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THE CRYSTAL AND MOLECULAR STRUCTURE OF HEXAAQUOALUMINUM HEXACHLORORUTHENATE TETRAHYDRATE

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CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, BERKELEY, CALIFORNIA

The Crystal and Molecular Structure of Hexaaquoaluminum Hexachlororuthenate Tetrahydrate.[1]

BY TED E. HOPKINS[2], ALLAN ZALKIN, DAVID H. TEMPLETON, AND MARTYN G. ADAMSON[3]

An X-ray diffraction study of a single crystal of $Al(H_2O)_6 \cdot RuCl_6 \cdot 4H_2O$ showed that it is monoclinic with $\underline{a}$ = 10.492 A, $\underline{b}$ = 11.415 A, $\underline{c}$ = 7.069 A, $\underline{\beta}$ = 92.69°, $\underline{Z}$ = 2, and $\underline{D_x}$ = 2.045 g cm^{-3}. The space group is $P2_1/n$. The ruthenium and aluminum ions are found to lie at the centers of slightly distorted octahedra of chlorines and water molecules, respectively. The hydrogen bond network connecting the octahedra is discussed. The average Ru-Cl and Al-O distances are found to be 2.375 and 1.880 Å.

Introduction

The aqueous ruthenium species are being studied in this laboratory by Professor R. E. Connick and others, and this research has provided a number of interesting ruthenium salts. We have investigated the structures of several of these compounds to help in the correlation of the optical spectra of the solutions with the environment of the ruthenium ion. Structures involving the aquo-tetrachloro and aquo-pentachloro ruthenium species are reported elsewhere.[4] In this paper we describe the structure of $A\ell(H_2O)_6RuC\ell_6 \cdot 4H_2O$, a salt of hexachlororuthenium (III).

Experimental Section

A solution of aluminum chloride in hydrochloric acid was prepared by dissolving 0.3 g analytical grade anhydrous $A\ell C\ell_3$ in 15 ml of concentrated $HC\ell$ with a minimum of heating; the resulting solution was then filtered and allowed to cool. A 0.15 M Ru(III) solution in concentrated $HC\ell$ was prepared by dilution of a pure Ru(III) stock solution.[5] Both solutions were deoxygenated by bubbling with pure nitrogen for half an hour. They were then mixed, and the resulting solution was allowed to stand under an atmosphere of nitrogen for 48 hours at room temperature. The light red plates which crystallized out of the solution were separated on a Buchner funnel, quickly washed with a minimum volume of ice-cold ethanol followed by ether, and then dried by suction. The crystals are stable in air at room temperature.

Anal. Calcd. for $A\ell RuC\ell_6(H_2O)_{10}$: $A\ell$, 5.18; Ru, 19.40; $C\ell$, 40.80; H, 3.84.
Found: $A\ell$, 5.21; Ru, 19.28; $C\ell$, 40.95; H, 3.82.

For taking the X-ray diffraction data, we used a single crystal in the form of a triangular plate 0.17 mm on an edge and 0.07 mm thick. A General Electric Co. XRD-5 X-ray diffraction unit equipped with a molybdenum tube (Mo $K\alpha_1$, $\lambda = 0.70296$ A), a scintillation counter, pulse height discriminator, and a quarter-circle Eulerian-cradle-type goniostat was used. The tube was operated at 50 kv and 20 ma, with a Zr filter at the receiving slit.

The crystal was oriented with the b axis coinciding with the ϕ axis, the polar axis of the goniometer head. The cell dimensions were obtained by measuring the 2θ (θ is the Bragg angle) values of the $h00$, $0k0$, and 00ℓ reflections whose α_1 and α_2 components were resolved. The β^* angle was measured directly from the angle between the $h00$ and 00ℓ sets of reflections.

A graph of the background was prepared for various values of χ and ϕ as a function of 2θ. Typical values were 18, 10 and 3 counts/sec for $2\theta = 6$, 9, and 15°. For 2θ greater than 28°, the background was constant at 1 count/sec. Individual backgrounds were determined for those reflections which were higher orders of strong reflections.

The stationary crystal, stationary counter technique was used with 10 second counting times for each reflection. Of the 1503 independent reflections measured (2θ less than 50°), 154 were recorded as zero intensity. The data were corrected for Lorentz-polarization effects, but no correction was made for either absorption or extinction. The calculated linear absorption coefficient is $\mu = 19.3$ cm^{-1} for molybdenum radiation. For the crystal used for the structure determination, $\mu R = 0.3$. The strongest reflection (011) gave a counting rate of 9931 counts/sec.

Fourier, least-squares and distance calculations were performed using our own unpublished programs. The full-matrix least squares program, which is a modification of an early unpublished version of one given us by P. Gantzel, R. Sparks, and K. Trueblood, minimizes the function $\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2$. F_o and F_c are the observed and calculated structure factors respectively, and w is the weighting factor. Atomic scattering factors for Ru^{+3}, Al^{+3}, Cl^{-1}, and neutral oxygen were taken from Cromer and Waber's compilation,[6] and neutral hydrogen from the International Tables.[7] Both the real and the imaginary parts of the anomalous dispersion for ruthenium, aluminum and chlorine[8] were included in the least squares calculations. w was set to $1.0/\sigma^2(F_o)$ with the exception that when $\sigma(I)$, I being the net count, was less than I then the reflection was given zero weight. The standard deviation of the observed structure factor was calculated as $\sigma(F_o) = F_o - \sqrt{(F_o^2 - s\sigma(I)/Lp)}$ where s is a scaling factor, $F_o = \sqrt{(sI/Lp)}$, and Lp is the Lorentz-polarization correction. In turn $\sigma(I) = \sqrt{(I + (pI)^2 + 2B + q^2)}$, where p is a fractional uncertainty in I, B is the background, and q represents an uncertainty in the background. p was set to 0.06 and q to 12.

The primitive cell contains two formula units of $Al(H_2O)_6RuCl_6 \cdot 4H_2O$. It is monoclinic with dimensions a = 10.492 ± 0.005, b = 11.415 ± 0.005, c = 7.069 ± 0.005 Å, and β = 92.69 ± 0.02°. The calculated density is 2.045 g/cc. The conditions limiting possible reflections were $h0l$: $h + l = 2n$, and $0k0$: $k = 2n$. These conditions correspond to space group $P2_1/n$.

Determination of the Structure

The cell contents and space group $P2_1/n$ require Ru and Al to be at centers of symmetry, and only three distinct combinations of such sites exist. The three-dimensional Patterson is consistent with only one of these, which can be taken as:

Al in 2(a): 0, 0, 0; 1/2, 1/2, 1/2

Ru in 2(b): 1/2, 0, 0; 0, 1/2, 1/2.

All other atoms are assigned to general positions:

4(e): ±(x, y, z; 1/2 − x, 1/2 + y, 1/2 − z).

Trial coordinates for the chlorines and the three water molecules coordinated to aluminum were derived from the Patterson function. Four cycles of least squares refinement with isotropic temperature factors of the form $\exp(-B\lambda^{-2}\sin^2\theta)$ gave a value of $R = 0.18$, where $R = \Sigma|\Delta F|/\Sigma|F_o|$ and $\Delta F = |F_o|-|F_c|$. The electron density function, phased with this structure, showed two additional waters of crystallization. Several more cycles of least squares with anisotropic thermal parameters reduced R to 0.054. The anisotropic temperature factor had the form $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}\ell^2-2\beta_{12}hk-2\beta_{13}h\ell-2\beta_{23}k\ell)$. In reporting the thermal parameters below we have converted β_{ij} to B_{ij} which is in units of $\mathring{A}^2$; the relation between these two quantities is $4\beta_{ij} = a_i^* a_j^* B_{ij}$, where a_i^* is the ith reciprocal axis. Possible hydrogen positions were deduced from hydrogen bonding and geometrical considerations and confirmed by the presence of some electron density in the difference Fourier at the estimated locations. Since these peaks were poorly resolved and did not refine well when attempted, the calculated positional parameters were used instead but not allowed to refine; however one isotropic temperature factor for all ten hydrogens was refined. The ten heavy atoms were all included with anisotropic temperature factors.

The final R value for 1238 non-zero weighted data is 0.036. The R value for all 1503 data is 0.049. The weighted R value, $\sqrt{(\Sigma w(\Delta F)^2/\Sigma wF_o^2)}$, is 0.048. The standard deviation of an observation of unit weight is 1.09. The observed and calculated structure factors are given in Table I. The final values of the parameters are listed in Table II. Table III lists the estimated hydrogen parameters.

Discussion of Structure

Figure 1 shows a clinographic projection of the unit cell. Figure 2 is a stereographic drawing of the environment around the ruthenium and aluminum atoms. In visualizing the structure it should be remembered that there are inversion centers at the centers of each octahedron. The ellipsoids show the 50% probablility enclosures, and were drawn using the version of ORTEP[9] written for the IBM 360/67.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $Al(H_2O)_6RuCl_6 \cdot 4H_2O$

OBSERVED AND CALCULATED STRUCTURE FACTORS OF AL(H2O)6RUCL6.4H2O
FCA(0,0,0) = 2590

L FOB FCA	-2 88 80	-1 24 27	5 82 83	H,K= 2, 12	3 78 78	2 732 737	3 31 29	5 42 42	6 80 77	6 84 82	0 730 742	-1 167 162	0 204 193
H,K= 0, 0	-1 20 12	0 198 217	6 109 109	-3 23 28*	4 26 22	3 94 94	4 154 146	6 0 10*	H,K= 6, 4	H,K= 7, 2	2 100 105	1 180 175	1 112 106
2 403 346	0 418 438	1 175 174	7 115 121	-2 138 139	5 193 194	4 233 231	H,K= 4, 11	H,K= 5, 7	-7 41 44	-7 74 75	4 405 401	3 288 286	2 184 181
4 790 791	1 21 32	2 25 26	8 62 63	-1 0 6*	6 57 53	5 94 92	-4 23 12*	-6 82 45	-6 76 80	-6 108 105	6 140 136	5 138 142	3 54 53
6 118 123	2 116 111	3 59 61	H,K= 2, 4	0 120 123	7 47 45	6 286 286	-3 126 119	-5 144 144	-5 81 87	-5 87 89	H,K= 8, 1	H,K= 9, 1	4 95 97
8 258 259	3 60 50	4 138 129	-7 31 22	1 0 17*	H,K= 3, 7	7 22 15*	-2 49 55	-4 193 188	-4 226 220	-4 98 94	-6 0 19*	-6 33 39	H,K= 10, 3
H,K= 0, 1	4 323 321	5 186 184	-6 275 266	2 101 105	-7 71 70	H,K= 4, 3	-1 92 99	-3 27 31	-3 0 9*	-3 54 52	-5 262 256	-5 22 26*	-5 267 265
1 781 695	5 146 145	6 45 48	-5 87 85	3 40 35	-6 0 16*	-7 110 116	0 0 5*	-2 58 64	-2 193 195	-2 259 264	-4 113 111	-4 219 204	-4 118 111
2 0 10*	6 219 228	H,K= 1, 9	-4 238 235	H,K= 2, 13	-5 0 25*	-6 79 74	1 68 69	-1 175 175	-1 166 162	-1 158 161	-3 199 201	-3 128 122	-3 184 185
3 158 158	7 21 18*	-6 66 70	-3 60 60	-2 58 76	-4 202 204	-5 203 205	2 0 8*	0 265 278	0 357 368	0 17 5*	-2 48 50	-2 0 19*	-2 124 126
4 179 178	8 73 76	-5 22 21*	-2 613 605	-1 197 192	-3 0 14*	-4 90 88	3 123 114	1 31 38	1 53 57	1 88 89	-1 388 393	-1 27 22	-1 261 268
5 298 297	H,K= 1, 2	-4 161 155	-1 189 193	0 84 80	-2 24 16	-3 323 321	4 0 7*	2 26 34	2 405 418	2 211 217	0 25 12	0 176 163	0 175 168
6 19 6*	-8 46 43	-3 34 28	0 325 343	1 0 16*	-1 58 57	-2 32 37	H,K= 4, 12	3 0 22*	3 99 105	3 163 161	1 236 237	1 72 69	1 105 101
7 98 95	-7 103 106	-2 80 79	1 133 138	2 75 76	0 280 292	-1 530 537	-3 103 107	4 135 131	4 96 95	4 74 76	2 26 37	2 156 159	2 114 116
8 102 96	-6 88 87	-1 37 33	2 66 71	H,K= 3, 0	1 190 199	0 33 32	-2 115 115	5 0 9*	5 30 21	5 101 102	3 171 165	3 0 5*	3 176 177
H,K= 0, 2	-5 180 185	0 57 41	3 100 103	-7 0 13*	2 0 8*	1 381 408	-1 94 91	6 23 34*	6 203 204	6 39 45	4 94 92	4 149 151	4 104 97
0 725 641	-4 103 107	1 26 24	4 377 377	-5 43 40	3 41 43	2 105 105	0 32 41	H,K= 5, 8	H,K= 6, 5	H,K= 7, 3	5 194 192	5 23 25*	H,K= 10, 4
1 13 13	-3 254 231	2 19 14*	5 55 50	-3 278 268	4 205 203	3 262 258	1 88 94	-6 41 45	-6 59 40	-6 0 8*	6 0 11*	H,K= 9, 2	-4 161 152
2 170 160	-2 554 535	3 48 47	6 125 125	-1 121 114	5 154 153	4 118 120	2 70 74	-5 74 77	-5 177 173	-5 97 100	H,K= 8, 2	-5 149 152	-3 0 23*
3 89 87	-1 195 180	4 0 14*	7 0 0*	1 160 161	6 55 55	5 222 210	H,K= 5, 0	-4 73 80	-4 122 122	-4 48 48	-6 51 56	-4 21 21*	-2 183 184
4 390 379	0 9 5*	5 0 8*	H,K= 2, 5	3 25 26	H,K= 3, 8	6 106 105	-7 223 229	-3 20 20*	-3 263 281	-3 74 73	-5 61 62	-3 71 74	-1 118 124
5 107 90	1 137 118	6 112 109	-7 92 96	5 124 124	-6 56 54	7 129 133	-5 19 10*	-2 43 43	-2 0 2*	-2 50 47	-4 264 253	-2 185 184	0 144 140
6 74 69	2 652 627	H,K= 1, 10	-6 41 46	7 223 226	-5 30 32	H,K= 4, 4	-3 152 158	-1 280 294	-1 193 201	-1 80 76	-3 43 51	-1 151 149	1 21 20*
7 0 1*	3 162 154	-5 60 61	-5 173 187	H,K= 3, 1	-4 117 112	-7 105 113	-1 214 206	0 155 162	0 197 191	0 0 7*	-2 49 38	0 72 53	2 105 104
8 165 173	4 146 147	-4 31 30	-4 153 158	-8 70 72	-3 332 336	-6 146 149	1 173 170	1 63 67	1 395 416	1 24 3	-1 25 28	1 20 24*	3 82 83
H,K= 0, 3	5 57 45	-3 160 158	-3 245 242	-7 21 14*	-2 32 27	-5 0 2*	3 64 66	2 28 32	2 0 10*	2 18 8*	0 307 294	2 210 209	4 193 201
1 345 298	6 175 181	-2 134 134	-2 15 14*	-6 27 30	-1 105 102	-4 329 324	5 0 11*	3 216 217	3 129 133	3 19 24*	1 0 2*	3 122 125	H,K= 10, 5
2 94 89	7 120 120	-1 19 24*	-1 555 555	-5 150 155	0 185 196	-3 137 142	H,K= 5, 1	4 107 105	4 106 112	4 115 112	2 33 39	4 107 104	-4 78 78
3 430 410	8 77 81	0 39 43	0 243 261	-4 69 61	1 221 234	-2 453 469	-7 66 62	5 0 12*	5 93 92	5 0 4*	3 59 67	5 0 5*	-3 96 102
4 115 121	H,K= 1, 3	1 155 152	1 82 91	-3 48 46	2 55 53	-1 48 53	-6 220 228	H,K= 5, 9	6 46 31	6 94 97	4 194 193	H,K= 9, 3	-2 0 14*
5 303 302	-8 149 152	2 80 82	2 15 15*	-2 433 427	3 33 36	0 699 741	-5 50 41	-5 0 1*	H,K= 6, 6	H,K= 7, 4	5 62 63	-5 51 46	-1 171 177
6 113 105	-7 0 14*	3 36 35	3 370 365	-1 72 67	4 81 87	1 35 36	-4 54 56	-4 38 32	-6 139 140	-6 75 76	6 82 77	-4 53 55	0 111 112
7 197 195	-6 152 151	4 22 14*	4 143 143	0 41 46	5 104 101	2 284 287	-3 161 161	-3 21 24*	-5 53 49	-5 21 37*	H,K= 8, 3	-3 62 51	1 93 94
8 77 77	-5 30 28	5 157 150	5 290 284	1 0 6*	6 52 52	3 145 147	-2 362 360	-2 164 173	-4 263 254	-4 127 126	-6 46 45	-2 192 185	2 0 18*
H,K= 0, 4	-4 72 75	H,K= 1, 11	6 51 51	2 356 364	H,K= 3, 9	4 311 309	-1 14 24*	-1 20 15*	-3 43 30	-3 236 238	-5 150 151	-1 71 64	3 201 204
0 206 197	-3 14 23*	-4 134 128	7 183 181	3 121 120	-6 24 27*	5 0 14*	0 197 177	0 219 227	-2 248 250	-2 26 22	-4 41 44	0 44 32	H,K= 10, 6
1 62 60	-2 178 171	-3 58 56	H,K= 2, 6	4 128 130	-5 0 9*	6 178 175	1 47 56	1 28 23	-1 0 8*	-1 88 92	-3 168 167	1 28 34	-3 0 8*
2 250 251	-1 83 77	-2 132 116	-7 64 65	5 47 44	-4 251 247	7 102 101	2 185 189	2 163 164	0 205 213	0 202 209	-2 0 3*	2 61 60	-2 111 109
3 184 181	0 83 78	-1 124 123	-6 185 186	6 329 340	-3 63 55	H,K= 4, 5	3 16 20*	3 21 23*	1 26 29	1 40 44	-1 123 121	3 21 15*	-1 0 6*
4 230 227	1 68 66	0 185 191	-5 58 53	7 48 43	-2 219 223	-7 65 69	4 43 39	4 151 143	2 273 297	2 61 61	0 26 37	4 0 10*	0 185 183
5 18 14*	2 235 226	1 62 63	-4 117 116	8 0 10*	-1 0 11*	-6 37 44	5 82 76	5 0 6*	3 81 81	3 88 90	1 213 210	5 0 12*	1 32 36
6 211 208	3 58 61	2 171 170	-3 69 77	H,K= 3, 2	0 235 247	-5 207 208	6 42 41	H,K= 5, 10	4 36 28	4 114 118	2 90 98	H,K= 9, 4	2 86 94
7 134 126	4 39 42	3 22 23*	-2 342 339	-8 77 79	1 42 49	-4 98 101	7 0 12*	-4 0 16*	5 58 55	5 87 89	3 184 194	-5 0 16*	3 47 47
8 94 90	5 120 110	4 122 121	-1 0 1*	-7 93 99	2 130 125	-3 148 149	H,K= 5, 2	-3 31 39	6 162 159	6 57 56	4 87 89	-4 147 146	H,K= 10, 7
H,K= 0, 5	6 0 6*	H,K= 1, 12	0 315 333	-6 155 161	3 20 23*	-2 32 33	-7 100 103	-2 135 130	H,K= 6, 7	H,K= 7, 5	5 109 115	-3 126 127	-2 0 17*
1 309 303	7 77 77	-3 51 51	1 15 12*	-5 207 212	4 67 64	-1 413 428	-6 74 75	-1 202 209	-6 41 27	-6 113 116	H,K= 8, 4	-2 0 7*	-1 107 112
2 58 55	8 52 62	-2 0 1*	2 196 197	-4 125 126	5 32 31	0 81 65	-5 76 77	0 21 29*	-5 233 235	-5 0 1*	-6 167 166	-1 167 177	0 133 137
3 473 462	H,K= 1, 4	-1 114 108	3 92 93	-3 291 294	H,K= 3, 10	1 223 235	-4 49 52	1 47 52	-4 118 117	-4 154 156	-5 0 8*	0 207 206	1 168 173
4 72 69	-8 53 51	0 31 3	4 385 387	-2 514 508	-5 0 4*	2 56 53	-3 201 204	2 86 84	-3 215 211	-3 103 103	-4 114 110	1 0 19*	2 0 21*
5 250 247	-7 196 200	1 156 147	5 59 62	-1 292 296	-4 0 5*	3 124 128	-2 335 333	3 174 175	-2 38 38	-2 353 367	-3 96 91	2 62 65	H,K= 10, 8
6 76 72	-6 40 38	2 22 22*	6 136 130	0 25 36	-3 229 226	4 32 17	-1 206 205	4 23 17*	-1 270 275	-1 89 85	-2 157 149	3 80 83	-1 58 56
7 183 187	-5 0 8*	3 141 132	7 69 67	1 336 332	-2 58 59	5 170 168	0 52 57	H,K= 5, 11	0 213 223	0 54 51	-1 19 17*	4 127 128	0 220 217
H,K= 0, 6	-4 259 254	H,K= 1, 13	H,K= 2, 7	2 420 412	-1 40 44	6 65 69	1 322 338	-3 40 35	1 140 139	1 69 75	0 56 61	5 0 20*	H,K= 11, 0
0 427 405	-3 72 76	-2 57 56	-7 157 151	3 141 145	0 44 48	7 121 119	2 377 384	-2 50 51	2 39 41	2 237 245	1 19 15*	H,K= 9, 5	-3 169 163
1 218 215	-2 58 52	-1 23 14*	-6 0 23*	4 113 110	1 189 199	H,K= 4, 6	3 152 157	-1 96 96	3 222 223	3 129 128	2 272 284	-5 0 21*	-1 65 63
2 726 715	-1 190 187	0 86 82	-5 91 87	5 129 125	2 111 105	-7 23 6*	4 144 141	0 0 4*	4 113 110	4 21 21*	3 84 90	-4 0 17*	1 79 81
3 110 111	0 511 544	1 69 70	-4 152 150	6 75 74	3 37 34	-6 31 30	5 227 229	1 31 37	5 96 87	5 22 33*	4 83 90	-3 89 90	3 33 43
4 287 284	1 272 261	2 97 86	-3 222 214	7 84 88	4 38 36	-5 109 106	6 148 148	2 0 18*	H,K= 6, 8	6 175 168	5 0 18*	-2 302 302	H,K= 11, 1
5 114 109	2 72 74	H,K= 2, 0	-2 56 57	H,K= 3, 3	5 96 91	-4 193 191	7 60 64	3 0 20*	-5 79 72	H,K= 7, 6	H,K= 8, 5	-1 20 21*	-4 52 41
6 320 316	3 239 235	-8 193 199	-1 180 184	-8 111 115	H,K= 3, 11	-3 94 92	H,K= 5, 3	H,K= 5, 12	-4 115 114	-6 23 19*	-5 112 112	0 89 93	-3 0 15*
7 23 20*	4 264 257	-6 129 136	0 288 307	-7 87 90	-4 33 32	-2 44 44	-7 0 8*	-2 33 5	-3 0 6*	-5 117 127	-4 98 101	1 41 46	-2 161 153
H,K= 0, 7	5 79 78	-4 255 264	1 366 387	-6 243 251	-3 22 31*	-1 172 187	-6 88 87	-1 0 28*	-2 220 228	-4 30 27	-3 279 271	2 203 204	-1 0 1*
1 314 311	6 118 113	-2 103 95	2 65 62	-5 127 128	-2 0 13*	0 231 243	-5 38 40	0 23 22*	-1 81 84	-3 224 220	-2 20 13*	3 0 3*	0 95 90
2 72 75	7 109 114	0 611 561	3 231 228	-4 321 322	-1 70 68	1 155 166	-4 230 237	1 23 29*	0 90 83	-2 51 48	-1 150 142	4 79 77	1 31 32
3 182 174	H,K= 1, 5	2 830 803	4 154 155	-3 93 80	0 0 8*	2 95 94	-3 47 48	H,K= 6, 0	1 77 80	-1 202 207	0 82 80	H,K= 9, 6	2 204 183
4 32 9	-7 91 89	4 287 286	5 254 255	-2 253 257	1 116 123	3 98 103	-2 127 129	-6 281 281	2 193 204	0 50 39	1 323 325	-4 23 27*	3 40 50
5 180 173	-6 225 226	6 286 291	6 22 24*	-1 101 103	2 72 75	4 191 185	-1 55 75	-4 323 321	3 21 22*	1 139 131	2 49 49	-3 159 157	H,K= 11, 2
6 106 104	-5 26 26	8 87 86	7 92 89	0 416 439	3 67 66	5 87 85	0 309 315	-2 429 423	4 165 162	2 0 10*	3 246 246	-2 48 46	-4 67 64
7 87 91	-4 72 72	H,K= 2, 1	H,K= 2, 8	1 25 27	4 0 20*	6 0 19*	1 0 9*	0 185 198	5 66 61	3 129 136	4 0 7*	-1 118 121	-3 170 163
H,K= 0, 8	-3 190 185	-8 0 17*	-6 190 185	2 365 362	H,K= 3, 12	H,K= 4, 7	2 215 218	2 105 108	H,K= 6, 9	4 0 3*	5 144 142	0 21 6*	-2 122 120
0 257 242	-2 485 480	-7 87 81	-5 92 88	3 21 15	-3 0 5*	-6 116 115	3 0 10*	4 314 308	-5 136 137	5 51 48	H,K= 8, 6	1 175 180	-1 90 97
1 93 78	-1 89 87	-6 105 106	-4 217 217	4 204 202	-2 23 28*	-5 199 202	4 306 307	6 68 64	-4 23 30*	H,K= 7, 7	-5 65 67	2 0 2*	0 22 6*
2 191 186	0 166 198	-5 291 295	-3 19 9*	5 0 11*	-1 0 10*	-4 20 17*	5 79 55	H,K= 6, 1	-3 57 65	-5 0 16*	-4 156 160	3 139 145	1 150 146
3 0 12*	1 79 84	-4 26 32	-2 170 172	6 83 85	0 0 14*	-3 217 213	6 175 171	-7 228 241	-2 115 120	-4 22 28*	-3 63 67	4 0 6*	2 108 103
4 52 49	2 618 604	-3 0 21*	-1 104 108	7 22 25*	1 63 72	-2 90 94	7 52 47	-6 87 84	-1 232 233	-3 0 13*	-2 384 381	H,K= 9, 7	3 74 72
5 55 55	3 151 150	-2 455 445	0 284 308	H,K= 3, 4	2 0 15*	-1 254 263	H,K= 5, 4	-5 216 225	0 21 29*	-2 212 225	-1 123 119	-4 0 30*	H,K= 11, 3
6 152 147	4 100 99	-1 521 482	1 111 107	-7 96 95	3 102 85	0 24 6	-7 0 13*	-4 18 11*	1 21 28*	-1 20 27*	0 204 211	-3 23 16*	-3 46 51
H,K= 0, 9	5 38 33	0 33 23	2 258 259	-6 105 100	H,K= 3, 13	1 195 204	-6 0 16*	-3 497 499	2 113 111	0 52 58	1 101 97	-2 119 113	-2 235 189
1 258 251	6 139 137	1 513 475	3 33 29	-5 281 288	-1 74 69	2 47 53	-5 251 254	-2 294 293	3 269 265	1 138 137	2 407 413	-1 115 118	-1 38 48
2 0 4*	7 70 76	2 439 431	4 159 161	-4 218 218	0 57 56	3 307 310	-4 215 213	-1 261 268	4 23 23*	2 210 220	3 71 76	0 53 35	0 182 187
4 36 26	H,K= 1, 6	3 654 632	5 95 91	-3 0 57*	1 0 16*	4 20 6*	-3 194 189	0 40 5	H,K= 6, 10	3 21 24*	4 149 140	1 0 13*	1 0 11*
5 185 180	-7 138 138	4 35 36	6 60 59	-2 40 40	H,K= 4, 0	5 130 134	-2 0 9*	1 277 281	-4 91 92	4 0 21*	5 47 46	2 134 137	2 163 162
6 23 17*	-6 73 73	5 195 193	H,K= 2, 9	-1 186 196	-8 41 44	6 82 84	-1 111 113	2 269 275	-3 32 31	5 121 113	H,K= 8, 7	3 0 22*	3 23 18*
H,K= 0, 10	-5 0 10*	6 102 102	-6 77 76	0 400 412	-6 330 338	H,K= 4, 8	0 349 358	3 191 191	-2 191 193	H,K= 7, 8	-5 94 100	H,K= 9, 8	H,K= 11, 4
0 262 248	-4 44 45	7 238 245	-5 144 144	1 339 344	-4 131 129	-6 135 142	1 229 244	4 19 15*	-1 38 38	-5 91 98	-4 23 24*	-3 134 135	-3 23 33*
1 138 121	-3 248 249	8 0 21*	-4 29 30	2 82 76	-2 372 375	-5 49 51	2 73 82	5 241 235	0 106 104	-4 81 79	-3 213 214	-2 0 19*	-2 0 9*
2 87 74	-2 34 34	H,K= 2, 2	-3 304 290	3 267 266	0 780 785	-4 285 281	3 163 162	6 69 74	1 65 68	-3 72 76	-2 87 83	-1 32 34	-1 159 164
3 29 25	-1 180 180	-8 157 165	-2 162 170	4 204 201	2 545 545	-3 0 13*	4 206 204	7 78 78	2 139 142	-2 30 24	-1 145 148	0 101 98	0 95 92
4 138 130	0 14 2*	-7 87 89	-1 83 84	5 199 195	4 60 64	-2 228 225	5 287 287	H,K= 6, 2	3 0 8*	-1 134 136	0 21 9*	1 134 134	1 126 129
5 114 114	1 395 395	-6 250 247	0 18 20*	6 51 53	6 225 223	-1 73 74	6 113 103	-7 76 83	H,K= 6, 11	0 135 130	1 228 226	2 23 27*	2 40 44
H,K= 0, 11	2 41 40	-5 46 50	1 369 380	7 0 7*	H,K= 4, 1	0 260 268	7 41 47	-6 151 148	-3 108 114	1 59 53	2 21 27*	H,K= 9, 9	H,K= 11, 5
1 251 229	3 283 275	-4 339 340	2 162 162	H,K= 3, 5	-8 74 87	1 71 79	H,K= 5, 5	-5 79 83	-2 40 46	2 21 27*	3 77 79	-2 0 5*	-2 23 20*
2 36 37	4 18 10*	-3 248 245	3 56 59	-7 81 87	-7 266 276	2 277 291	-7 70 70	-4 225 222	-1 154 161	3 147 149	4 0 6*	-1 0 4*	-1 65 62
3 164 156	5 172 171	-2 437 423	4 36 35	-6 75 81	-6 20 19*	3 0 4*	-6 22 23*	-3 200 194	0 39 36	4 65 64	H,K= 8, 8	0 33 30	0 154 149
4 0 3*	6 0 13*	-1 155 154	5 133 127	-5 19 20*	-5 192 195	4 288 290	-5 20 2*	-2 296 289	1 94 98	H,K= 7, 9	-4 77 80	1 0 17*	1 33 37
H,K= 0, 12	7 125 131	0 460 445	6 71 71	-4 138 141	-4 154 164	5 54 60	-4 317 319	-1 41 41	2 47 50	-4 70 66	-3 0 11*	H,K= 10, 0	2 0 4*
0 250 228	H,K= 1, 7	1 218 222	H,K= 2, 10	-3 160 157	-3 448 446	6 88 93	-3 138 144	0 308 315	H,K= 7, 0	-3 32 38	-2 153 152	-4 111 119	H,K= 11, 6
1 118 105	-7 23 20*	2 364 390	-5 32 32	-2 225 221	-2 48 48	H,K= 4, 9	-2 126 127	1 159 158	-7 138 137	-2 0 15*	-1 53 57	-2 172 171	-1 47 54
2 163 157	-6 135 132	3 212 208	-4 170 170	-1 92 98	-1 181 177	-5 104 122	-1 0 18*	2 289 297	-5 243 244	-1 0 4*	0 91 97	0 251 247	0 41 39
3 121 110	-5 167 162	4 256 253	-3 29 27	0 241 256	0 12 18*	-4 21 8*	0 149 167	3 112 115	-3 40 37	0 30 27	1 53 58	2 257 264	1 53 53
H,K= 0, 13	-4 26 30	5 0 0*	-2 121 124	1 111 113	1 330 335	-3 253 248	1 61 64	4 279 278	-1 366 360	1 43 48	2 73 76	4 79 80	H,K= 12, 0
1 86 81	-3 55 50	6 180 177	-1 56 54	2 15 27*	2 28 29	-2 0 14*	2 85 89	5 29 21	1 201 225	2 66 70	3 0 2*	H,K= 10, 1	-2 167 163
2 0 8*	-2 288 277	7 71 73	0 194 209	3 172 173	3 493 476	-1 183 187	3 51 60	6 168 166	3 237 238	3 0 14*	H,K= 8, 9	-5 134 126	0 33 46
H,K= 1, 0	-1 214 218	8 99 95	1 74 65	4 298 294	4 142 140	0 38 26	4 161 159	7 41 38	5 75 70	H,K= 7, 10	-3 107 107	-4 0 4*	H,K= 12, 1
-7 36 42	0 31 35	H,K= 2, 3	2 204 201	5 43 44	5 200 195	1 177 184	5 21 22*	H,K= 6, 3	H,K= 7, 1	-3 23 27*	-2 0 9*	-3 103 96	-2 23 31*
-3 474 450	1 63 66	-8 70 63	3 21 11*	6 30 26	6 0 5*	2 0 6*	6 54 55	-7 106 110	-7 23 1*	-2 32 28	-1 116 115	-2 176 165	-1 80 76
-1 343 328	2 279 271	-7 194 197	4 126 122	7 79 85	7 180 182	3 340 333	H,K= 5, 6	-6 96 87	-6 149 154	-1 135 138	0 39 29	-1 229 232	0 0 2*
1 342 330	3 25 18	-6 114 111	5 33 34	H,K= 3, 6	H,K= 4, 2	4 31 29	-6 67 76	-5 20 7*	-5 108 107	0 50 45	1 123 124	0 20 7*	1 168 169
3 358 356	4 59 54	-5 472 466	H,K= 2, 11	-7 40 46	-8 89 89	5 83 77	-5 229 235	-4 192 191	-4 212 210	1 23 28*	2 0 7*	1 222 214	H,K= 12, 2
5 359 362	5 29 18	-4 273 271	-4 0 1*	-6 21 20*	-7 22 7*	H,K= 4, 10	-4 39 36	-3 222 221	-3 0 1*	2 65 68	3 24 10*	2 155 156	-2 242 240
7 212 213	6 178 179	-3 413 405	-3 153 147	-5 66 68	-6 325 336	-5 100 100	-3 45 46	-2 219 219	-2 38 42	H,K= 7, 11	H,K= 8, 10	3 165 162	-1 0 17*
H,K= 1, 1	7 57 66	-2 319 324	-2 70 65	-4 18 17*	-5 80 83	-4 136 138	-2 50 54	-1 104 107	-1 16 19*	-1 41 57	-2 82 80	4 0 2*	0 139 139
-8 145 144	H,K= 1, 8	-1 849 849	-1 127 126	-3 38 22	-4 212 213	-3 22 22*	-1 130 131	0 315 323	0 456 465	0 124 127	-1 70 73	H,K= 10, 2	1 0 14*
-7 51 54	-6 59 51	0 520 550	0 41 35	-2 56 59	-3 66 65	-2 252 238	0 17 7*	1 497 512	1 17 27*	1 97 97	0 153 155	-5 66 75	H,K= 12, 3
-6 63 66	-5 107 103	1 31 35	1 187 188	-1 0 6*	-2 759 767	-1 110 106	1 0 5*	2 196 199	2 35 35	H,K= 8, 0	1 52 60	-4 182 177	-1 224 206
-5 34 43	-4 90 91	2 307 311	2 64 63	0 15 22*	-1 32 28	0 127 125	2 0 10*	3 214 225	3 78 79	-6 32 51	H,K= 9, 0	-3 140 133	0 41 31
-4 515 512	-3 320 310	3 322 319	3 139 135	1 172 180	0 288 288	1 89 96	3 32 33	4 189 181	4 308 316	-4 508 498	-5 199 205	-2 213 210	1 169 166
-3 164 164	-2 66 64	4 268 264	4 0 2*	2 0 7*	1 13 6*	2 248 259	4 0 6*	5 273 263	5 47 37	-2 310 248	-3 57 48	-1 0 2*	

*Zero-weighted data.

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TABLE II

POSITIONAL AND THERMAL PARAMETERS IN $A\ell(H_2O)_6 \cdot 4H_2O$[a,b]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Aℓ	0.0[c]	0.0[c]	0.0[c]	1.66(8)	2.38(9)	2.16(8)	-.04(8)	.12(7)	-.10(7)
Ru	0.5[c]	0.0[c]	0.0[c]	1.50(2)	2.33(3)	1.75(2)	.01(2)	.18(2)	-.07(2)
Cℓ(1)	.3768(1)	-.1037(1)	.2176(2)	2.12(5)	3.15(6)	2.37(5)	-.07(5)	.44(4)	.42(5)
Cℓ(2)	.3649(1)	-.0675(1)	-.2551(2)	2.15(5)	3.42(6)	2.11(5)	-.21(5)	.00(4)	-.29(5)
Cℓ(3)	.3732(1)	.1717(1)	.0301(2)	2.03(5)	2.65(6)	3.11(6)	.17(4)	.17(4)	-.22(5)
O(1)	.0980(3)	.1182(3)	-.1090(5)	2.3(2)	3.1(2)	2.7(2)	-.6(1)	.2(1)	.3(1)
O(2)	.1091(3)	-.0023(3)	.2194(5)	2.4(1)	3.3(2)	2.4(2)	.3(1)	-.2(1)	-.4(1)
O(3)	.0980(3)	-.1152(3)	-.1136(5)	2.1(2)	2.7(2)	3.2(2)	-.1(1)	.6(1)	-.2(1)
O(4)	.1113(4)	.1447(3)	.5164(5)	4.4(2)	3.1(2)	2.9(2)	.1(2)	.3(2)	-.2(1)
O(5)	.3732(4)	.1726(4)	.4869(5)	3.8(2)	3.1(2)	3.1(2)	.6(2)	.5(1)	.1(1)

[a]The standard deviation of the least significant figure is given in parenthesis.

[b]The thermal parameters are in units of $Å^2$.

[c]Parameter fixed by symmetry.

TABLE III

ESTIMATED HYDROGEN PARAMETERS[a]

Atom	x	y	z
H(1)	.190	.136	-.063
H(2)	.102	.127	-.234
H(3)	.193	-.037	.218
H(4)	.109	.046	.318
H(5)	.186	-.099	-.161
H(6)	.107	-.186	-.080
H(7)	.199	.153	.506
H(8)	.072	.217	.480
H(9)	.424	.105	.542
H(10)	.383	.174	.346

[a]These atoms were included in the least-squares calculation but their positional parameters were not refined. One isotropic temperature factor was used for all ten atoms, and it is $B = 4.9 \pm 0.7$ Å^2.

Interatomic distances and angles are reported in Tables IV and V. The chlorine and oxygen octahedra are nearly regular. There is no significant difference among the Ru - Cℓ distances or the Aℓ - O distances. The anion-anion distances and the corresponding angles at the central atom differ by as much as 15 estimated standard deviations and are likely to be significant in terms of the accuracy of the experiment. These distortions are trivial for most chemical purposes and probably reflect the unsymmetrical arrangement of the hydrogen bonds which tie the structure together.

Bond distances and angles permit assignment of several hydrogen atoms to hydrogen bonds. In each of the water molecules coordinated to Aℓ, these bonds are to another water molecule and to a chlorine atom. The coordinates in Table III are calculated from the heavy atom positions; for these atoms they are confirmed approximately by peaks of electron density of from 0.6 to 0.9 electrons/A^3 in the difference function. For the uncoordinated water molecules, the hydrogen positions are less obvious. The short distance between these two molecules corresponds to a hydrogen bond, and the angles at O(4) imply that one of its hydrogen atoms is in this bond. If its other hydrogen atom is then approximately tetrahedral with respect to the other three bonds to this atom, it is pointed between two near chlorine atoms of type Cℓ(1) and Cℓ(3). In the difference function, peaks of about 0.5 electrons/A^3 coincide approximately with these two hydrogen positions. This suggested location for the second hydrogen atom corresponds to the geometry which has been referred to in other crystals as a "bifurcated hydrogen bond". We use the term in the present case to describe the geometrical arrangement, without intending to imply anything about the magnitude of bond energy, if any.

TABLE IV

PRINCIPAL INTERATOMIC DISTANCES IN $Al(H_2O)_6RuCl_6 \cdot 4H_2O$

Atoms	Dist(Å)	Atoms	Dist(Å)	Atoms	Dist(Å)
Al - 2 O(1)	1.883(3)	O(1) - O(4)	2.676(5)[b]	O(4) - Cl(3)	3.266(4)[c]
Al - 2 O(2)	1.884(4)	O(1) - Cl(3)	3.068(4)[b]	O(5) - Cl(1)	3.369(4)[c]
Al - 2 O(3)	1.873(4)	O(2) - O(3)	2.632(5)[a]	O(5) - Cl(2)	3.295(4)[c]
Ru - 2 Cl(1)	2.372(2)	O(2) - O(3)	2.681(5)[a]	O(5) - Cl(3)	3.229(5)[b]
Ru - 2 Cl(2)	2.370(2)	O(2) - O(4)	2.687(5)[b]	Cl(1) - Cl(2)	3.342(2)[d]
Ru - 2 Cl(3)	2.384(2)	O(2) - Cl(1)	3.038(4)[b]	Cl(1) - Cl(2)	3.363(3)[d]
O(1) - O(2)	2.631(5)[a]	O(3) - O(5)	2.596(6)[b]	Cl(1) - Cl(3)	3.313(2)[d]
O(1) - O(2)	2.697(5)[a]	O(3) - Cl(2)	3.066(4)[b]	Cl(1) - Cl(3)	3.411(2)[d]
O(1) - O(3)	2.647(5)[a]	O(4) - O(5)	2.783(6)[b]	Cl(2) - Cl(3)	3.329(2)[d]
O(1) - O(3)	2.665(6)[a]	O(4) - Cl(1)	3.319(4)[c]	Cl(2) - Cl(3)	3.393(2)[d]

[a]Edge in Al octahedron.

[b]Hydrogen bond.

[c]Bifurcated hydrogen bond.

[d]Edge in Ru octahedron.

TABLE V

PRINCIPAL ANGLES IN $A\ell(H_2O)_6RuC\ell_6 \cdot 4H_2O$

Atoms	Angle(°)	Atoms	Angle(°)
Octahedral angles		Angles involving hydrogen bonds	
O(1) - Aℓ - O(2)	91.4(2)	O(4) - O(1) - Cℓ(3)	101.7(2)
O(1) - Aℓ - O(3)	90.4(2)	O(4) - O(2) - Cℓ(1)	105.5(2)
O(2) - Aℓ - O(3)	91.1(2)	O(5) - O(3) - Cℓ(2)	100.7(2)
Cℓ(1) - Ru - Cℓ(2)	90.4(1)	O(5) - O(4) - Cℓ(1)	78.7(2)[a]
Cℓ(1) - Ru - Cℓ(3)	91.7(1)	O(5) - O(4) - Cℓ(3)	133.5(2)[a]
Cℓ(2) - Ru - Cℓ(3)	91.1(1)	Cℓ(1) - O(5) - Cℓ(3)	125.7(1)[a]
		Cℓ(2) - O(5) - Cℓ(3)	123.5(1)[a]

[a]Angles involving bifurcated hydrogen bonds.

The other uncoordinated water molecule is an acceptor for two hydrogen bonds. It has no other neighbors at distances appropriate for ordinary hydrogen bonds. If its hydrogen atoms are approximately tetrahedral with respect to the two external hydrogen bonds, then one is in the geometry of the "bifurcated bond" with respect to the pair of chlorine atoms, Cℓ(1) and Cℓ(2), and one points to the Cℓ(3). The difference function shows peaks of about 0.25 electrons/A^3 at (0.41, 0.10, 0.60) and (0.42, 0.17, 0.40). These locations are near the predicted ones, but the low density implies that these atoms have considerable freedom of motion or, alternately, have a disordered structure.

In summary, the structure consists of $A\ell(H_2O)_6$ and $Ru(C\ell)_6$ octahedra, tied together with hydrogen bonds to each other or to the uncoordinated water molecules. Of the ten independent hydrogen atoms, four are in bonds of type O - H . . . O, three in bonds of type O - H . . . Cℓ, and three are not in simple hydrogen bonds.

The Ru - Cℓ distance reported here is slightly larger, by about 0.03 Å, than the distances that were found for the tetra and penta chlorides involving Ru(III).[4,10] The octahedron of water molecules around the aluminum is less symmetrical than the octahedron found by Okaya et al., in monomethylammonium aluminum sulfate alum.[11] In that compound, the aluminum is at a site of point symmetry $\bar{3}$, and there is less than 0.01 A spread in the O - O distances. They found an average O - O distance of 2.669 A, compared to our 2.659 Å, and reported an Aℓ - O distance of 1.886 Å compared to 1.880 Å in the compound we have studied.

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(1) Work done under the auspices of the U. S. Atomic Energy Commission.

(2) Department of Chemistry, Stanford University, Stanford, California.

(3) Chemistry Division, Atomic Energy Research Establishment, Harwell, England.

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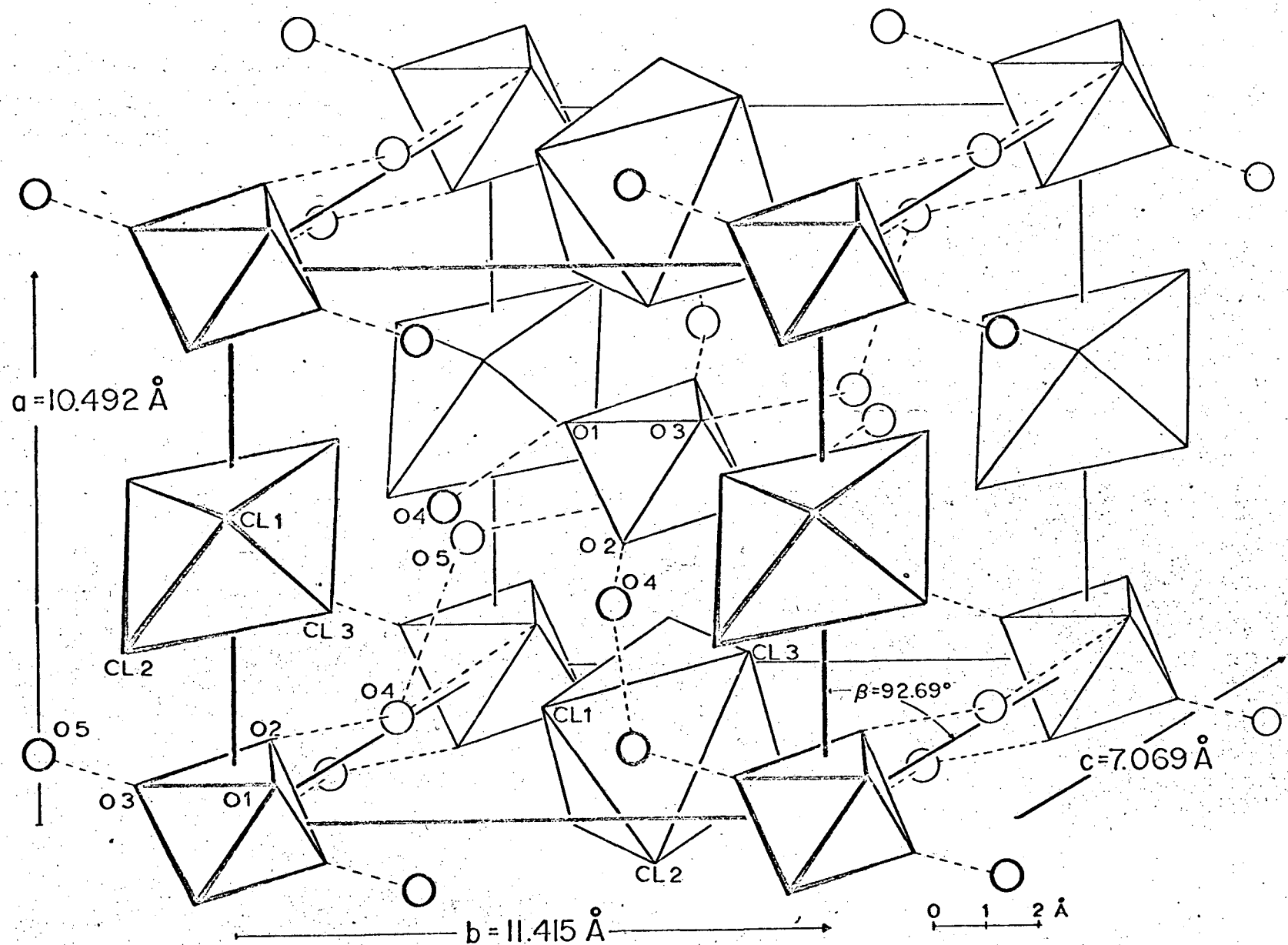
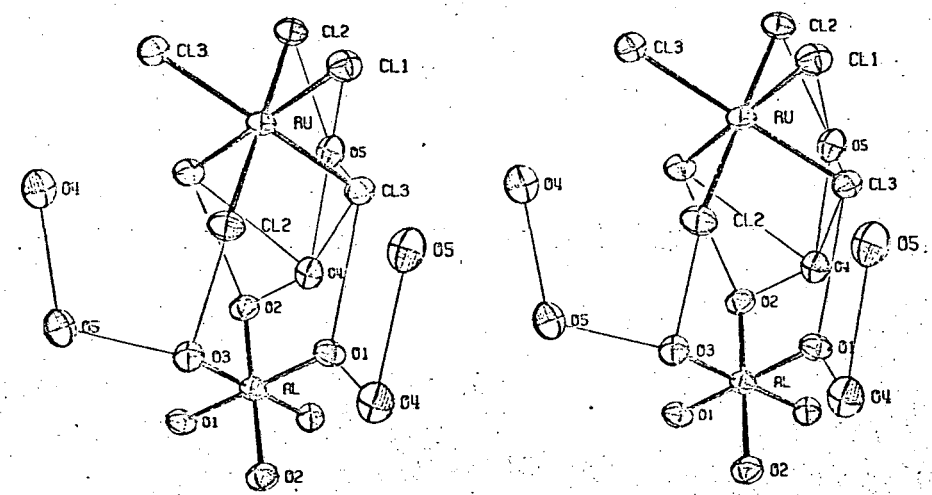


Figure 1. Unit cell of $Al(H_2O)_6RuCl_6 \cdot 4H_2O$.

Figure 2. Stereographic views of the environment around the metal ions.



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