5	228	-235	-13	222	247		H,12,0		8	167	161	4	407	394	-10	98	43			
6	215	212	-12	86	121				10	244	268	6	320	-335	-8	224	224			
7	350	-378	-11	217	-250	-6	126	-132				10	231	-278	-7	186	189			
8	178	-196	-10	155	-196					H,-3,1					-5	91	-49			
10	146	-156	-8	82	90		H,-11,1						H,2,1		-4	356	377			
12	181	198	-7	92	34				-10	159	-184				-3	140	118			
			-5	196	196	1	136	-115	-9	139	-140	-11	185	-206	-1	145	159			
	H,1,0		-4	90	88	2	148	-113	-7	195	186	-10	169	-188	0	169	199			
			-3	453	-458	5	127	127	-6	102	145	-9	211	233	1	102	91			
-13	87	95	-2	86	-87	6	130	148	-5	96	77	-7	342	345						
-12	123	-149	-1	1131	1158				-3	659	623	-6	428	447		H,8,1				
-11	97	14	0	335	351		H,-10,1		-2	70	50	-5	136	125						
-10	69	72	1	126	105				-1	712	707	-4	252	-273	-12	179	-193			
-8	391	-392	3	256	-265	0	194	-233	0	536	504	-3	229	218	-9	143	-136			
-7	336	333	4	86	35	1	224	-243	1	367	-368	-2	330	328	-7	220	227			
-6	909	-910	5	241	249	2	177	-193	2	1192	-1189	-1	58	-35	-1	132	110			
-5	1282	-1326	9	97	-137	6	131	-136	3	318	315	0	243	228	1	117	-108			
-4	711	700	10	92	-33	8	134	115	4	999	-1035	1	125	117	5	109	127			
-3	101	84	11	111	46				5	162	-131	2	142	119						
-2	395	-372					H,-9,1		6	191	167	4	315	331		H,9,1				
-1	561	560		H,6,0					7	135	-120	5	250	321						
0	511	492				-4	198	213	8	109	122	6	105	-66	-9	111	-115			
1	240	232	-12	86	124	-3	178	197	9	216	243	7	137	142	-4	148	168			
2	760	766	-10	85	-118	3	202	-218	10	112	104	10	119	-97	-3	241	265			
3	455	-454	-9	75	42	5	108	-106							-1	291	-320			
4	65	-64	-8	289	322	7	116	133		H,-2,1			H,3,1		0	209	-256			
5	509	528	-7	260	-259	8	287	304												
6	453	-488	-6	753	-763	9	212	215	-10	107	-69	-12	100	-79		H,10,1				
7	411	-425	-4	150	151	10	185	200	-9	126	-141	-11	227	-285						
9	178	-186	-3	363	360				-8	95	40	-10	100	-60	-8	136	-129			
10	172	-197	-2	109	102		H,-8,1		-6	183	-187	-8	67	-105	-6	242	250			
12	115	103	0	205	250				-4	598	579	-6	273	266	-5	103	147			
			1	439	462	-4	101	28	-3	177	127	-4	186	183	-3	148	167			
	H,2,0		3	137	133	-2	141	125	-2	544	-520	-3	372	-357	0	146	128			
			4	91	84	0	133	125	-1	795	753	-2	160	-154						
-12	304	-339	5	116	-119	2	423	-469	0	396	-390	-1	713	-683		H,-12,2				
-11	218	249	6	110	-102	3	543	-592	1	594	586	0	541	539						
-10	88	89	8	146	-130	4	175	-162	2	659	-618	1	336	-340	1	131	-100			
-8	180	-163	9	110	-38	5	203	-201	3	1579	-1581	2	566	-559	3	116	133			
-6	428	-419				7	109	-104	4	1260	-1291	3	687	-704	4	132	87			
-5	210	-212		H,7,0		9	149	169	5	124	-112	4	332	-355	11	139	-78			
-4	407	-412				10	139	155	8	133	-143	5	105	90	12	124	-98			
-3	166	180	-13	192	-216				9	170	-185	6	265	327						
-2	864	847	-12	107	139		H,-7,1		10	146	144	7	169	-201		H,-11,2				
-1	660	-643	-11	124	135							8	101	-116						
0	954	-935	-9	155	-144	-3	165	188		H,-1,1		9	103	102	0	211	-215			
1	1111	1108	-6	343	-360	-1	104	-77				10	101	47	1	121	-101			
4	168	184	-5	473	-487	0	156	165	-11	107	-44				4	121	-128			
5	576	599	-4	129	-125	1	112	105	-10	178	170		H,4,1		7	209	217			
6	241	-243	-3	96	77	3	229	-232	-8	167	170				9	125	48			
8	98	-111	-2	114	-85	4	589	-619	-7	180	-175	-12	204	-190	12	143	-132			
9	140	-126	-1	76	47	6	131	105	-6	117	79	-9	144	122						
			0	114	140	7	124	-117	-5	139	-139	-6	279	-287		H,-10,2				
	H,3,0		2	111	115	8	170	-188	-4	79	29	-4	638	645						
			3	92	72	10	183	-150	-3	1018	1019	-3	500	456	-3	121	-89			
-8	84	-85	6	131	-112				-2	1488	1437	-2	473	475	-2	122	-13			
-7	274	-284	7	101	-120		H,-6,1		-1	288	286	-1	125	105	2	250	-250			
-6	817	834							0	138	151	0	764	-765	3	186	-197			
-4	198	-201		H,8,0		-6	115	-44	1	270	-265	1	353	-408	5	138	141			
-2	766	749				-2	300	302	2	46	34	2	389	401	6	245	237			
-1	678	-661	-13	126	-137	-1	429	441	3	482	487	3	258	-263	7	280	280			
0	731	-722	-11	184	178	0	138	-128	4	830	807	4	323	-345	8	163	145			
1	322	317	-10	90	108	2	251	245	5	616	-633	6	176	-163						
2	234	229	-9	121	-145	3	266	250	7	294	-310	7	112	-112		H,-9,2				
3	455	455	-8	87	-47	4	213	191	9	156	-168	10	154	136						
4	272	294	-7	190	198	5	450	458	10	192	200				1	160	-143			
6	86	101	-6	126	117	6	148	-176					H,5,1		2	157	-175			
7	209	208	-5	97	-55	8	256	-292		H,0,1					5	184	-224			
8	110	-95	-2	153	161	9	102	-72				-11	240	242	6	191	-179			
10	98	47	1	140	137	10	112	-113	-10	280	290	-10	152	-124	8	145	150			
11	123	-161	2	228	225		H,-5,1		-8	249	-267	-7	244	-260	10	116	99			
12	90	-80	3	193	198				-7	107	87	-5	737	759	11	134	160			
									-4	120	-75	-4	159	189	12	198	217			
	H,4,0			H,9,0		-8	126	104	-3	101	106	-2	494	491						
						-7	138	-162	-2	513	-485	-1	159	161		H,-8,2				
-13	118	160	-12	115	-116	-2	116	137	-1	349	341	1	380	369						
-12	95	91	-8	151	-170	-1	416	-417	1	424	-380	2	163	-165	-7	125	-64			
-11	297	-327	-7	100	59	0	508	-508	2	806	778	4	105	-119	-2	127	-144			
-10	88	-97	-6	146	151	1	310	-329	3	363	365	5	253	-290	0	163	135			
-8	112	-101	-4	95	-88	2	457	459	4	691	654	7	108	95	1	119	-76			
-7	570	-562	-3	153	-164	3	302	305	5	548	-569				2	206	-187			
-6	498	494	-2	177	-186	4	161	-167	6	369	-374		H,6,1		3	148	-135			
-3	171	-164	3	126	-85	5	328	-329	7	221	-217				6	338	-339			
-2	375	-380				6	446	-449	8	100	79	-10	133	-141	7	464	-507			
-1	726	-692		H,10,0		9	148	-170	9	210	-202	-7	186	-224	9	114	132			
0	298	-282										-6	221	245	12	194	185			
1	380	-395	-11	148	-158		H,-4,1			H,1,1		-4	117	-114						
2	231	238	-6	98	67							-3	179	-180		H,-7,2				
3	234	256	-4	165	-170	-6	178	178	-9	108	-68	-2	267	-302						
4	435	-442	-2	184	169	-5	222	218	-8	191	-186	-1	177	189	-10	144	74			
5	223	-239	-1	105	78	-4	300	301	-7	263	262	0	371	370	-2	115	73			
6	289	332	1	104	-121	-3	101	-124	-5	762	750	1	179	-188	0	209	-188			
7	85	-54	2	126	-151	-2	130	120	-4	1097	-1048	2	151	-178	1	402	401			
8	80	38				-1	173	-176	-3	653	-627	4	158	-155						

Table 5. Continued.

	H_7-7,2		-3	133	-118	1	568	-599	-3	267	-270		H_7-4,3		3	257	-261
			-2	305	302	2	350	-376	-2	147	-161				4	175	-171
3	408	379	-1	985	-918	3	140	164	2	132	-127	-9	125	-98	5	244	263
4	261	245	0	766	789	4	267	293	3	198	-187	-4	432	-411	6	506	525
5	133	126	1	887	860	5	506	-541				-3	343	-339	7	182	203
6	330	-347	2	627	-578	6	186	192		$H_7$9,2		-2	624	-582			
7	143	-150	3	271	263	7	169	225				0	95	-93		$H_7$2,3	
8	143	148	4	315	308	9	175	202	-3	167	149	1	254	-236			
9	294	282	5	558	-576	11	142	-107	-2	129	120	2	437	-411	-11	180	-210
13	238	238	6	319	-327				-1	142	123	3	131	-138	-7	287	-318
			7	223	238		$H_7$3,2		0	141	144	5	79	46	-5	158	-152
	H_7-6,2		8	146	132				2	135	-149	6	138	126	-4	210	201
			9	170	147	-12	273	278		H_7-11,3		7	280	270	-3	208	-191
-9	139	-18	10	147	140	-11	156	-114							-2	333	-315
-8	124	87	12	162	155	-10	181	-204					H_7-3,3		-1	175	-146
-6	176	194				-9	108	16	-2	124	113				0	289	-298
-5	144	179		H_7-1,2		-8	106	-82	0	112	-146	-9	168	135	1	520	-544
-4	294	-318				-6	154	164	3	110	87	-7	114	-112	3	131	-118
-3	223	-216	-13	126	23	-5	247	258	5	139	116	-6	169	-153	4	230	-237
-2	134	-127	-10	135	116	-4	127	133				-5	116	-71	5	267	253
-1	469	-457	-8	101	-59	-3	94	76		H_7-10,3		-4	342	-311	6	323	355
3	158	-142	-7	267	269	-2	670	-676				-3	378	-362	7	115	-83
4	129	-151	-6	781	771	-1	94	98	1	233	230	-2	443	-403			
5	127	-89	-5	543	-521	0	397	410	2	143	151	-1	184	-163		$H_7$3,3	
6	444	433	-4	83	-89	1	756	-765	5	125	-129	0	902	890			
8	231	-234	-3	70	28	2	232	-200	8	103	82	1	170	-163	-13	131	88
9	130	158	-2	603	-562	3	203	-193				2	324	-295	-10	109	115
11	267	-240	-1	469	-451	4	410	-449		H_7-9,3		4	447	446	-8	226	234
12	125	-159	0	703	892	5	145	-139				6	202	186	-6	479	-469
13	172	191	1	425	414	6	168	155	-4	224	-224	7	148	124	-5	118	106
			2	253	-246	8	266	264	-3	158	-142	8	102	-111	-4	129	139
	H_7-5,2		3	136	-143	9	113	125	0	193	212				-3	164	-152
			4	121	-119	11	129	10	3	161	141		H_7-2,3		-2	184	207
-10	147	-40	6	168	166				4	134	-144				-1	529	520
-9	141	133	7	337	-331		$H_7$4,2		5	233	-246	-10	159	229	0	343	-335
-7	139	133	8	182	180							-9	298	307	2	159	154
-6	232	212	10	146	-80	-11	113	127		H_7-8,3		-6	122	-129	3	231	252
-5	135	-115	11	118	-101	-10	136	-112				-5	470	-451	4	255	296
-4	208	-186	12	235	256	-9	126	-43	-7	132	66	-3	341	-318	6	151	-145
-3	288	-324				-7	444	427	-6	125	-77	-2	187	-221	7	117	76
-2	103	-99		$H_7$0,2		-6	147	-147	-5	138	-152	-1	286	280			
-1	185	199				-5	447	451	-3	186	-190	0	788	883		$H_7$4,3	
1	766	-729	-12	198	-252	-4	364	365	-1	372	376	1	358	-458			
3	415	-394	-10	240	261	-3	105	-107	0	111	105	2	456	465	-12	222	219
5	458	457	-9	116	86	-1	620	632	1	129	148	3	305	-302	-11	248	257
6	1008	1013	-7	537	552	0	242	223	2	283	334	4	568	606	-8	132	129
7	191	163	-6	221	216	2	343	-362	3	259	280	5	433	424	-7	341	-357
8	274	-278	-5	547	-522	3	384	-425	4	131	124	6	172	-190	-6	322	-318
10	132	102	-4	784	-783	5	150	120	5	261	290	7	243	-221	-4	204	-200
			-3	81	-39				8	113	-16				-3	179	-196
	H_7-4,2		-2	199	-191		$H_7$5,2						H_7-1,3		-2	547	-602
			-1	166	175					H_7-7,3					-1	373	-394
-9	149	156	0	1201	-1242	-13	159	-177				-11	125	165	0	156	168
-8	122	84	1	327	-307	-11	193	147	-8	139	120	-9	115	90	1	280	280
-6	269	-313	2	417	-439	-7	107	124	-7	119	-65	-8	59	-61	3	183	184
-5	111	92	3	150	144	-6	167	-167	-6	143	-140	-6	505	-510	4	118	-124
-4	369	378	4	151	-151	-5	235	-224	-4	198	-206	-5	107	-52	5	298	-283
-3	298	280	5	517	543	-4	127	-122	-3	211	-199	-3	66	-46	6	139	-133
-2	192	-167	6	124	129	-3	182	184	-2	101	78	-2	110	95	8	113	16
-1	500	-461	7	226	-237	-2	102	124	1	183	192	-1	1524	-1535			
0	302	-308	9	102	-82	-1	204	-182	2	106	-134	0	787	-989		$H_7$5,3	
1	156	-222	11	147	96	0	236	-245	3	155	145	1	837	856			
2	456	433				1	316	-321	4	366	353	2	328	321	-12	207	215
3	423	425		$H_7$1,2		2	226	-256	5	358	379	3	75	-44	-9	114	-58
4	444	-456				3	97	-81	6	138	135	4	84	84	-8	128	96
5	190	193	-12	153	-140	6	109	-136	7	111	-154	5	175	-179	-7	278	286
6	469	491	-10	259	258				8	143	-154	6	354	-384	-5	465	-468
7	556	548	-9	188	207		$H_7$6,2					7	125	138	-4	335	-340
9	97	27	-8	274	300					H_7-6,3					-1	107	115
11	285	319	-6	201	200	-13	164	-168					H_7C,3		0	174	167
13	167	-209	-5	475	464	-11	134	140	-5	219	-215				1	91	7
			-4	152	146	-10	217	249	-4	129	102	-11	149	138	4	119	111
	H_7-3,2		-3	167	154	-7	135	141	-3	268	280	-10	163	-205	8	110	-61
			-2	195	-197	-6	277	308	-2	134	-109	-7	165	159			
-11	144	144	-1	63	-40	-5	187	201	-1	410	-398	-6	505	521		$H_7$6,3	
-10	119	13	0	1360	-1491	-4	130	141	0	569	-551	-5	164	160			
-6	414	-428	1	585	570	-3	136	-119	1	320	-317	-4	321	-299	-10	125	138
-4	412	397	2	923	955	-1	134	-150	2	563	539	-3	389	393	-7	294	347
-3	283	-254	3	102	-66				3	579	564	-2	358	356	-6	161	132
-2	422	-398	4	82	-30		$H_7$7,2		4	372	394	-1	141	-149	-5	130	-147
0	622	-594	5	435	453				6	134	173	1	55	112	0	159	168
1	793	-761	6	119	141	-13	112	-30	7	91	-60	2	167	-155	5	136	157
2	716	-679	7	325	369	-12	131	-148	8	167	164	3	322	329	6	135	136
3	66	-87	8	129	110	-9	147	95				4	107	-91			
5	99	75	10	121	109	-7	135	147		H_7-5,3		5	552	583		$H_7$7,3	
6	897	-894	12	134	-129	-6	226	226				6	197	205			
7	467	478				-5	116	96	-9	134	-118	7	240	244	-12	198	-160
10	174	198		$H_7$2,2		0	184	-162	-5	190	218				-8	107	-121
11	256	271				1	112	-119	-3	127	-120		$H_7$1,3		-5	104	-48
12	172	-155	-12	117	184	2	147	187	-2	226	-236				0	322	-329
13	113	-20	-11	167	-193	3	141	166	0	89	-46	-11	163	-199	1	146	-132
			-8	296	287	4	122	-56	1	225	229	-10	129	-194	2	125	-86
	H_7-2,2		-7	325	-307				2	115	112	-6	450	477	3	131	-134
			-6	173	145		$H_7$8,2		3	196	192	-5	109	-73			
-13	119	-30	-5	376	361				4	442	424	-4	179	178		$H_7$8,3	
-11	197	200	-4	493	-466	-11	123	-138	5	218	228	-3	218	-220			
-8	211	211	-3	74	-46	-10	110	-119	6	651	674	-2	167	202	-7	140	-135
-7	140	-134	-2	765	740	-9	128	-38	7	202	212	-1	292	-313	-3	212	193
-6	148	130	-1	780	-773	-6	101	79	8	127	155	0	417	-435	-2	179	153
-4	245	243	0	1075	-1083	-5	145	113				2	70	-78			

Table 5. Continued.

H, 8, 3

-1	144	-149
0	124	-127
3	184	145

H, -13, 4

1	110	-47
8	133	-67
12	122	-112

H, -12, 4

5	144	-106
6	101	-40
7	109	90
8	132	106

H, -11, 4

-2	120	82
-1	183	202
0	234	247
1	122	175
3	214	-211

H, -10, 4

-3	190	155
-2	120	154
0	134	101
2	170	-158
6	119	-97
7	337	-331
8	209	-211
10	108	-78

H, -9, 4

-2	106	-98
1	152	123
2	464	491
3	98	122
4	175	-162
5	213	198
7	241	-247
8	168	-211

H, -8, 4

-8	134	26
-7	116	44
-3	189	-191
-2	218	223
0	435	-448
2	528	523
3	366	390
4	171	179
6	189	-177
8	278	-259
9	147	-152
10	125	-112
11	146	-171
12	202	-196
13	110	79

H, -7, 4

-6	123	164
-5	141	115
-4	169	-186
-3	184	-219
-2	138	-129
-1	205	-218
0	204	213
1	108	127
2	96	91
3	258	242
4	89	-72
5	293	-274
6	281	266
7	328	319
8	287	-293
9	287	-317
10	113	-98
11	245	-295
13	141	-47

H, -6, 4

-5	141	-136
-2	99	-51
-1	448	475
0	676	689
1	156	-163
2	145	-164
3	571	562
4	91	85
5	160	123
6	356	378
7	151	101
9	117	-84
11	117	-68
12	139	86
13	231	-209

H, -5, 4

-6	385	-455
-5	290	-279
-4	411	428
-3	235	226
-2	152	-131
-1	457	464
0	94	-101
2	127	-105
3	146	-135
4	190	-177
5	375	350
6	492	-471
7	89	-92
8	314	301
11	195	211
13	119	-129

H, -4, 4

-9	227	-218
-7	198	-228
-6	276	-259
-5	107	48
-2	352	344
-1	207	-225
0	89	-113
1	929	968
2	609	-575
3	522	-477
4	365	361
5	268	-272
6	457	-452
7	134	126
8	154	135
10	194	186

H, -3, 4

-12	120	94
-10	150	22
-8	139	-141
-7	97	-103
-6	423	440
-5	208	-218
-4	378	-353
-3	739	736
-2	285	292
-1	358	-330
1	177	-173
2	355	332
3	696	668
4	204	191
5	592	-562
6	111	123
7	185	-175
8	140	159
11	235	-227
12	139	94

H, -2, 4

-11	116	-128
-8	225	-253
-7	245	271
-6	366	369
-4	555	-545
-3	639	-596
-2	330	-323
-1	577	562
0	227	-250
1	394	-416
3	370	-352
5	156	137
6	248	217
7	350	-343
8	129	-133
9	143	-110
10	299	-305
11	141	-99

H, -1, 4

-12	126	-121
-11	180	-173
-9	147	140
-7	130	119
-5	424	407
-4	306	-281
-2	92	83
-1	399	422
0	108	-100
2	284	296
3	215	208
4	237	238
5	506	513
7	115	-128
8	116	-120
9	162	-182
10	179	-193

H, 0, 4

-11	165	-141
-10	124	-134
-9	117	133
-7	308	-291
-6	433	-421
-5	391	371
-4	522	521
-3	111	99
-2	198	210
-1	52	-32
0	145	119
1	347	333
2	360	338
4	366	367
6	135	-141
8	202	-186

H, 1, 4

-12	119	131
-10	287	-303
-9	135	-138
-8	189	-192
-7	411	-394
-6	311	-319
-4	161	135
-3	65	-23
-1	111	-105
0	725	742
1	72	19
2	102	-84
3	105	-75
4	171	-179
5	233	-254
7	180	-167
9	143	152

H, 2, 4

-11	132	160
-10	154	-163
-9	196	-189
-8	239	-270
-6	316	-317
-5	208	-198
-4	388	372
-3	288	282
-2	184	188
-1	288	285
0	388	387
1	547	559
2	410	423
4	218	-221
7	120	65

H, 3, 4

-11	200	186
-9	132	-163
-8	147	-149
-6	107	-67
-5	359	-358
-4	539	-538
-3	221	-233
-2	188	197
-1	430	438
0	339	346
2	271	-266
5	114	95
7	129	-43
8	120	-86

H, 4, 4

-13	116	7
-10	184	191
-7	153	-135
-6	182	-139
-5	307	-315
-4	97	-95
-3	155	-166
0	146	-171
2	111	134
4	162	167

H, 5, 4

-10	153	163
-9	103	118
-7	117	-76
-6	96	11
-5	120	137
-4	154	174
-3	112	111
-1	163	-205
1	149	143
2	187	195
3	288	313

H, 6, 4

-12	114	15
-11	115	-81
-10	152	-131
-2	175	-181
0	134	-122
2	108	96

H, 7, 4

-10	110	-136
-9	119	-105
-8	104	-44
-5	124	82
0	170	170
1	229	229

H, 8, 4

-11	123	-21
-5	197	-204
-4	141	-111
-3	123	97
-2	174	201
-1	213	231

H, -13, 5

1	113	-53
2	138	-102
4	121	-71

H, -11, 5

-1	159	-123
1	141	123
5	312	-322
6	177	-211

H, -10, 5

-2	110	-105
-1	155	149
0	235	252
3	98	82
6	115	-107
7	176	-175

H, -9, 5

-7	153	116
-6	136	-37
7	151	-165
5	131	121
7	143	-128

H, -8, 5

-2	108	106
-1	126	-110
0	187	-185
1	118	-142
2	232	-246
3	490	-500
4	108	-74
5	165	146
6	166	115
7	165	-155
8	191	-216

H, -7, 5

-5	121	126
-4	274	258
-3	458	473
-2	257	258
-1	270	-276
0	212	-195
1	132	-124
3	81	-41
4	88	-46
5	205	-200
6	296	280
7	214	209
8	148	-104

H, -6, 5

-8	115	-166
-6	138	106
-5	171	190
-4	331	333
-3	141	178
-2	223	-226
-1	89	27
0	115	122
1	218	-217
2	150	153
4	642	-647
5	308	-312
7	340	331
8	103	42

H, -5, 5

-10	127	-71
-9	118	-133
-6	102	-59
-5	102	81
-3	370	-366
-2	369	364
-1	464	458
1	165	-169
2	336	-332
3	93	-99
4	124	114
5	230	-234
6	577	-583
7	188	192

H, -4, 5

-9	136	104
-7	139	-139
-6	126	131
-5	94	-72
-4	133	-121
-3	115	121
-2	165	175
-1	80	-69
0	1011	1002
1	383	401
2	354	-383
3	70	61
4	127	121
6	210	-183
7	184	-195

H, -3, 5

-11	112	-55
-7	126	114
-6	94	-7
-5	454	-454
-4	233	223
-3	222	225
-2	118	-102
0	167	-202
2	57	97
3	208	-197
4	243	-237
6	355	-395
7	527	-523

H, -2, 5

-8	101	84
-5	190	159
-4	249	229
-3	418	401
-2	457	415
-1	230	-214
0	853	-940
1	409	462
2	361	385
3	151	-137
4	467	-446
5	77	-72
6	202	-203
7	118	-117

H, -1, 5

-10	191	-161
-9	141	-142
-6	475	495
-5	576	557
-3	205	195
-2	526	512
-1	225	211
0	115	-123
1	418	431
3	223	-223
4	311	-299
5	279	-276
6	161	177
7	242	239
8	111	-67

H, 0, 5

-12	139	61
-11	246	-263
-10	176	-185
-8	95	-75
-7	212	-203
-6	194	177
-4	102	-146
-3	298	282
-2	271	270
-1	422	415
0	164	175
1	813	-837
2	275	-298
3	219	203
4	329	-316
5	375	-384
6	214	204
7	125	-91

H, 1, 5

-11	131	-108
-8	128	-153
-6	302	-303
-5	114	139
-4	412	404
-3	212	-206
-2	81	-43
-1	1155	1173
0	482	511
1	236	-222
3	126	-141
4	124	137
5	178	187
6	115	-139

H, 2, 5

-11	200	187
-9	112	-107
-7	119	-147
-6	561	-563
-5	124	112
-4	94	111
-2	101	113
0	125	134
1	344	333
3	130	153
4	267	276
5	112	-140
6	322	-320
7	137	-109

H, 3, 5

-13	119	116
-11	157	170
-6	89	-88
-5	235	-231
-4	106	-101
-3	109	110
-2	280	-286
-1	416	-435
0	110	74
1	191	214
2	109	122
5	174	-166
6	185	-161
7	106	-53

H, 4, 5

-12	122	-39
-7	346	379
-6	432	443
-4	105	-141
-2	106	39
0	247	257
1	137	156

H, 5, 5

-12	221	-195
-11	172	-161
-7	101	121
-6	124	88
0	227	-216
1	137	-139
2	102	44
3	167	-142
5	138	84

H, 6, 5

-11	119	-123
-9	116	30
-7	145	-110

Table 5. Continued.

H_5,6,5		
-5	173	183
-2	209	240
-1	138	137
0	113	-48
1	104	-78
2	217	-184
4	138	71
H_5,7,5		
-9	123	43
-7	206	-195
-5	123	183
-4	249	256
-3	214	234
-1	117	61
0	108	93
H_5,8,5		
-9	122	-110
-8	122	-103
-7	113	-113
-6	138	-123
H_5-12,6		
0	107	68
2	167	-162
3	238	-206
9	106	90
H_5-11,6		
0	129	-120
1	137	-163
3	102	78
9	105	105
12	123	82
H_5-10,6		
-2	143	-105
-1	130	-105
0	188	-225
1	122	-109
2	114	129
3	131	145
6	93	122
7	103	93
H_5-9,6		
-3	138	-123
-1	150	-152
0	269	-294
1	280	-272
2	95	-89
5	136	-132
7	216	202
8	179	135
12	107	-121
H_5-8,6		
-6	110	118
-5	159	158
-4	119	101
-1	95	-114
2	313	-313
3	122	-141
5	224	-237
6	89	87
7	246	269
8	251	224
10	117	77
H_5-7,6		
-9	124	-9
-6	124	119
-3	192	211
-1	263	235
0	423	455
1	307	-300
2	777	-761
3	238	-257
5	167	148
6	90	83
7	236	-244
8	112	133
9	162	222
10	116	55
11	140	156
H_5-6,6		
-8	122	-22
-6	134	-190
-5	153	-88
-4	214	251
-3	185	163
-2	92	-68
-1	125	114
0	166	-189
3	568	-576
4	236	-223
5	107	127
6	298	-297
7	243	-239
9	100	104
10	157	147
11	246	300
H_5-5,6		
-7	106	-118
-5	179	200
-4	120	-133
-2	334	330
-1	288	-267
0	151	-144
1	459	456
2	300	307
3	199	-203
4	141	165
5	167	-148
6	80	-105
7	96	67
9	95	98
10	234	239
11	137	113
H_5-4,6		
-6	194	226
-5	96	-75
-4	376	-371
-1	443	-430
0	88	-79
1	104	-103
2	154	178
3	154	157
4	129	-129
5	398	-393
6	143	142
7	124	128
8	95	-72
11	167	-97
12	146	109
H_5-3,6		
-12	116	-0
-7	184	200
-6	115	97
-4	77	-48
-3	296	-303
-2	398	-401
1	126	-409
3	52	35
4	470	-451
5	143	138
6	272	256
10	252	-226
H_5-2,6		
-8	228	267
-7	206	169
-5	119	123
-4	368	329
-3	121	-116
-2	292	292
-1	432	439
0	276	-312
1	341	-376
2	204	-209
3	270	-265
4	205	203
5	530	507
6	142	-114
9	114	-45
11	115	96
H_5-1,6		
-10	131	-81
-9	106	16
-8	107	102
-7	204	-232
-5	250	235
-4	413	408
-3	182	184
-1	575	-613
1	138	131
2	497	-507
3	325	-329
5	191	-182
8	126	-90
10	167	175
12	129	-15
$H_5$0,6		
-8	108	-108
-6	162	151
-4	323	305
-3	365	366
-2	79	-81
-1	82	-70
2	187	184
3	82	94
4	273	-271
5	164	-186
9	118	132
$H_5$1,6		
-10	114	79
-9	124	-112
-7	170	164
-6	92	85
-4	177	-164
-3	118	-88
-2	119	135
1	184	162
2	160	197
3	123	111
4	168	-152
5	169	-162
$H_5$2,6		
-6	124	112
-5	159	-160
-4	460	-470
-3	389	-401
-2	216	-232
1	122	-124
2	126	-122
$H_5$3,6		
-11	138	-56
-10	123	142
-9	217	209
-8	208	234
-7	123	150
-5	130	-89
-3	101	98
-2	116	117
0	157	-140
1	184	-162
3	132	168
4	224	236
8	118	-25
$H_5$4,6		
-7	118	57
-5	174	183
-4	193	207
-2	235	-219
-1	192	-167
0	96	-86
1	138	-144
2	111	-96
5	107	61
$H_5$5,6		
-10	118	-89
-5	178	190
-4	144	152
-3	118	89
-2	96	-1
-1	233	-204
0	242	-199
2	109	-106
$H_5$6,6		
-6	248	221
-5	156	145
-3	189	176
0	140	99
$H_5$7,6		
-1	193	129
H_5-13,7		
2	113	-4
4	116	112
6	104	-69
H_5-12,7		
-2	149	-86
-1	167	-110
2	111	127
H_5-11,7		
-3	113	-106
2	128	114
5	159	149
6	162	142
13	136	72
H_5-10,7		
-4	133	-82
-1	113	-122
0	158	-159
5	174	128
6	160	174
7	93	103
11	105	-39
H_5-9,7		
-2	107	-46
1	209	-183
2	163	-144
3	85	-60
4	89	58
5	172	171
6	220	198
7	150	137
10	139	141
12	112	-81
13	156	-111
H_5-8,7		
-4	155	106
-3	98	109
3	216	219
5	164	-173
6	96	-96
7	181	164
8	121	163
11	103	60
13	127	-140
H_5-7,7		
-3	115	-78
-2	139	-138
-1	80	46
0	128	148
1	155	164
4	100	-107
5	280	-262
6	326	-318
7	111	94
8	261	220
13	133	-28
H_5-6,7		
-5	148	-142
-4	285	-278
-3	109	-110
-2	132	148
-1	268	263
0	318	304
1	224	235
3	117	124
4	214	222
5	72	67
6	97	-77
8	176	154
9	114	16
10	117	-141
11	117	-76
13	120	75
H_5-5,7		
-5	259	-252
-4	264	-274
0	103	-87
1	100	110
2	121	150
4	292	301
5	384	361
6	141	147
7	227	-227
10	127	-81
H_5-4,7		
-10	155	132
-5	106	-68
-4	240	-236
-3	176	-175
-2	213	-221
-1	245	-248
0	321	-360
1	71	-185
3	73	46
4	287	282
5	446	442
6	256	274
7	185	-187
8	142	-131
9	102	28
H_5-3,7		
-6	96	-54
-5	294	293
-4	171	182
-3	132	-122
-2	386	-375
-1	304	-328
0	314	-444
2	472	515
3	166	154
5	149	172
6	214	222
7	247	245
9	126	53
H_5-2,7		
-9	101	46
-7	131	-76
-5	278	288
-4	137	-126
-3	389	-377
-2	157	-161
-1	217	-216
1	78	-79
2	176	-167
5	256	-254
6	145	147
7	227	259
11	128	-66
H_5-1,7		
-5	275	-251
-4	111	-118
-2	127	-134
-1	247	247
0	474	473
1	328	-326
2	231	-246
8	104	95
$H_5$0,7		
-11	114	123
-10	137	121
-7	152	127
-6	275	-281
-5	159	-212
-4	195	199
-1	235	244
0	209	213
1	100	140
4	135	118
5	193	179
8	103	35
$H_5$1,7		
-11	193	185
-6	193	-160
-5	200	-234
-4	200	-184
-1	269	-270
0	260	-274
4	158	150
5	127	85
7	122	-38
$H_5$2,7		
-8	101	-38
-6	222	222
-5	116	86
-2	198	-193
-1	486	-478
0	125	-130
1	263	240
2	146	143
6	195	157
7	132	118
$H_5$3,7		
-11	146	-113
-7	108	155
-6	258	285
-2	209	-181
-1	120	-122
0	118	-115
1	205	-186
5	117	101
6	174	172
$H_5$4,7		
-3	186	-194
-2	104	-35
0	237	-229
1	197	-197
2	145	-120
3	139	-114
$H_5$5,7		
-5	147	123
-4	110	87
0	142	91
2	134	-79
$H_5$6,7		
-6	120	-118
H_5-13,8		
1	101	70
8	137	-165
10	109	-9
H_5-12,8		
-1	155	123
3	171	191
4	103	105
5	121	88
7	132	-131
8	160	-142
H_5-11,8		
2	104	118
6	100	-39
9	141	-119
H_5-10,8		
1	125	104
4	101	54
5	85	-106
6	91	-34
7	90	93
9	116	-19
11	123	-82
12	124	-110
H_5-9,8		
-3	165	134
0	155	187
1	80	63
4	125	-145
6	139	134
10	119	-74
H_5-8,8		
-5	109	-101
-4	121	-72
-2	164	148
-1	281	293
1	82	-70
3	155	-158
4	94	-76
5	119	106
6	112	-80
7	169	-150
8	127	-101
10	120	-121
11	143	83
12	103	46
H_5-7,8		
-7	129	-86
-6	114	-141
-2	253	254
1	133	155
2	217	225
3	264	269
4	243	236
6	219	-212
7	139	-123
8	161	-169

Table 5. Continued.

H,-7,8

9	194	-173
11	125	83

H,-6,8

-8	129	-33
-7	153	-166
-3	139	-110
-2	178	-152
0	216	224
1	314	329
2	409	431
3	355	365
4	130	159
7	99	-46
8	204	-158
9	151	-153
11	125	-104

H,-5,8

-5	146	-148
-4	96	-77
-3	204	-165
-2	183	-181
-1	209	-209
0	88	-78
1	215	266
2	256	328
3	296	305
5	89	-84
8	99	-16
9	117	-34
10	201	-186
11	190	-204

H,-4,8

-9	113	-74
-7	111	83
-5	91	-94
-4	83	-60
-2	67	-68
-1	133	119
0	91	120
3	98	94
5	251	264
6	219	210
7	126	71
8	134	120
10	153	-136
11	121	-66

H,-3,8

-10	133	-44
-5	82	-52
-4	97	-61
-2	187	182
-1	261	252
0	108	-130
1	191	-249
2	211	-274
3	146	-162
4	119	117
5	164	175
6	108	59

H,-2,8

-9	135	3
-8	130	-121
-7	202	-205
-3	147	158
-2	63	57
0	114	-141
1	159	-161
2	77	-77
6	87	-31

H,-1,8

-10	125	97
-8	156	-142
-5	123	115
-1	145	167
0	196	198
1	113	143
2	100	111
3	159	166

H,0,8

-4	124	-112
-3	142	-120
-2	258	-231
-1	108	-96
0	138	143
1	173	171
2	203	197
3	144	127
6	98	-45
8	106	-15

H,1,8

-7	125	101
-5	172	-169
-4	179	-177
-3	111	-134
-1	83	65
0	135	119
1	104	126
3	87	33
4	214	186
5	135	133

H,2,8

-5	122	-110
-4	88	-39
-3	110	93
4	146	132
5	146	137

H,3,8

-8	157	-138
-7	134	-136
-4	119	94
-1	152	-150
0	164	-169
3	104	-79

H,4,8

-7	115	-88
-5	107	91
-2	138	129

H,-13,9

1	117	67

H,-11,9

2	103	-99
4	109	79
7	102	69
9	161	-120

H,-10,9

-3	102	87
0	184	172
1	86	-62
2	226	-239
4	111	119

H,-9,9

-5	117	-58
-4	165	152
-3	132	126
0	95	77
1	102	-59
4	96	-91
6	253	-266
7	259	-247

H,-8,9

1	437	439
2	164	182
3	271	-296
4	165	-168
5	161	-146
6	229	-206
7	85	-108
9	91	1

H,-7,9

-8	133	44

-7	105	40
-6	130	123
-4	221	-225
-3	104	114
-2	222	228
0	109	128
1	160	177
2	79	83
4	68	-75
5	114	-85
6	105	86
7	80	-67
8	148	-159

H,-6,9

-5	138	-83
-1	126	112
1	237	-267
2	93	90
3	57	63
4	95	-99
5	120	107
6	208	183
7	99	-93
8	205	-189
9	125	-98

H,-5,9

-9	122	32
-5	170	163
-4	221	177
-3	98	-116
-1	139	144
0	117	-142
1	88	-201
4	132	120
5	201	194

H,-4,9

-6	134	-95
-5	263	248
-4	278	276
-1	161	-151
2	97	-103
4	111	87
5	168	-158
6	116	-102
7	181	164

H,-3,9

-7	95	-48
-4	123	99
-3	122	103
-2	158	-150
0	254	308
2	172	-206
3	126	-129
4	256	-254
5	248	-243

H,-2,9

-9	111	-89
-7	175	181
-5	237	-245
-3	222	231
-2	221	223
-1	234	249
0	94	114
1	77	77
2	74	86
3	75	-71
4	167	-150
6	123	-96

H,-1,9

-5	132	-120
-4	140	-116
-2	250	263
-1	149	153
6	138	-138
7	147	-144

H,0,9

-7	97	-93
-2	87	111
1	89	46
2	96	75
3	98	65

H,1,9

-7	120	-107
-5	211	197
-3	102	79
-2	93	-25
0	88	76
2	132	97
3	157	145

H,2,9

-2	89	-94
-1	125	115
0	103	74
1	107	-80

H,3,9

-6	114	-100
-3	119	90
-2	119	117
-1	95	77

H,-12,10

0	112	-116
2	96	10
4	93	20
5	98	79
8	121	70

H,-11,10

-1	111	-126
7	138	154
8	114	107
9	106	122

H,-10,10

-2	96	-48
1	108	-106
2	105	-62
4	210	-229
5	151	-147
7	99	113
9	114	98

H,-9,10

-3	145	-125
-1	202	228
0	103	-76
1	190	-228
2	82	-63
6	110	-89
7	90	-51

H,-8,10

-2	112	121
0	110	-105
2	99	-98
4	212	213
6	128	-162

H,-7,10

-4	100	86
-3	85	92
-2	216	-195
-1	251	-258
2	123	-128

H,-6,10

-5	93	54
-4	180	165
-3	113	72
-2	179	-176
-1	69	-82
0	74	-63
4	190	-177
5	108	78
6	184	157
9	102	102

H,-5,10

-7	123	112
-5	142	128
-2	88	99
-1	71	43
0	121	-154
3	258	-253
4	155	-142
7	135	143

H,-4,10

-5	82	10
-4	134	-140
-3	96	56
-2	213	217
1	167	-298
2	234	-289
5	132	-133

H,-3,10

-7	105	-58
-6	54	-37
-4	127	115
-3	109	78
-1	139	126
0	77	80
1	127	-132
5	130	-118
6	116	-117

H,-2,10

-4	85	125
-2	87	-101
-1	70	-49
1	144	138
4	93	-69
5	112	-105
6	163	-122

H,-1,10

-7	129	76
-2	95	-51
-1	162	-150
1	107	101
3	128	-104
4	92	-75
6	97	-25

H,0,10

-7	166	128
-6	168	155
-3	122	88
1	92	19

H,1,10

-4	328	29
-3	90	80
0	229	-199
1	176	-182

H,-12,11

1	96	-48

H,-11,11

1	94	-44

H,-10,11

-1	142	-74

H,-9,11

-3	98	-103
-1	102	-104
0	113	-122
1	76	120
2	193	206
4	92	-95
5	91	18

H,-8,11

-3	126	-119
-1	115	-86
6	100	117
7	109	117

H,-7,11

-2	74	-63
1	179	-238
2	42	-89
6	114	94

H,-6,11

-4	159	163
-1	167	164
1	76	-172
2	50	-80
4	130	151
5	135	132
6	102	-65
8	94	132

H,-5,11

-6	103	-64
-4	127	56
1	34	111
2	107	-138
3	139	-126
6	96	-65
8	142	90

H,-4,11

-2	70	-82
-1	55	-111
3	70	-54
4	104	-121
6	92	93

H,-3,11

-5	166	-148
-4	157	-132
-3	76	-54
1	67	-56
2	78	82
4	82	-46
6	95	70

H,-2,11

-4	111	-109
-3	167	-156
0	185	-175
1	72	-73

H,-1,11

-1	84	-88
0	78	-46
3	136	128
4	162	150

H,-9,12

0	86	-54

H,-7,12

6	135	113

H,-6,12

-1	94	91

H,-5,12

-2	110	101
0	42	80
3	82	104
4	109	122

H,-4,12

1	94	83
2	91	105

H,-3,12

-2	133	-123
1	124	99

phases were determined by a modification of the GIER algol program ML4, written by M. S. Lehmann.[6] After that phase refinements were performed by the program N16 [7] according to the method described by Karle and Karle.[5] The results of the phase refinements were 894 phases for each possibility. Table 3 shows the 4 possibilities with corresponding R_E-values (eqn. 5.2 in Karle and Karle).[5] The second set was selected as the most probable and a fourier synthesis was calculated.[8] Chlorine atoms were placed at the positions of the 12 highest peaks and the R-values were calculated [9] to 46 %. By successive fourier synthesis and R calculations it was possible to determine positions for 39 atoms and it appeared eventually that the formula was $Mg(PO_2Cl_2)_2(POCl_3)_2$. The R-value was now 26 % and the structure was seen to be centrosymmetric. By full matrix least squares refinement using the program ORFLS in the X-ray-63 system,[10] the R-value was reduced to 10 %. As anisotropic factors were used, the computer (IBM 7090) was too small for the total matrix, so the refinement was made in blocks containing as many atoms as possible. Atomic scattering factors were selected from *International Tables*.[11] Table 4 shows the final parameters. The observed and calculated structure factors are shown in Table 5 as printed by the LISTFC program.[10]

DISCUSSION

The structure of $Mg(PO_2Cl_2)_2(POCl_3)_2$ is similar to the structure of $Mn(PO_2Cl_2)_2(CH_3COOC_2H_5)_2$. In both cases the metal atom is octahedrally coordinated by oxygen. Four of the oxygen atoms belong to four PO_2Cl_2 groups which form bridges to two other metal atoms. The remaining two oxygen atoms are in *cis* positions. In the magnesium compound they belong to two phosphoryl chloride groups, in the manganese compound they belong to two ethyle acetate groups. The infinite chains formed by the dichlorophosphate groups run in the direction of the c-axis. Fig. 1 shows an MgO octahedron with the attached groups.

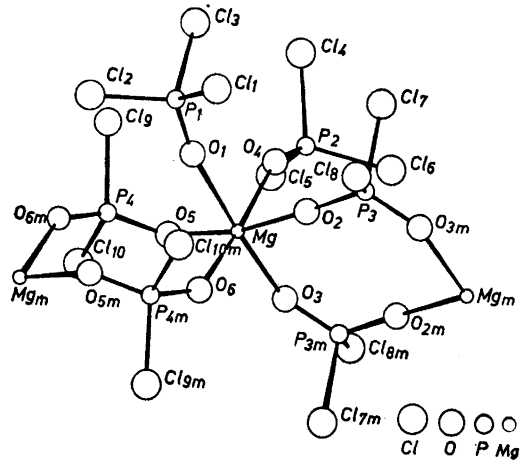

Fig. 1. MgO octahedron with the attached groups.

The similarity between the two solved structures now explains why the magnesium compound when dissolved in organic solvents such as ketones or esters is crystallized as $Mg(PO_2Cl_2)_2$ (solvent)$_2$.[1,2]

Table 6.

Distances	Å	$\sigma \times 10^3$	Angles	Degrees	$\sigma \times 10$
$Mg-O_1$	2.146	13	O_1-Mg-O_2	85.5	4
$Mg-O_2$	2.003	9	O_1-Mg-O_3	177.1	7
$Mg-O_3$	1.993	12	O_1-Mg-O_4	85.1	6
$Mg-O_4$	2.122	18	O_1-Mg-O_5	87.7	4
$Mg-O_5$	2.019	8	O_1-Mg-O_6	89.9	6
$Mg-O_6$	2.010	16	O_2-Mg-O_3	94.1	5
			O_2-Mg-O_4	87.7	5
			O_2-Mg-O_5	170.4	5
			O_2-Mg-O_6	92.6	5
			O_3-Mg-O_4	92.1	6
			O_3-Mg-O_5	92.4	4
			O_3-Mg-O_6	93.0	6
			O_4-Mg-O_5	85.0	5
			O_4-Mg-O_6	174.9	5
			O_5-Mg-O_6	94.2	5
P_1-O_1	1.410	12	$Mg-O_1-P_1$	167.0	8
P_1-Cl_1	1.955	7	$O_1-P_1-Cl_1$	114.3	5
P_1-Cl_2	1.895	11	$O_1-P_1-Cl_2$	113.1	6
P_1-Cl_3	1.948	10	$O_1-P_1-Cl_3$	113.0	8
			$Cl_1-P_1-Cl_2$	106.1	5
			$Cl_1-P_1-Cl_3$	103.7	4
			$Cl_2-P_1-Cl_3$	105.7	5
P_2-O_4	1.429	19	$Mg-O_4-P_2$	152.6	8
P_2-Cl_4	1.944	8	$O_4-P_2-Cl_4$	112.1	7
P_2-Cl_5	1.944	7	$O_4-P_2-Cl_5$	113.7	6
P_2-Cl_6	1.917	8	$O_4-P_2-Cl_6$	114.0	6
			$Cl_4-P_2-Cl_5$	105.4	4
			$Cl_4-P_2-Cl_6$	105.5	5
			$Cl_5-P_2-Cl_6$	105.5	4
P_3-O_2	1.440	10	$Mg-O_2-P_3$	162.0	11
P_3-O_{3m}	1.434	12	$O_2-P_3-O_{3m}$	122.0	6
P_3-Cl_7	2.005	8	$O_2-P_3-Cl_7$	108.3	6
P_3-Cl_8	1.995	7	$O_2-P_3-Cl_8$	108.0	7
			$O_{3m}-P_3-Cl_7$	108.6	7
			$O_{3m}-P_3-Cl_8$	107.3	5
			$Cl_7-P_3-Cl_8$	100.8	3
P_4-O_5	1.441	10	$Mg-O_5-P_4$	144.2	7
P_4-O_{6m}	1.440	16	$O_5-P_4-O_{6m}$	122.3	8
P_4-Cl_9	2.010	7	$O_5-P_4-Cl_9$	108.7	6
P_4-Cl_{10}	1.997	5	$O_5-P_4-Cl_{10}$	108.1	5
			$O_{6m}-P_4-Cl_9$	107.0	5
			$O_{6m}-P_4-Cl_{10}$	107.9	4
			$Cl_9-P_4-Cl_{10}$	100.8	3

Distances and angles were calculated by the BONDLA program.[10] The values are shown in Table 6. The estimated standard deviations are of the order 0.01 Å for the distances and 0.5° for the angles. Mean values of the equivalent distances are shown in Table 7. The values were tested at the 5 % significance level. None of the equivalent distances are significantly different.

Table 7. Mean values of equivalent distances.

Number of dist.	Type	Mean dist., Å
4	MgO	2.006
2	MgO	2.134
2	PO in $POCl_3$	1.420
4	PO in PO_2Cl_2	1.439
6	PCl in $POCl_3$	1.934
4	PCl in PO_2Cl_2	2.002

The two sets of Mg—O distances have a significant difference of 0.13 Å, the P—Cl distances in $POCl_3$ and PO_2Cl_2 are significantly different by 0.07 Å. The P—O distances in the $POCl_3$ groups and the PO_2Cl_2 groups are not significantly different.

The dimensions of free $POCl_3$ as determined from electron diffraction measurements[12] are 1.45 Å for the P—O distance, 1.99 Å for the P—Cl distance, and 103.5° for the Cl—P—Cl angle. The $POCl_3$ groups in the present structure are thus only slightly distorted. There is no significant difference between the structure of PO_2Cl_2 in the magnesium compound and the manganese compound.

The temperature parameters vary in a way which is consistent with the geometric structure. Magnesium and phosphorus have the smallest temperature factor as these atoms are located at the center of an octahedron and a tetrahedron, respectively. The chlorine atoms and especially those in the $POCl_3$ groups have the greatest temperature factors. The anisotropic temperature parameters indicate that the main motion of the $POCl_3$ groups is an oscillation around the P—O bonds, and the main motion of the PO_2Cl_2 group is an oscillation in a plane perpendicular to the O—O direction.

Table 8. The shortest van der Waals contacts, Å.

$Cl_9 - Cl_3$	a	3.404	a: $1-x, -y, -z$
$Cl_7 - Cl_2$	b	3.479	b: $x, y, 1+z$
$Cl_8 - Cl_5$	c	3.513	c: $x, 1+y, 1+z$
$Cl_8 - Cl_{10}$	c	3.539	d: x, y, z
$Cl_8 - Cl_1$	d	3.610	e: $1-x, 1-y, 1-z$
$Cl_7 - Cl_1$	e	3.650	f: $-x, -1-y, -1-z$
$Cl_{10} - Cl_{10}$	f	3.667	g: $-x, -y, -z$
$Cl_8 - Cl_3$	e	3.679	
$Cl_9 - Cl_4$	a	3.693	
$Cl_{10} - Cl_1$	g	3.695	

The shortest van der Waals contacts are given in Table 8. The packing of the chains is dominated by the Cl—Cl interactions. The shortest distance is 3.404 Å and four of the distances are shorter than the most ordinary van der Waals distance of 3.6 Å.

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