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HEXACHLORORUTHENATE TETRAHYDRATE

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

The Crystal and Molecular Structure of Hexaquoaluminum
Hexachlororuthenate Tetrahydrate.¹

BY TED E. HOPKINS², ALLAN ZALKIN, DAVID H. TEMPLETON, AND MARTYN
G. ADAMSON³

An X-ray diffraction study of a single crystal of $\text{Al}(\text{H}_2\text{O})_6 \cdot \text{RuCl}_6 \cdot 4\text{H}_2\text{O}$ showed that it is monoclinic with $a = 10.492 \text{ \AA}$, $b = 11.415 \text{ \AA}$, $c = 7.069 \text{ \AA}$, $\beta = 92.69^\circ$, $Z = 2$, and $D_x = 2.045 \text{ g cm}^{-3}$. 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 $\text{\AA}$.

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 $\text{Al}(\text{H}_2\text{O})_6\text{RuCl}_6 \cdot 4\text{H}_2\text{O}$, 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 AlCl_3 in 15 ml of concentrated HCl with a minimum of heating; the resulting solution was then filtered and allowed to cool. A 0.15 M Ru(III) solution in concentrated HCl 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 $\text{AlRuCl}_6(\text{H}_2\text{O})_{10}$: Al, 5.18; Ru, 19.40; Cl, 40.80; H, 3.84.

Found: Al, 5.21; Ru, 19.28; Cl, 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 ($\text{Mo K}\alpha_1$, $\lambda = 0.70296 \text{ \AA}$), 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 a_1 and a_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 $\mu = 19.3 \text{ cm}^{-1}$ 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 $\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$. 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 chlorine⁸ 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 $a = 10.492 \pm 0.005$, $b = 11.415 \pm 0.005$, $c = 7.069 \pm 0.005$ Å, and $\beta = 92.69 \pm 0.02^\circ$. 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(c): $\pm(x, y, z; 1/2 - x, 1/2 + y, 1/2 - z)$.

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 $R = \sum |\Delta F| / \sum |F_o|$ 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 $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. In reporting the thermal parameters below we have converted β_{ij} to B_{ij} which is in units of $\text{\AA}^2$; the relation between these two quantities is $4\beta_{ij} = a_i^* a_j^* B_{ij}$, where a_i^* is the i th 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, $\sqrt{\sum w(\Delta F)^2 / \sum w F_o^2}$, 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% probability enclosures, and were drawn using the version of ORTEP⁹ 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 $Al(H_2O)_6RuCl_6 \cdot 4H_2O$

FCA(0,0,0) = 2590

L FOR FCA	-2	88	80	-1	24	27	5	82	83	H,K,M	2, 12	3	78	78	2 732 737	3	31 29	5	42 42	6	80 77	6	84 82	G 730 742	-1	167 162	0	204 193	
H,K,M	0, 0	-1	20	12	0	158 217	6	109 109	-3	-23 28	4	26 22	3	94 94	4	154 146	6	0 10*	H,K,M	6, 4	H,K,M	7, 2	2 100 105	1	180 175	1	112 106		
0	1	161 438	1	113 174	1	113 174	1	113 174	1	113 174	1	113 174	1	113 174	1	113 174	1	113 174	1	113 174	1	113 174	1	113 174	1	113 174	1	113 174	
4	790 791	1	21 32	5	26 8	62 63	-1	0 1*	6*	57 53	5	94 92	-4	23 12*	-6	82 45	-6	76 80	-6	108 105	-6	104 136	5	138 142	3	54 53			
6	128 123	2	116 111	3	59 61	H,K,M	2, 1	4	0 120 123	7	47 45	6	286 286	-3	126 119	-5	144 144	-5	81 87	-5	87 89	H,K,M	8, 1	H,K,M	9, 1	4 95 97			
8	258 259	3	60 50	4	138 129	-7	31 22	1	0 17*	H,K,M	3, 7	7 22 15*	-2	49 55	-4	193 188	-4	226 220	-4	98 94	-4	0 19*	-6	33 39	H,K,M	10, 3			
H,K,M	0, 0	4	323 321	5	166 184	-6	275 266	2	161 105	-7	71 70	H,K,M	3, 3	-1	92 99	-3	27 31	-3	27 31	-3	27 31	-3	27 31	-3	27 31	-3	27 31	-3	27 31
1	707 695	1	21 32	5	26 8	62 63	-1	0 1*	6*	57 53	5	94 92	-4	23 12*	-6	82 45	-6	76 80	-6	108 105	-6	104 136	5	138 142	3	54 53			
2	0 10*	6	219 228	H,K,M	1, 9	-4	238 235	H,K,M	2, 13	-5	0 25*	-6	79 74	1	68 69	-1	175 175	-1	166 162	-1	158 161	-3	193 201	-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 59	-2	48 50	-2	0 19*	-2	124 126		
4	179 178	8	73 76	-5	22 21*	-2	613 605	-1	157 152	-3	0 14*	-4	90 88	3	123 114	1	31 38	1	33 57	1	18 89	-1	388 393	-1	27 22	-1	261 268		
5	225 227	9	74 77	-6	114 115	-3	124 125	-2	161 150	-4	202 204	-5	203 205	2	0 8*	0	265 278	0	357 368	0	17 59	-2	48 50	-2	0 19*	-2	124 126		
6	19 19*	-8	46 43	-3	34 28	0	325 343	1	0 16*	-1	58 57	-2	32 37	H,K,M	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,M	3, 0	1	190 199	0	33 32	-1	115 115	5	0 9*	5	90 94	5	101 102	3	171 165	3	5 3	3	176 177		
9	125 125	-7	140 135	0	41 30	-4	117 103	-5	70 72	3	332 334	-6	146 148	-6	146 148	-6	146 148	-6	146 148	-6	146 148	-6	146 148	-6	146 148	-6	146 148		
10	725 641	-4	103 107	0	26 24	4	377 377	-5	43 40	3	41 43	3	205 205	0	32 41	H,K,M	5, 9	H,K,M	6, 5	H,K,M	7, 3	5 194 192	5	23 25	H,K,M	10, 4			
1	13 13	-3	254 231	2	19 14*	-3	278 268	4	205 203	3	262 258	1	88 94	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77		
2	170 160	-2	554 535	3	48 47	6	125 125	-1	112 114	5	154 153	4	118 120	2	70 74	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77		
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 59	-2	48 50	-2	0 19*	-2	124 126		
4	179 178	8	73 76	-5	22 21*	-2	613 605	-1	157 152	-3	0 14*	-4	90 88	3	123 114	1	31 38	1	33 57	1	18 89	-1	388 393	-1	27 22	-1	261 268		
5	225 227	9	74 77	-6	114 115	-3	124 125	-2	161 150	-4	202 204	-5	203 205	2	0 8*	0	265 278	0	357 368	0	17 59	-2	48 50	-2	0 19*	-2	124 126		
6	19 19*	-8	46 43	-3	34 28	0	325 343	1	0 16*	-1	58 57	-2	32 37	H,K,M	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,M	3, 0	1	190 199	0	33 32	-1	115 115	5	0 9*	5	90 94	5	101 102	3	171 165	3	5 3	3	176 177		
9	125 125	-7	140 135	0	41 30	-4	117 103	-5	70 72	3	332 334	-6	146 148	-6	146 148	-6	146 148	-6	146 148	-6	146 148	-6	146 148	-6	146 148	-6	146 148		
10	725 641	-4	103 107	0	26 24	4	377 377	-5	43 40	3	41 43	3	205 205	0	32 41	H,K,M	5, 9	H,K,M	6, 5	H,K,M	7, 3	5 194 192	5	23 25	H,K,M	10, 4			
1	13 13	-3	254 231	2	19 14*	-3	278 268	4	205 203	3	262 258	1	88 94	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77		
2	170 160	-2	554 535	3	48 47	6	125 125	-1	112 114	5	154 153	4	118 120	2	70 74	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77		
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 59	-2	48 50	-2	0 19*	-2	124 126		
4	179 178	8	73 76	-5	22 21*	-2	613 605	-1	157 152	-3	0 14*	-4	90 88	3	123 114	1	31 38	1	33 57	1	18 89	-1	388 393	-1	27 22	-1	261 268		
5	225 227	9	74 77	-6	114 115	-3	124 125	-2	161 150	-4	202 204	-5	203 205	2	0 8*	0	265 278	0	357 368	0	17 59	-2	48 50	-2	0 19*	-2	124 126		
6	19 19*	-8	46 43	-3	34 28	0	325 343	1	0 16*	-1	58 57	-2	32 37	H,K,M	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,M	3, 0	1	190 199	0	33 32	-1	115 115	5	0 9*	5	90 94	5	101 102	3	171 165	3	5 3	3	176 177		
9	125 125	-7	140 135	0	41 30	-4	117 103	-5	70 72	3	332 334	-6	146 148	-6	146 148	-6	146 148	-6	146 148	-6	146 148	-6	146 148	-6	146 148	-6	146 148		
10	725 641	-4	103 107	0	26 24	4	377 377	-5	43 40	3	41 43	3	205 205	0	32 41	H,K,M	5, 9	H,K,M	6, 5	H,K,M	7, 3	5 194 192	5	23 25	H,K,M	10, 4			
1	13 13	-3	254 231	2	19 14*	-3	278 268	4	205 203	3	262 258	1	88 94	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77		
2	170 160	-2	554 535	3	48 47	6	125 125	-1	112 114	5	154 153	4	118 120	2	70 74	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77		
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 59	-2	48 50	-2	0 19*	-2	124 126		
4	179 178	8	73 76	-5	22 21*	-2	613 605	-1	157 152	-3	0 14*	-4	90 88	3	123 114	1	31 38	1	33 57	1	18 89	-1	388 393	-1	27 22	-1	261 268		
5	225 227	9	74 77	-6	114 115	-3	124 125	-2	161 150	-4	202 204	-5	203 205	2	0 8*	0	265 278	0	357 368	0	17 59	-2	48 50	-2	0 19*	-2	124 126		
6	19 19*	-8	46 43	-3	34 28	0	325 343	1	0 16*	-1	58 57	-2	32 37	H,K,M	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,M	3, 0	1	190 199	0	33 32	-1	115 115	5	0 9*	5	90 94	5	101 102	3	171 165	3	5 3	3	176 177		
9	125 125	-7	140 135	0	41 30	-4	117 103	-5	70 72	3	332 334	-6	146 148	-6	146 148	-6	146 148	-6	146 148	-6	146 148	-6	146 148	-6	146 148	-6	146 148		
10	725 641	-4	103 107	0	26 24	4	377 377	-5	43 40	3	41 43	3	205 205	0	32 41	H,K,M	5, 9	H,K,M	6, 5	H,K,M	7, 3	5 194 192	5	23 25	H,K,M	10, 4			
1	13 13	-3	254 231	2	19 14*	-3	278 268	4	205 203	3	262 258	1	88 94	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77		
2	170 160	-2	554 535	3	48 47	6	125 125	-1	112 114	5	154 153	4	118 120	2	70 74	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77	-5	74 77		
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 59	-2	48 50	-2	0 19*	-2	124 126		
4	179 178	8	73 76	-5	22 21*	-2	613 605	-1	157 152	-3	0 14*	-4	90 88	3	123 114	1	31 38	1	33 57	1	18 89	-1	388 393	-1	27 22	-1	261 268		
5	225 227	9	74 77	-6	114 115	-3	124 125	-2	161 150	-4	202 204	-5	203 205	2	0 8*	0	265 278												

* Zero-weighted data.

TABLE II

POSITIONAL AND THERMAL PARAMETERS IN $\text{Al}(\text{H}_2\text{O})_6 \cdot 4\text{H}_2\text{O}^{\text{a}, \text{b}}$

Atom	$\bar{x}$	$\bar{y}$	$\bar{z}$	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)

^aThe standard deviation of the least significant figure is given in parenthesis.^bThe thermal parameters are in units of $\text{\AA}^2$.^cParameter 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

^aThese 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 $B = 4.9 \pm 0.7 \text{ \AA}^2$.

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/A³ 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 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/A³ 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 $\text{Al}(\text{H}_2\text{O})_6\text{RuCl}_6 \cdot 4\text{H}_2\text{O}$

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

^aEdge in Al octahedron.

^bHydrogen bond.

^cBifurcated hydrogen bond.

^dEdge in Ru octahedron.

TABLE V
PRINCIPAL ANGLES IN $\text{Al}(\text{H}_2\text{O})_6\text{RuCl}_6 \cdot 4\text{H}_2\text{O}$

Atoms	Angle(°)	Atoms	Angle(°)
<u>Octahedral angles</u>		<u>Angles involving hydrogen bonds</u>	
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

^aAngles 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/ $\text{\AA}^3$ 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 $\text{Al}(\text{H}_2\text{O})_6$ and $\text{Ru}(\text{Cl})_6$ 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 $\text{\AA}$, 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 $\text{\AA}$ spread in the O - O distances. They found an average O - O distance of 2.669 $\text{\AA}$, compared to our 2.659 $\text{\AA}$, and reported an Al - O distance of 1.886 $\text{\AA}$ compared to 1.880 $\text{\AA}$ in the compound we have studied.

References

- (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.
- (4) T. E. Hopkins, A. Zalkin, D. H. Templeton and M. G. Adamson,
J. Inorg. Chem., 5, 1427, 1431 (1966).
- (5) D. A. Fine, Ph. D. Thesis, University of California at Berkeley, 1958.
- (6) D. T. Cromer and J. T. Waber, Acta Cryst., 18, 104(1965).
- (7) "International Tables for X-Ray Crystallography", Vol. III,
The Kynoch Press, Birmingham, England, 1962.
- (8) D. T. Cromer, Acta Cryst., 18, 17(1965).
- (9) Carrol K. Johnson, Oak Ridge National Laboratory Rept 3794(1965).
- (10) T. S. Khodashova, Zh. Strukt. Khim., 1, 333(1960).
- (11) Y. Okaya, M. S. Ahmed, R. Pepinsky and V. Vand, Z. Krist., 109, 367(1957).

Figure 1. Unit cell of $\text{Al}(\text{H}_2\text{O})_6\text{RuCl}_6 \cdot 4\text{H}_2\text{O}$.

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

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