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The Crystal Structure of Hydroxylammonium Perchlorate ($\text{NH}_3\text{OH}^+\text{ClO}_4^-$) at -150°C

BY BRIAN DICKENS*

Research and Development Department, Naval Ordnance Station, Indian Head, Maryland 20640, U.S.A.

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Three crystalline phases of hydroxylammonium perchlorate have been examined by X-ray diffraction. The crystal structure of the most stable phase, which is orthorhombic with space group $P2_1cn$ and cell dimensions $a=7.52(2)$, $b=7.14(1)$, $c=15.99(2)$ Å at 25°C , has been determined at -150°C with data collected by the use of the equi-inclination photographic technique. The final $R=\sum ||F_o|-|F_c||/\sum |F_o|=0.09$ for 1757 observed reflections. The structure consists of chains of perchlorate ion tetrahedra held together by hydrogen bonding from parallel chains of NH_3OH^+ ions. The NH_3OH^+ ions may be rotating with the N-O vector as axis.

Introduction

Hydroxylammonium perchlorate (HAP) crystallizes as colorless but very hygroscopic needles from a mixture of ethanol and chloroform. When the crystals so obtained (called phase A here) are heated, they crack near 55°C (*i.e.*, 54 – 56°C) but retain their external form. Simultaneously, colors appear under the polarizing microscope in a crystal which previously had been in an extinction position. Differential thermal analysis (DTA) studies (Cziesla, 1966; Crisler, 1966) on phase A crystals show an absorption of heat at about 55°C . The above evidence is consistent with a phase change. The phase change is apparently not immediately reversible, although absorption of heat in the DTA studies reappears after the high temperature phase has either been cooled to liquid nitrogen temperatures or has been allowed to stand for about a week.

As part of the elucidation of this phase change and as part of a study of the physical and chemical properties of HAP, the crystal structure at -150°C of the room temperature form (phase A) has been determined and crystals of the high temperature form (phase B,

melting at about 89 – 91°C) were examined at 70°C . A third phase (phase C) which melts at about 58°C at atmospheric pressure, presumably the phase the possible existence of which was suggested earlier in order to explain anomalous DTA results (Cziesla, 1966), has been grown in capillaries and examined by single-crystal X-ray diffraction.

Since phase A undergoes the phase transition near 55°C and the closely related phases B and C melt near 90°C and near 58°C respectively, and since disorder or rotation has been reported in perchlorate groups (Gomes de Mesquita, MacGillavry & Eriks, 1965; Karle & Karle, 1966; Sundaralingam & Jensen, 1966) and NH_4^+ groups (Smith & Levy, 1962), the X-ray data on phase A were collected at about -150°C with a Weissenberg camera which had been modified slightly (Dickens, 1966) for routine low temperature work.

Determination of the structure

Roughly cylindrical needle-like crystals of phase A, not more than 0.35 mm in cross-section ($\mu_{\text{Mo}}=8.5$ cm $^{-1}$) were examined under a microscope attached to a dry box (Crisler, 1964) and were sealed into capillaries. The crystals were found to be orthorhombic, with the cell dimensions in Table 1 and space group $P2_1cn$ or $Pmcn$. Space group $P2_1cn$ ($x, y, z; \frac{1}{2}+x, \bar{y}, \bar{z};$

* Present address: Institute for Materials Research, Dental Research Section, National Bureau of Standards, Washington, D.C. 20234, U.S.A.

$\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z; x, \frac{1}{2}-y, \frac{1}{2}+z$) was indicated in the Patterson map, where the centrosymmetric peaks $2x, 2y, 2z$ were missing. The choice was substantiated by the eventual refinement of a chemically reasonable structure in $P2_1cn$. The unit cell, therefore, has two formula weights in the asymmetric unit. The observed density is 2.02 and the calculated density is 2.13 g. cm⁻³ at 25°C.

1757 intensity data taken with Mo radiation on $0 \rightarrow 8kl$ a -axis equi-inclination photographs (a is the needle axis) were estimated visually and corrected for the combined spot extension and Lp effects, but not for absorption. Preliminary estimates of the scale factors for the various equi-inclination levels were obtained in the calculation of quasi-normalized structure factors (Dickinson, Stewart & Holden, 1966).

The form factors for atoms other than hydrogen were taken from *International Tables for X-ray Crystallography* (1962), and those of hydrogen were taken from McWeeny (1951). All form factors used were for isolated neutral atoms.

The structure was solved from the sharpened Patterson function, calculated from the $E^2 - 1$ coefficients, and from subsequent F_o Fourier syntheses. It was refined by full-matrix least-squares procedures. The nitrogen atoms were identified by their higher temperature factors ($B_N = 1.5, B_O = 0.85$) when they were introduced into the refinement as oxygen atoms. In these refinements the weights for the reflections were calculated from $10/[\text{maximum of } (F_o/2 + 5) \text{ or } 10]$ and the quantity minimized was $\sum_{hkl} w|F_o - F_c|^2$. The x coordinate of the atom Cl(2) was used to define $x = 0$.

The few reflections with $F_c > 60$ at this stage of the refinement apparently suffered from extinction and were, therefore, labeled appropriately and given zero weights in the refinements.

Hydrogen atoms were sought in several difference syntheses, including one at $R = 0.09$, but were not found, presumably in part because of the imprecise phasing present in acentric structure determinations

Table 1. *Cell parameters** of HAP phases

Phase A		Phase B (at 23°C)	
	25°C		-150°C
<i>a</i>	7.52 ± 0.02 Å	7.46 ± 0.01 Å	7.52 ± 0.03 Å
<i>b</i>	7.14 ± 0.01	7.12 ± 0.01	24.28 ± 0.03
<i>c</i>	15.99 ± 0.02	15.70 ± 0.02	7.13 ± 0.03
<i>z</i>	4		β $95^\circ \pm 1^\circ$
	8 F. Wts. per cell		<i>z</i> 4
	$P2_1cn$		12 F. Wts. per cell
			$P2_1/n$
Phase C (at 50°C)			
	C-centered cell	<i>F</i> -centered cell	Body-centered cell
<i>a</i>	11.67 ± 0.03 Å	16.46 Å	10.21 Å
<i>b</i>	16.34 ± 0.03	16.34	16.34
<i>c</i>	10.00 ± 0.03	11.52	10.03
β	$124^\circ 35' \pm 1^\circ$	$90^\circ 35'$	$109^\circ 45'$
<i>z</i>	4 or 8		
	16 F. Wts. per unit cell		
	$C2/m, C2$ or Cm		

* Cell dimensions of phase A determined from Weissenberg and oscillation films and standardized from a superimposed powder pattern of Al taken at room temperature. Other cell dimensions measured from precession films taken with single crystals and not standardized.

Table 2. *Atomic parameters in phase A of HAP*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
ClO_4^- group	Cl(1) 0.1421 (4)	0.1456 (2)	0.1836 (1)	0.32 (2) Å ²
	O(1) -0.0093 (11)	0.0123 (7)	0.1861 (3)	0.83 (6)
	O(2) 0.2580 (11)	0.1069 (9)	0.2551 (4)	0.93 (8)
	O(3) 0.0673 (12)	0.3322 (9)	0.1895 (4)	0.99 (8)
	O(4) 0.2405 (11)	0.1213 (9)	0.1059 (4)	1.05 (8)
	Cl(2) 0.0000	0.2450 (2)	0.4372 (1)	0.35 (2)
ClO_4^- group	O(5) 0.1087 (10)	0.0931 (9)	0.4679 (4)	1.05 (8)
	O(6) 0.1141 (10)	0.4011 (8)	0.4144 (3)	0.76 (7)
	O(7) -0.0993 (12)	0.1811 (10)	0.3646 (4)	1.38 (10)
	O(8) -0.1229 (11)	0.3025 (8)	0.5043 (3)	0.79 (7)
	N(1) -0.0104 (12)	0.7893 (8)	0.0282 (3)	0.61 (6)
	O(9) -0.0032 (11)	0.6509 (7)	0.0927 (3)	0.61 (5)
NH_3OH^+	N(2) 0.1379 (13)	0.6689 (8)	0.2776 (3)	0.65 (6)
	O(10) 0.1222 (10)	0.7952 (8)	0.3461 (3)	0.73 (6)

x coordinate of Cl(2) used to define origin along *a*.

Average value of shift/error for final cycle = 0.005.

Maximum value of shift/error for final cycle = 0.019.

Table 3. Observed and calculated structure factors for phase A
Columns are I , $10F_0$, $10F_C$.

0,0,L		0,+L		6 -93 70 177		2 314 282 755		5 231 203 850		20 110 99 881		12 126 121 813		14 133 120 861		16 252 242 968	
4	85 48 0	1	407 325 0	9	193 178 982	5	218 211 808	7	396 430 739	22	154 172 89	14	418 495	178	19 184 187	660	12 220 238 973
6	126 137 0	2	530 560 500	10	292 288 704	6	391 382 302	8	273 329 174	23	148 134 319	16	134 135 316	20	265 262 161	13	118 78 405
8	554 575 500	4	119 113 506	11	634 625 341	7	158 145 377	9	149 117 377	24	184 204 862	18	324 353	177	21 126 114 141	14 130 114 593	
10	212 775 0	5	105 114 500	12	466 537 785	8	270 284 142	10	259 292 31	29	98 104 345	20	146 142 71	71	22 113 115 231	15 172 197 591	
12	311 311 0	6	122 522 500	13	211 208 759	11	206 206 111	12	250 250 70	30	133 127 645	23	126 126 701	71	23 126 111 173	17 173 173 593	
14	215 222 500	7	178 127 0	14	264 268 688	10	207 210 271	13	190 204 880	31	92 52 726	24	143 130 822	28	147 139 724	18 100 74 523	
16	351 398 0	10	438 433	17	99 89 356	13	145 159 434	14	190 217 433	35	147 123 183	19	130 146 994				
18	145 139 500	11	84 74	C	183 176 176	14	191 161 760	15	323 341 341	34	2,7,L	20	92 76 918				
22	165 165 0	13	264 288 290	19	107 109 956	15	258 150 151	16	150 151 485			21	227 259 549				
24	154 152 500	15	244 250 500	20	294 296 327	17	137 137 523	18	137 137 523			22	236 236 417				
26	150 150 0	15	143 500	21	166 166 749	18	157 157 484	2	337 338 622	1	247 203 832	1	213 183 744	23	177 177 123		
32	310 340 0	18	125 131 500	22	166 165 263	21	128 182 194	22	202 198	4	221 222 461	3	329 339	24	102 100 14		
0,+L		22 325 369 0		23	148 131 967	23	135 160 396	23	137 130 734	5	312 312 234	4	220 227 280	6	189 154 176	26 155 161 979	
22	132 122 500	24	132 122 500	25	120 120 715	24	112 99 192	26	207 207 500	7	187 187 345	8	187 187 345	9	187 187 345	30 149 150 495	
3	417 497 500	26	120 120 500	27	120 120 500	28	119 119 918	29	256 256 330	10	169 151 300	11	169 151 300	12	165 165 300	34 112 941	
4	124 161 910 0	32	135 136 500	29	119 93 866	1,8,L	22 116 116	29	113 119 855	12	113 126 15	9	339 317	13	168 162 696		
5	264 244 500	33	128 120 319	1	236 170 296	2	133 139 217	3	128 120 217	4	187 187 205	5	128 120 205	6	187 187 205	4,3,L	
7	248 244 500	0,7,L		1,3,L	4	306 305 703	31	320 320 156	14	201 201 976	11	311 311 325	7	153 167 186	2 493 466 448		
11	308 304 0	1	128 88	0	5 239 242 500	5	229 192 436	30	105 116 555	15	146 146 966	12	151 162 880	16 270 273 695			
13	640 511 500	3	470 434 500	1	267 247 54	6	161 166 710	34	102 88 441	14	151 154 144	13	234 198 368	17 160 155 632			
16	187 178 0	4	161 122 500	2	233 197 780	9	166 157 835	17	150 150 177	18	129 121 485	14	343 345 688	18 115 113 746			
17	197 187 0	5	212 212 500	11	204 204 228	10	110 110 177	17,3,L	19 86 151 831	19	151 150 155	21	152 152 155	15 154 154 96			
19	165 167 500	6	167 162 500	5	161 161 221	11	149 301	2,3,L	21 24 24 20	22	120 121 211	21	121 121 211	22 122 122 545			
23	154 173 0	7	289 280 500	7	322 290 290	12	207 207 326	1,3,L	21 24 24 20	22	120 121 211	21	121 121 211	22 122 122 545			
25	120 126 500	10	245 234	8	209 196 352	13	221 232 286	2,2,L	27 193 332	21	139 128 435	19	257 243 128	24 110 113 180			
27	166 164 0	9	197 181	9	360 421	700	17 136 136 446	3,0,L	260 260 260	15	155 157 54	23	202 193 202	11 412 475 54			
28	419 399 500	13	177 175 500	100	126 171 274	19	159 184 875	4	387 400 368	27	151 150 247	21	126 114 652	12 216 216 516			
36	125 149 0	11	167 161 500	11	167 161 212	12	157 157 193	2,8,L	21 120 120 212	22	120 121 211	21	121 121 211	22 122 122 545			
G,2,L		18	200 198 500	13	248 251 24	28	166 166 322	19	196 166 409	2,6,L	21 120 120 212	20	174 140 278	16 78 328	13 130 130 518		
20	159 159 500	14	235 373 384	817	1,9,L	187 166 103	0	2,1,L	188 132	3,3,L	4 144 128 835	20 257 257 538					
0	1024E+1413 500	26	121 90	0	15 234 266 458	11	265 305 969	1	223 245 726	2,3,L	5 211 197 500	25 224 224 500	1	262 205 63			
1	309E+211 500	27	161 171 173	0	1,3,L	4 306 305 703	31	320 320 156	14	201 201 976	11	311 311 325	7	153 167 186	2 493 466 448		
2	507 507 500	0,8,L		17 18 198	0	344 353 356	13	226 237 358	7	187 187 303	6	276 276 619	693	24 153 153 909			
5	233 102 500	18	243 290 790	1	153 133 362	14	225 225 217	5	156 116 310	1	551 559 307	7	86 88 592	24 91 88 991			
6	146 72 500	19	70 84	665	2 167	112 94 6	16	118 98 310	6	215 215 390	2	337 331 599	8 79 70 603	25 143 140 555			
7	180 113 0	0	351 302 302	26	108 92 681	5	110 119 322	17	132 148 822	7	154 149 803	4 249 234 205	9 102 108 202	26 139 110 952			
9	164 120 0	1	126 226 226	50	25 25 25 25	10	119 119 234	2,1,L	12 120 120 217	10	151 151 217	11 216 216 545					
9	55 55 500	6	214 204	26	119 119 234	7	159 145 193	2,2,L	274 274 274	9	203 203 316	6 379 381 368	11 121 121 205				
10	224 229 0	6	217 248 248	500	25 119 107 415	8	341 382 785	23	182 172 515	10	168 169 394	3 393 392 138	12 181 181 223	29 90 98 572			
11	194 171 500	12	120 129 500	25	138 146 276	9	120 123 508	21	153 153 938	11	113 83 404	8 432 502 19	13 219 234 163	30 93 93 994			
13	242 261 500	8	398 397 399	500	25 129 129 426	10	129 129 426	14	171 165 362	12	146 146 216	9 362 374 713	14 154 154 310				
14	333 333 500	30	156 156 140	140	262 262 802	15	160 160 202	16	174 174 362	17	161 161 362	10 379 379 379	11 111 111 114				
15	302 302 500	13	164 164 175 500	16	184 184 206	24	123 123 206	19	120 120 206	11	122 122 206	12 162 162 206	13 162 162 206				
16	202 222 500	14	94 113 500	1,4,L	22 120 120 500	25	207 229 323	16	215 216 119	12	107 82 715	19 121 118 212					
17	92 92 500	16	246 246 283	0	24 263 261 609	26	105 105 177	15	124 124 124	13	265 277 125	20 25 20 97	107 741	0 633 544 2			
18	154 182 500	21	211 211 211	0	2 442 465 861	27	113 106 829	19	100 112 939	14	181 155 646	4 145 129 393	4 130 113 887				
21	144 152 500	23	134 141 160	0	2 474 487 270	28	186 186 971	21	120 120 330	12	162 162 330	3 142 142 330	3 142 142 330				
24	237 237 222 0	0	24 233 238 653	3	182 182 188 893	2,4,L	125 125 188	24	124 124 224	2,4,L	194 193 267	1 142 142 314	3 142 142 314				
25	143 148 0	8	95 104 147	4	270 280 327	2,5,L	79 79 580	5	74 82 286	1	280 224 220	210 175 175 220	1 101 72 103				
27	143 148 0	9	85 85 85	401	4 158 173 629	28	125 119 892	6	282 332 904	14	116 95 513	4 145 136 516					
29	118 109 0	0	20 213 195 300	8	276 276 342	15	111 107 899	20	161 172 127	3 193 135 307	3 142 132 307						
30	204 204 195 0	16	314 266 265	311	9 161 161 31	31	123 135 900	10	190 191 857	17	132 119 343	4 154 129 238					
32	301 272 0	12	7298E+061 311	31	9 161 161 31	8 7876E+05 631	32	123 135 900	11	71 71 565	12 168 168 62	6 668 686 518					
37	221 213 183 500	13	125 125 257	361	1 250 250 250	2,5,L	13 125 125 250	13	71 71 565	12 168 168 62	6 668 686 518						
38	134 128 0	14	363 367 367	11	1 250 250 250	2,6,L	13 125 125 250	13	71 71 565	12 168 168 62	6 668 686 518						
39	161 201 156 0	15	201 196 196	44	1 250 250 250	2,7,L	13 125 125 250	13	71 71 565	12 168 168 62	6 668 686 518						
40	255 255 205 0	3	175 175 183	63	1 250 250 250	2,8,L	13 125 125 250	13	71 71 565	12 168 168 62	6 668 686 518						
41	282 281 500	5	218 203 203	71	1 250 250 250	2,9,L	13 125 125 250	13	71 71 565	12 168 168 62	6 668 686 518						
42	287 281 500	6	166 166 175	291	7 212 212 313	2,10,L	24 24 24 205	28	190 190 173	3,1,L	139 139 139	10 109 989					
43	281 281 500	7	166 166 175	291	7 212 212 313	2,11,L	13 191 214 267	4	184 144 616	5	172 144 291	7 32 32 320					
44	436 436 500	6	261 251 258	75	4 909E+127 135	14	215 234 587	5	199 188 717	6	226 224 757</						

Table 3 (cont.)

	4,7,L	12	335	335	150	5,5,L	5,10,L	6,4,L	6,9,L	7,4,L	7,10,L	8	222	228	400			
18	178	192	500	14	377	403	312	0	509	477	279	2	332	271	345			
19	168	182	62	18	386	398	862	1	162	152	22	4	179	161	113			
20	148	141	46	20	331	390	654	2	167	155	5	162	152	22	208			
21	93	94	76	22	161	191	767	3	138	110	806	8	120	111	328			
22	116	127	519	4	161	133	807	9	126	101	126	8	126	101	236			
25	97	98	86	5	197	199	256	12	168	162	593	5	72	52	928			
28	134	154	10	6	282	280	580	14	111	103	789	6	296	263	478			
				3	90	93	615	10	202	190	33	18	106	134	336			
				4	143	151	580	8	395	306	845	6,0,L	10	252	248	436		
D	349	371	979	6	331	288	826	12	111	111	369	12	104	91	323			
1	314	296	82	7	414	454	3	13	115	94	71	8	594	605	422			
2	202	194	9	8	164	160	614	14	160	157	17	14	160	157	303			
3	116	111	584	9	291	278	635	15	171	144	712	14	204	139	50			
5	137	80	545	10	343	356	776	16	313	324	340	18	186	179	136			
6	207	203	543	14	319	313	334	19	99	94	91	24	291	200	437			
7	167	145	102	15	136	157	191	81	97	463	18	182	144	241	226			
8	111	101	51	17	129	127	150	21	82	910	32	225	207	918	24			
9	156	155	554	17	133	133	38	19	13	211	26	137	114	529	135			
10	158	156	570	18	307	334	298	24	180	180	817	30	140	129	910			
11	170	182	453	23	121	132	458	6,1,L	6	80	72	121	121	57	6,5,L			
14	204	223	54	21	113	117	506	2	230	267	98	7,0,L	1	127	108	78		
15	143	140	50	22	101	104	21	3	311	328	344	7,1,L	1	96	83	326		
16	126	140	420	23	184	183	699	2	240	252	809	6,2,L	505	0	280	228		
17	103	106	100	24	186	183	699	2	252	235	169	5,3,L	3	136	126	505		
18	144	166	10	25	105	94	543	3	212	167	705	9	166	159	420			
				4	211	195	294	17	162	167	603	6	322	299	292			
				5	245	229	521	11	138	174	768	7	79	78	180			
				6	80	80	121	12	166	166	57	8,0,L	3	196	176	690		
1	67	66	996	1	93	67	143	7	87	75	845	10	191	191	426			
2	321	280	43	2	233	188	219	108	91	882	14	139	161	73	11	181	157	186
3	156	138	580	3	437	420	528	1	229	603	16	93	79	823	12	245	245	556
4	866	4	202	251	315	11	182	164	457	17	130	113	903	13	176	179	318	
5	163	151	502	5	279	252	553	12	166	166	457	14	204	192	509			
6	213	297	21	6	347	376	248	14	151	157	688	19	229	247	391			
12	316	284	532	7	120	110	529	17	132	140	444	20	247	264	970			
11	80	96	115	8	96	78	734	12	129	127	146	21	101	95	865			
13	109	122	323	10	319	338	450	19	159	195	922	22	106	132	27			
14	177	169	545	11	306	324	939	21	77	88	432	25	103	95	320			
15	112	137	475	12	154	140	638	26	136	133	668	26	106	106	251			
18	164	190	53	13	174	186	588	5,7,L	27	82	105	907	6,6,L	21	81	73	859	
20	89	62	626	14	235	255	541	9	222	224	712	29	196	195	429			
				17	135	136	921	1	194	172	992	30	113	112	543			
				18	240	250	269	2	220	181	714	5,8,L	6	175	150	908		
2	158	124	397	19	253	281	573	178	162	631	3	392	320	511	7,2,L			
3	207	157	196	5	167	156	628	1	221	231	231	1	232	212	21			
4	266	224	152	13	171	171	233	6	180	171	233	2	245	245	252			
10	167	132	22	22	146	154	298	7	249	241	16	1	258	265	336			
14	297	312	525	17	174	192	199	3	346	359	563	1	191	192	166			
16	95	68	48	5,3,L	9	248	247	443	3	272	278	765	13	111	110	606		
18	150	123	519	12	194	212	233	5	180	176	233	2	201	201	460			
20	151	104	556	0	563	481	703	13	104	108	317	4	176	156	596			
22	115	118	54	1	291	281	360	5	182	176	366	5	306	303	352			
				2	269	228	806	15	198	199	498	2	352	364	352			
				3	120	89	138	2	254	253	793	17	100	88	838			
4	4	66	283	17	168	192	981	9	361	447	949	18	161	161	564			
6	147	147	520	6	436	410	411	21	110	128	448	11	82	89	227			
8	155	141	974	7	451	445	490	13	118	145	983	13	129	115	338			
9	152	167	521	8	414	497	327	24	129	131	255	14	143	115	543			
10	221	218	519	9	215	213	219	5,6,L	15	240	256	782	6,7,L	1	125	125	625	
14	109	130	992	12	97	86	798	9	177	171	245	1	152	127	751			
17	90	85	38	13	157	142	426	1	219	246	166	3	181	231	240			
18	97	92	124	14	133	140	771	2	206	186	830	17	171	199	866			
19	102	102	550	15	132	224	981	3	144	146	522	14	162	142	561			
				17	201	166	445	5	123	207	941	20	103	103	577			
				18	79	77	602	6	101	172	888	25	113	102	777			
4,11,L	4	6	115	94	14	94	278	3	321	309	828	15	117	131	971			
5	120	119	519	5	100	99	227	2	103	103	185	40	114	114	547			
6	142	145	519	6	133	127	155	6	339	389	472	21	120	110	842			
7	121	270	238	7	272	127	155	665	6	339	389	472	21	120	110	842		
8	156	157	519	8	107	109	473	7	105	109	473	6,8,L	9	92	88	661		
12	199	213	526	2	270	238	719	27	127	155	665	6,9,L	1	239	288	935		
				3	338	321	94	21	128	86	44	7	195	204	699			
				4	659	639	817	8	107	109	473	6,10,L	15	120	121	721		
				5	126	126	498	9	104	104	473	6,11,L	15	120	121	721		
4,14,L	4	5	117	507	5	126	126	498	5,9,L	9	135	118	681	7,8,L	15	120	121	721
16	167	197	530	5	305	334	136	11	79	100	159	1	329	288	935			
8	8	222	211	353	2	265	232	140	19	75	2	205	193	74	14	214	214	214
4,15,L	9	231	244	928	12	136	126	148	241	13	183	204	829	3	102	88	956	15
12	137	155	301	11	123	121	225	12	121	121	225	2	103	117	134	226		
				12	328	308	719	9	133	127	247	286	853	8	323	317	449	
				13	127	126	247	19	127	126	247	286	853	9	127	126	247	
				14	138	181	974	10	133	125	468	6	202	184	594	15		
6	324	264	550	13	125	125	328	11	130	130	93	10	124	119	604	15		
6	323	307	847	20	211	224	847	15	152	152	328	28	130	107	27	13		
8	151	136	39	21	83	82	599	16	205	212	129	14	100	112	73	24		
10	393	419	354	17	167	111	420	16	232	285	909	33	132	124	742	7		

(Olovsson & Templeton, 1959) but possibly also because of oscillation or rotation of the NH_3OH^+ group. A smeared model with half the hydrogen atoms in suitable positions was used to refine the heavier atom parameters to the values reported in Table 2. The observed and calculated structure factors are listed in Table 3.

The largest correlation coefficients are 0.34 between the scale factors and the Cl isotropic temperature factors, 0.25 between the scale factors themselves, 0.21 between the Cl isotropic temperature factors, and 0.1 between the Cl temperature factors and the other temperature factors. All other correlation coefficients are

much less than 0.1. The systematically high correlations between the scale factors and the β_{11} (for a axis data) temperature factors prevent the direction of maximum vibrations of individual atoms from being picked out and make anisotropic refinement worthless. Since the crystal was kept at -150° during the data collection the thermal motion should, however, be relatively small.

Discussion of the structure of phase A</h3

perchlorate ion tetrahedra in infinite chains along **c** which are held together by hydrogen bonding from parallel chains of NH_3OH^+ ions. The different chains alternate along **a** and **b**. The closest approach of ClO_4^- tetrahedra, $\text{O}(4)\cdots\text{O}(8) = 3.03 \text{ \AA}$, is between neighboring groups in the chain along **c**. The NH_3OH^+ ions are arranged with parallel pairs of N–O vectors (Fig. 1) one pair having the N–O vectors roughly 45° and the other -45° to **b**. The ClO_4^- groups present their edges irregularly to six surrounding NH_3OH^+ ions, which are, therefore, arranged in an irregular large octahedron around each ClO_4^- ion. There are seventeen ($\text{N–O}\cdots(\text{ClO}_4^-)$) distances less than the $\text{O}(4)\cdots\text{O}(8)$ inter- ClO_4^- closest approach.

The intra-ionic distances and angles are given in Table 4 and the inter-ionic distances, which must include those between hydrogen bonded atoms, in Table 5. The Cl–O distances in the ClO_4^- groups [average value $1.45 \pm 0.01 \text{ \AA}$ uncorrected for any rotation-oscillation effect (Cruickshank, 1956, 1961)] are in good agreement with those of $1.46 \pm 0.01 \text{ \AA}$ (NO_2ClO_4 , Trutter, Cruickshank & Jeffrey, 1960) and $1.462 \pm 0.004 \text{ \AA}$ (low temperature form of $\text{H}_3\text{O}^+\text{ClO}_4^-$, Nordman, 1952). The O–Cl–O angles (average value $109.5 \pm 0.04^\circ$) show the ClO_4^- group to be essentially tetrahedral, as expected. The average O–O distance in the ClO_4^- group is $2.36 \pm 0.01 \text{ \AA}$. The average N–O distance of $1.41 \pm 0.01 \text{ \AA}$ in the NH_3OH^+ group is near to that expected when the sum ($1.47 \pm 0.02 \text{ \AA}$) of the sp^3 covalent radii (Giguère & Schomaker, 1943) of nitrogen (0.735 \AA) and oxygen (0.735 \AA) is corrected (Schomaker &

Stevenson, 1941) by $-0.08 |x_A - x_B| = -0.08 |3.0 - 3.5| = -0.04 \text{ \AA}$ to $1.43 \pm 0.02 \text{ \AA}$ to account for the difference in the electronegativities of these atoms. In room temperature structure determinations of NH_3OHC and NH_3OHBr , 1.45 \AA has been found (Jerslev, 1948) for the N–O distance.

The X–H \cdots Y distances for possible hydrogen bonds in phase A are given in Table 5 and the environments of the two NH_3OH^+ groups are shown in Fig. 2 and 3. Since hydrogen can form hydrogen bonds to two or more atoms simultaneously (Baur, 1965) in keeping with the predominantly electrostatic nature (see for example Coulson, 1957) of the hydrogen bond, the X \cdots Y distance is a poor criterion of the strength. However, various X \cdots Y distances for N and O given in Baur (1965) and Coulson (1957) suggest that the hydrogen bonding in phase A is weak. Further, preliminary nuclear magnetic resonance results (Farrar, 1967) indicate that the NH_3OH^+ group in phase A is rotating faster than 10^5 times per second at room temperature. This is substantiated by preliminary measurements (Rush, 1967) of total neutron cross sections as a function of neutron wavelength (Rush, Taylor & Havens, 1962; Rush & Taylor, 1964) which indicate that the NH_3OH^+ ions in phase A have a low barrier (of the order of 1 kcal) to either one- or three-dimensional rotation at room temperature. This rotation is expected to persist well below -150°C .

The N and O atoms show no greater thermal motion than the O's in the ClO_4^- groups (Table 3) so any such rotation is obviously approximately about the N–O

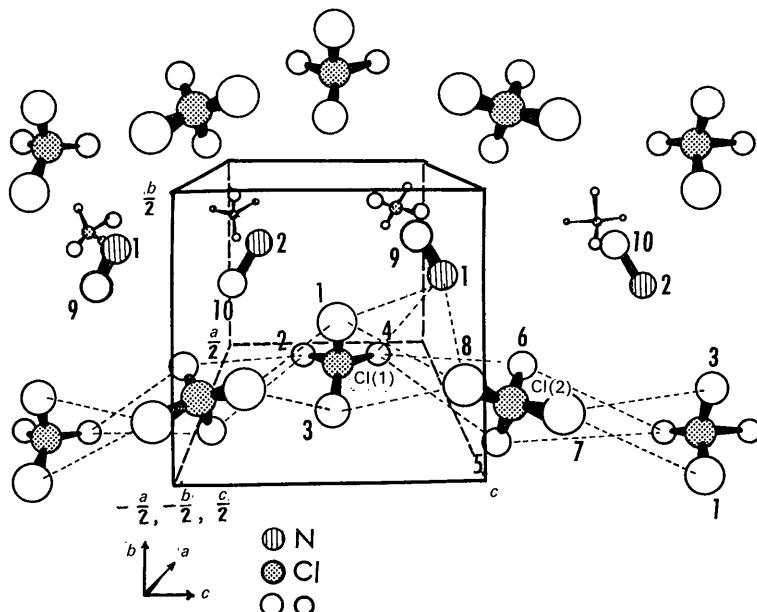


Fig. 1. The crystal structure of HAP.

vector. It is proposed* to examine possible partial or complete rotation about the N–O vector in the various HAP phases of either the complete NH_3OH^+ group or the $-\text{NH}_3^+$ group by further subthermal neutron scattering experiments.

Other phases of HAP: phase B

If a single crystal of phase A in an extinction position is heated on the hot stage of the polarizing microscope to about 55°C it cracks and develops 'polarization colors'. X-ray examination of a single crystal of HAP before and after the cracking, and especially of a single crystal of the phase produced above 55°C by repeated recrystallization at 85°C from the melt (melting point 89–91°C), showed that the cracking is a result of a first order phase transformation from phase A to a second phase, phase B. To grow phase B and subsequently examine the crystal on the precession camera, it has been found convenient to seal a crystal of phase A in a 0.2 mm diameter glass capillary and keep it on the camera in a stream of air heated to 85°C by a nichrome wire heating coil in the glass tube delivery nozzle. The solid may be recrystallized by melting it from each end alternately with a small soldering iron. A very small part of the solid should be left unmelted each time to act as a seed. When phase B was cooled to room temperature, after annealing for one hour

at 85°C, and then warmed up past 60°C, it did not crack or develop polarization colors before melting at 90°C. Phase B is monoclinic with the unit-cell parameters given in Table 1. It is related to phase A (cell dimensions at room temperature $a = 7.52$, $c = 15.99$ and $b = 7.13$ Å) since the c of phase A increases by $\frac{3}{2}$ and becomes the b axis of phase B. This was substantiated by comparing precession and Weissenberg photographs of the cracked crystal with those of the parent crystal.

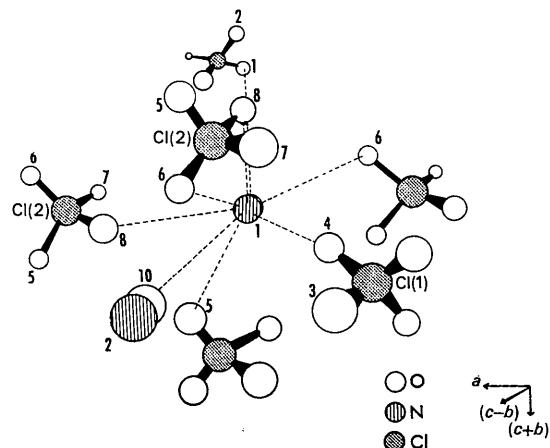


Fig. 2. The environment of the $\text{N}(1)-\text{O}(9)$ NH_3OH^+ group
The dotted lines represent $\text{N}(1)-\text{X}$ distances quoted in Table 5

Table 4. Intra-ionic distances and angles in phase A of HAP

ClO_4^- group 1		ClO_4^- group 2	
Atoms	Distance Å	Atoms	Angle
$\text{Cl}(1)-\text{O}(1)$	1.476 (8)	$\text{O}(1)-\text{Cl}(1)-\text{O}(2)$	108.4 (4)°
$\text{Cl}(1)-\text{O}(2)$	1.444 (3)	$\text{O}(1)-\text{Cl}(1)-\text{O}(3)$	107.1 (5)
$\text{Cl}(1)-\text{O}(3)$	1.444 (8)	$\text{O}(1)-\text{Cl}(1)-\text{O}(4)$	109.6 (4)
$\text{Cl}(1)-\text{O}(4)$	1.434 (7)	$\text{O}(2)-\text{Cl}(1)-\text{O}(3)$	110.9 (4)
$\text{O}(1)-\text{O}(2)$	2.37 (1)	$\text{O}(2)-\text{Cl}(1)-\text{O}(4)$	109.4 (5)
$\text{O}(1)-\text{O}(3)$	2.35 (1)	$\text{O}(3)-\text{Cl}(1)-\text{O}(4)$	111.3 (4)
$\text{O}(1)-\text{O}(4)$	2.38 (1)		
$\text{O}(2)-\text{O}(3)$	2.38 (1)		
$\text{O}(2)-\text{O}(4)$	2.35 (1)		
$\text{O}(3)-\text{O}(4)$	2.38 (1)		
ClO_4^- group 2			
$\text{Cl}(2)-\text{O}(5)$	1.435 (7)	$\text{O}(5)-\text{Cl}(2)-\text{O}(6)$	109.3 (4)
$\text{Cl}(2)-\text{O}(6)$	1.445 (7)	$\text{O}(5)-\text{Cl}(2)-\text{O}(7)$	108.7 (4)
$\text{Cl}(2)-\text{O}(7)$	1.433 (8)	$\text{O}(5)-\text{Cl}(2)-\text{O}(8)$	108.9 (4)
$\text{Cl}(2)-\text{O}(8)$	1.455 (7)	$\text{O}(6)-\text{Cl}(2)-\text{O}(7)$	110.6 (4)
$\text{O}(5)-\text{O}(6)$	2.35 (1)	$\text{O}(6)-\text{Cl}(2)-\text{O}(8)$	109.5 (4)
$\text{O}(5)-\text{O}(7)$	2.33 (1)	$\text{O}(7)-\text{Cl}(2)-\text{O}(8)$	109.8 (5)
$\text{O}(5)-\text{O}(8)$	2.35 (1)		
$\text{O}(6)-\text{O}(7)$	2.37 (1)		
$\text{O}(6)-\text{O}(8)$	2.37 (1)		
$\text{O}(7)-\text{O}(8)$	2.36 (1)		
NH_3OH^+			
$\text{N}(1)-\text{O}(9)$	1.414 (8)		
$\text{N}(2)-\text{O}(10)$	1.406 (8)		

The standard errors are those obtained from the parameter errors from the final full-matrix least-squares refinement and the errors in the cell dimensions.

The 24 Å spacing was along the direction which had previously been 16 Å and the phase A $hk0$ reciprocal lattice plane had split into two $h0l$ planes, with a common c in the monoclinic phase B. The equivalent cell volumes and hence the densities of the two phases are equal within 0.5%. Phase B can exist as a clear single crystal from minutes to perhaps two days at room temperature, provided the crystal has been annealed at about 75°C and cooled slowly to room temperature. In the X-ray beam it gradually becomes cloudy even when held between 60°C and 90°C, and after a week gives only a powder pattern. The phase into which it changes at these temperatures has not been established. Good crystals of phase B (and phase C) can be regrown from a crystal which has become cloudy and gives only a powder pattern, which suggests that only a change in phase has taken place. An attempt to supercool a single crystal of phase B fairly slowly to liquid nitrogen temperatures, to freeze the crystal as phase B, produced only a powdered phase.

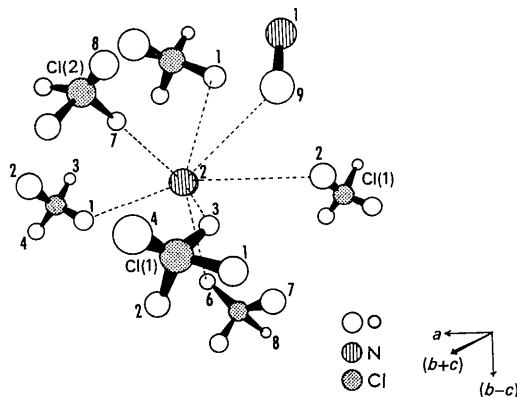


Fig. 3. The environment of the N(2)-O(10) NH_3OH^+ group. The dotted lines represent N(2)-X distances quoted in Table 5.

Phase B has, qualitatively, a high birefringence as does phase A.

Phase C

If the cracked crystal obtained on heating phase A in a capillary is allowed to melt entirely, then on over 50% of the occasions it will not solidify until below 57–58°C when it forms a solid melting at 57–58°C. Single crystals of this phase (phase C) have been grown in capillaries from a completely molten sample of HAP and have been shown to be monoclinic with the unit cell parameters in Table 1. The calculated density is 2.26 g. cm⁻³. This phase, like phase A, has an axis of nearly 16 Å, which is the unique monoclinic axis. The cell is most easily indexed as face-centered or body-centered. Phase C will persist at room temperature for a few minutes.

The determination of the crystal structures of phases B and C has not been attempted because of their instabilities and presumed high thermal motion, although it is feasible especially if the data are collected rapidly by an automated system.

The metastability of the phases B and C at room temperature suggests that oscillation of the perchlorate groups is not the determining factor in the transition.

Most of the calculations were done with the use of the *X-ray 63* crystallographic computing system assembled under the editorship and guidance of J. M. Stewart, University of Maryland. A. L. Milstead of the Naval Ordnance Station, Indian Head, Maryland, 20640, helped with the visual estimation of the raw X-ray intensity data.

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Table 5. *Inter-ionic distances** in phase A of HAP

NH ₃ OH ⁺ group 1 [N(1)-O(9)]		NH ₃ OH ⁺ group 2 [N(2)-O(10)]	
Atoms	Distance	Atoms	Distance
O(9)-O(5)	2.75 Å	O(10)-O(2)	2.83 Å
O(9)-O(3)	2.78	O(10)-O(5)	2.86
O(9)-O(1)	2.96	O(10)-O(6)	3.01
O(9)-O(2)	3.00	O(10)-N(1)	3.09
O(9)-O(5)	3.08	O(10)-O(8)	3.10
O(9)-O(7)	3.09	O(10)-O(1)	3.11
O(9)-N(2)	3.09	N(2)-O(3)	2.82
N(1)-O(4)	2.88	N(2)-O(6)	2.88
N(1)-O(8)	2.94	N(2)-O(2)	2.91
N(1)-O(1)	2.94	N(2)-O(1)	2.92
N(1)-O(6)	2.99	N(2)-O(7)	2.97
N(1)-O(5)	3.02	N(2)-O(1)	3.04
N(1)-O(8)	3.05	N(2)-O(9)	3.09
N(1)-O(6)	3.05		
N(1)-O(10)	3.09		
N(1)-O(5)	3.17		

* All standard errors are 0.01 Å.

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The Structure of $C_9Cl_7(COOH) \cdot (O_2C_2H_4)$, a Condensed Cage Pentacyclononane Compound, Determined by the Symbolic Addition Method*

BY Y. OKAYA

Chemistry Department, State University of New York at Stony Brook, Stony Brook, New York 11790, U.S.A.

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The crystal structure of $C_9Cl_7(COOH) \cdot (O_2C_2H_4)$, a pentacyclononane derivative, was studied to obtain information on the configuration of the basic carbon cage structure which can be derived from a cube by adding one apex carbon atom. The crystal is monoclinic and the cell constants are: $a = 17.496 \pm 0.004$, $b = 8.005 \pm 0.003$, $c = 24.193 \pm 0.004 \text{ \AA}$, $\beta = 95.6 \pm 0.1^\circ$; the space group is $I2/a$. Three-dimensional intensity data were collected on the CCXD, a computer-controlled diffractometer, which is operated by an IBM 1620 under a stored data-collection program. The crystal structure was determined by systematic application of the symbolic addition method and refined by a full-matrix least-squares program on an IBM 7094. The molecule can be called 6,6-ethylenedioxyheptachloropentacyclo-[5.2.0.0^{2,5}.0^{3,9}.0^{4,8}]nonane-3-carboxylic acid. The configurations of the cyclobutane and cyclopentane rings in the condensed cage molecule are discussed in detail. The carboxyl group is involved in the formation of centrosymmetric dimers which are stacked in the structure with the usual van der Waals contacts.

Introduction

Scherer, Lunt & Ungefug (1965) reported ring contraction through Favorskii rearrangement of chlorinated pentacyclodecanones by the action of alkali on I and III. In each case a pentacyclononane carboxylic acid has been formed (see Fig. 1). The position of the carboxyl group in IV could be uniquely assigned since the starting decanone possesses a symmetric cage structure; whereas for II the choice between the two non-equivalent sites for the group was decided by measuring the pK_a value of the acid V obtained by a hydrolysis of II which effected a removal of the ethylene glycol residue.

Crystals of II and IV were studied as a part of our continuing effort to determine the shape and size of condensed poly-ring carbon cage structures. Although

IV is a simpler molecule than II, the crystallographic data revealed that there are two non-equivalent molecules per asymmetric unit. This led to determination of the crystal structure of II, which possesses an extra ethylenedioxy group on the apex carbon.

Experimental

Crystals of II, $C_9Cl_7(COOH)(O_2C_2H_4)$, were obtained from CH_2Cl_2 solution of the sample supplied by Professor K. Scherer. One such crystal was ground into an approximately spherical shape and mounted on a G.E. Goniostat on CCXD, a computer-controlled diffractometer system, operated by an IBM 1620 in a closed-loop manner (Cole, Okaya & Chambers, 1963). The crystallographic constants were measured on the diffractometer and used as input parameters to the subsequent data-collection program; the values were $a = 17.496 \pm 0.004$, $b = 8.005 \pm 0.003$, $c = 24.193 \pm 0.004 \text{ \AA}$,

* The experimental part of this work was performed at IBM Research Center, Yorktown Heights, New York.