of a single (2.14 Å) and a double (1.94 Å) P–S bond.[27d] (B) The four independent P–O bonds average 1.58 (2) Å in length, compared with the hypothetical lengths of a single (1.76 Å) and double (1.44 Å) P–O bond.[29] The following two results are also noteworthy: (C) Within the coordination sphere of each phosphorus atom, the S–P–S angle is larger than the O–P–O angle. (D) The oxygen valency angle, P–O–C, is considerably larger (average 123 (7)°) than a tetrahedral angle. These four results are fully consistent with the bond lengths and angles found in the other known molecular O,O-dialkylphosphorodithioates, $Ni[(C_2H_5O)_2PS_2]_2$,[30] $Ni[(C_2H_5O)_2PS_2]_2 \cdot 2C_2H_5N$,[31] and $Te[(CH_3O)_2PS_2]_2$,[32] and may be interpreted variously in terms of sp^3d hybridization,[33,34] repulsion of valence shell electron pairs,[35] π bonding due to delocalization of lone-pair electrons from one atom (*e.g.*, oxygen or sulfur) into the vacant orbitals of another (*e.g.*, phosphorus),[29,33,35c,36–38] and electronegativity effects on atom hybridization.[39]

(29) E. A. Robinson, *Can. J. Chem.*, **41**, 3021 (1963).
(30) (a) J. F. McConnell and V. Kastalsky, *Acta Cryst.*, **22**, 853 (1967); (b) Q. Fernando and C. D. Green, *J. Inorg. Nucl. Chem.*, **29**, 647 (1967).
(31) S. Ooi and Q. Fernando, *Inorg. Chem.*, **6**, 1558 (1967).
(32) S. Husebye, *Acta Chem. Scand.*, **20**, 24 (1966).
(33) D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).
(34) F. A. Cotton, *J. Chem. Phys.*, **35**, 228 (1961).
(35) (a) R. J. Gillespie and R. S. Nyholm, *Quart. Rev.* (London), **11**, 339 (1957); (b) R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963); (c) R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1963); (d) R. J. Gillespie, *J. Am. Chem. Soc.*, **82**, 5978 (1960).
(36) (a) E. A. Robinson, *Can. J. Chem.*, **39**, 247 (1961); (b) E. A. Robinson, *ibid.*, **41**, 173 (1963); (c) R. J. Gillespie and E. A. Robinson, *ibid.*, **41**, 2074 (1963); (d) E. A. Robinson and M. W. Lister, *ibid.*, **41**, 2988 (1963); (e) R. J. Gillespie and E. A. Robinson, *ibid.*, **42**, 2496 (1964).
(37) P. Haake, W. B. Miller, and D. A. Yysser, *J. Am. Chem. Soc.*, **86**, 3577 (1964).
(38) U. Blindheim and T. Gramstad, *Spectrochim. Acta*, **21**, 1073 (1965).
(39) (a) H. A. Bent, *Can. J. Chem.*, **38**, 1235 (1960); (b) H. A. Bent, *J. Inorg. Nucl. Chem.*, **19**, 43 (1961).

Molecular Packing.—The crystals are tabular with the plate surface having Miller indices (001) (parallel with the *ab* plane). The molecules (Figure 2) are aligned in such a way as to form layers or sheets of dimeric molecules with the longest dimension of the dimer approximately normal to these planes. These sheets intersect the unit cell *c* axis at the points $^1/_4$ and $^3/_4$. The sheets and all molecules within the sheets are held together by van der Waals forces. All van der Waals contacts between dimers involve only the center carbon (and associated hydrogen) atoms, terminal methyl groups, and sulfur atoms. There are approximately twice as many C$\cdots$S contacts involving carbon atoms in the isopropyl groups at P(7) as compared with those at P(6) [in crystals of $Zn_2(dtp)_4$, six *vs.* two such contacts and in $Cd_2(dtp)_4$, seven *vs.* four, at distances ≤ 4.5 Å]. The C$\cdots$C contacts (≤ 4.5 Å) are about equal in number for each of the four isopropyl groups, averaging about five such contacts per group. Thus, forces between the sheets are probably considerably less than those within the sheets, thereby enabling the sheets to slide over one another and form cleavage planes. This would explain the greasy-like feel of the crystals. The spiral-staircase growth effect parallel to *c* occasionally exhibited by these crystals is also similarly explained.

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

BY TED E. HOPKINS, ALLAN ZALKIN, DAVID H. TEMPLETON, AND MARTYN G. ADAMSON

An X-ray diffraction study of a single crystal of $Al(H_2O)_6RuCl_6 \cdot 4H_2O$ showed that it is monoclinic with $a = 10.492$ (5) Å, $b = 11.415$ (5) Å, $c = 7.069$ (5) Å, $\beta = 92.69$ (2)°, $Z = 2$, and $D_x = 2.045$ 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 (5) and 1.880 (4) 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 aquotetrachloro and aquopentachloro ruthenium species are reported elsewhere.[2] In this paper we

(2) T. E. Hopkins, A. Zalkin, D. H. Templeton, and M. G. Adamson, *Inorg. Chem.*, **5**, 1427, 1431 (1966).

describe the structure of $Al(H_2O)_6RuCl_6\cdot 4H_2O$, a salt of hexachlororuthenium (III).

Experimental Section

A solution of aluminum chloride in hydrochloric acid was prepared by dissolving 0.3 g of 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.[3] Both solutions were deoxygenated by bubbling with pure nitrogen for 0.5 hr. They were then mixed, and the resulting solution was allowed to stand under an atmosphere of nitrogen for 48 hr at room temperature. The light red plates which crystallized from the solution were separated on a Büchner 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 $AlRuCl_6(H_2O)_{10}$: 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.

An opaque crystal, having the shape of an equilaterally triangular plate of dimensions 0.17 mm on edge and 0.07 mm thick, was selected and glued to the end of a Pyrex fiber in air. The crystallographic b axis was in the plane of the plate.

A General Electric XRD-5 X-ray diffraction apparatus equipped with a molybdenum X-ray tube (Mo $K\alpha_1$, λ 0.70926 Å), a scintillation counter, a pulse height discriminator, and a quarter-circle Eulerian-cradle type of goniostat was used. The X-ray tube was operated at 50 kV and 20 mA; a 0.003-in. Zr filter was used on the receiving slit. The crystal was oriented such that the b axis was parallel to the φ axis of the instrument. The cell dimensions were obtained from carefully measured 2θ values of the $0k0$, $h00$, 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 $00l$ set of reflections.

A total of 1503 independent intensities were measured, of which 154 were recorded as having zero intensity. A stationary-crystal, stationary-counter technique with a 10-sec count for every reflection was used. The diffractometer was set at a $4°$ takeoff angle to the tube. The maximum 2θ angle was $50°$ [$(\sin\theta)/\lambda = 0.596$]. The maximum observed raw intensity was 9931 cps for the 011 reflection. Background was plotted for various values of χ and φ as a function of 2θ and these values were used for most of the intensities; in the cases where background was seriously affected by streaking, individual backgrounds were measured. The absorption parameter is 19 cm^{-1}, which we estimate causes the absorption factor to vary by a factor of 1.25 between the most extreme cases. Variations of the intensity of the 020 reflection when the φ setting was changed $90°$ ($\chi = 90°$) were about 25%. Lorentz and polarization corrections were made, but no correction was made for either absorption or extinction.

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 $\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2$. 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^-, and neutral oxygen were taken from Cromer and Waber's compilation,[4] and for neutral hydrogen from ref 5. Both the real and imaginary parts of the anomalous dispersion for ruthenium, aluminum, and chlorine[6] were included in the least-squares calculations. For each reflection w was set to $1.0/\sigma^2(F_o)$ with the exception that when I(net count) $\leq \sigma(I)$, then $w = 0$. The standard deviation of the observed structure factor was calculated as $\sigma(F_o) = F_o - [F_o^2 - (s\sigma(I)/Lp)]^{1/2}$,

(3) D. A. Fine, Ph.D. Thesis, University of California at Berkeley, 1958.
(4) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).
(5) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.
(6) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

where s is a scaling factor, $F_o = (sI/Lp)^{1/2}$, and Lp is the Lorentz-polarization correction. $\sigma(I) = (I + (pI)^2 + 2B + q^2)^{1/2}$, where p is a fractional uncertainty in I, B is the background, and q represents an uncertainty in the background. Values of p and q were 0.06 and 12.

The primitive cell contains two formula units of $Al(H_2O)_6$-$RuCl_6\cdot 4H_2O$. 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 $\beta = 92.69 \pm 0.02°$. The calculated density is 2.045 g/cm^3. 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 map is consistent with only one of these, which can be taken as Al in 2(a), Ru in 2(b), and all other atoms in the general position 4(e). Trial coordinates for the chlorine ions and the three independent 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 partial structure, showed two additional waters of crystallization. Several more cycles of least-squares calculations with anisotropic thermal parameters reduced R to 0.054. The anisotropic temperature factors have 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 square ångströms; 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 supported by the presence of some electron density in the difference Fourier at the estimated locations. Since these peaks were poorly resolved and did not respond well to attempted refinement, the original calculated positional parameters were used but not allowed to refine; however one isotropic temperature factor for all 10 hydrogens was refined. The 10 heavy atoms were all refined with anisotropic temperature factors.

The final R value for 1238 data with nonzero weights is 0.036. The R value for all 1503 data is 0.049. The weighted R value, $(\Sigma w(\Delta F)^2/\Sigma wF_o^2)^{1/2}$, 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

TABLE I

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

OBSERVED AND CALCULATED STRUCTURE FACTORS OF AL(H2O)6RUCL6.4H2O
FCA(0,0,0) = 2593

[Dense multi-column table of observed and calculated structure factors — columns of L, FOB, FCA values grouped by H,K index.]

[a] Asterisks indicate zero-weighted data.

enclosures and were drawn using the version of ORTEP[7] written for the IBM 360/67.

Interatomic distances and angles permit the identification of several hydrogen bonds and the calculation of approximate hydrogen atom positions. O(1), O(2), and O(3) represent the oxygen atoms of the three water molecules coordinated to the Al atom, and each of these is hydrogen bonded to a noncoordinated water

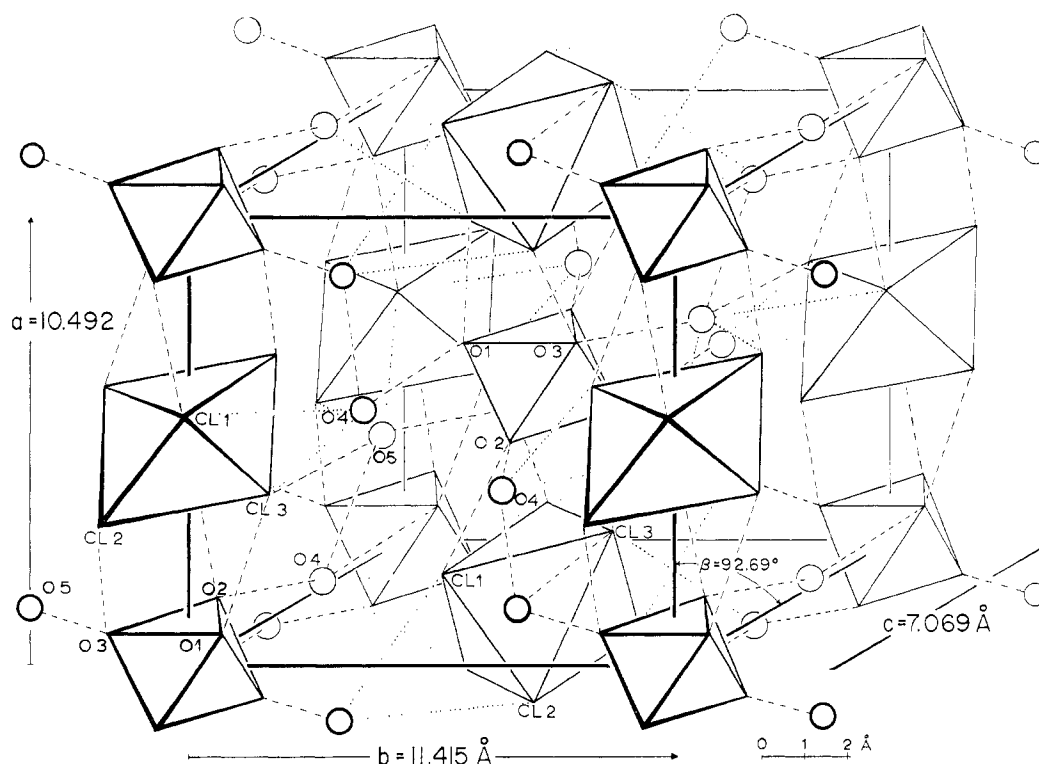(7) C. K. Johnson, Oak Ridge National Laboratory Report 3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

molecule and a chloride ion. Tables IV and V indicate the hydrogen bonds and their distances and angles. The hydrogen atoms of the above three water molecules were calculated to be at one-third the distance from the water oxygen to the atom to which it is hydrogen bonded. These estimated hydrogen atom positions are H(1) through H(6) in Table III. The difference Fourier map shows electron density peaks of 0.6–0.9 $e^-/\text{Å}^3$ near these calculated positions and these six peaks are found among the top 10 peaks in the map; the

Figure 1.—Unit cell of $Al(H_2O)_6RuCl_6 \cdot 4H_2O$. Hydrogen bonding is indicated by dashed and dotted (for bifurcated) lines.

TABLE II

POSITIONAL AND THERMAL PARAMETERS IN $Al(H_2O)_6RuCl_6 \cdot 4H_2O^{a,b}$

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)	−0.04 (8)	0.12 (7)	−0.10 (7)
Ru	0.5^c	0.0^c	0.0^c	1.50 (2)	2.33 (3)	1.75 (2)	0.01 (2)	0.18 (2)	−0.07 (2)
Cl(1)	0.3768 (1)	−0.1037 (1)	0.2176 (2)	2.12 (5)	3.15 (6)	2.37 (5)	−0.07 (5)	0.44 (4)	0.42 (5)
Cl(2)	0.3649 (1)	−0.0675 (1)	−0.2551 (2)	2.15 (5)	3.42 (6)	2.11 (5)	−0.21 (5)	0.00 (4)	−0.29 (5)
Cl(3)	0.3732 (1)	0.1717 (1)	0.0301 (2)	2.03 (5)	2.65 (6)	3.11 (6)	0.17 (4)	0.17 (4)	−0.22 (5)
O(1)	0.0980 (3)	0.1182 (3)	−0.1090 (5)	2.3 (2)	3.1 (2)	2.7 (2)	−0.6 (1)	0.2 (1)	0.3 (1)
O(2)	0.1091 (3)	−0.0023 (3)	0.2194 (5)	2.4 (1)	3.3 (2)	2.4 (2)	0.3 (1)	−0.2 (1)	−0.4 (1)
O(3)	0.0980 (3)	−0.1152 (3)	−0.1136 (5)	2.1 (2)	2.7 (2)	3.2 (2)	−0.1 (1)	0.6 (1)	−0.2 (1)
O(4)	0.1113 (4)	0.1447 (3)	0.5164 (5)	4.4 (2)	3.1 (2)	2.9 (2)	0.1 (2)	0.3 (2)	−0.2 (1)
O(5)	0.3732 (4)	0.1726 (4)	0.4869 (5)	3.8 (2)	3.1 (2)	3.1 (2)	0.6 (2)	0.5 (1)	0.1 (1)

[a] The standard deviation of the least significant figure is given in parentheses. [b] The thermal parameters are in square ångströms. [c] Parameter fixed by symmetry.

TABLE III

ESTIMATED HYDROGEN PARAMETERS[a]

Atom	x	y	z
H(1)	0.190	0.136	−0.063
H(2)	0.102	0.127	−0.234
H(3)	0.198	−0.037	0.218
H(4)	0.109	0.046	0.318
H(5)	0.186	−0.099	−0.161
H(6)	0.107	−0.186	−0.080
H(7)	0.199	0.153	0.506
H(8)	0.072	0.217	0.480
H(9)	0.424	0.105	0.542
H(10)	0.383	0.174	0.346

[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 10 atoms, and it is $B = 4.9 \pm 0.7 \text{ Å}^2$.

largest peak in the map is 1.1 $e^-/\text{Å}^3$ and is near the Ru atom. For the two noncoordinated water molecules, O(4) and O(5), the situation is more complex. O(4) is a hydrogen-bond acceptor from O(1) and O(2) and has a

close approach to O(5). If it is assumed that its two hydrogen atoms are approximately tetrahedral to the two hydrogen bonds from O(1) and O(2), then it is the donor of the hydrogen to the hydrogen bond with O(5), and its other hydrogen is directed toward a point between Cl(1) and Cl(3) suggesting a "bifurcated hydrogen bond;" this is a term we use in the present case to describe the geometrical arrangement without intending to imply anything about the magnitude of the bond energy. In the difference Fourier maps, peaks of $\sim$0.5 $e^-/\text{Å}^3$ are near the two calculated hydrogen positions and rank as the 11th and 18th peaks in magnitude. In a similar fashion, O(5) is a hydrogen-bond acceptor for O(3) and O(4), but it has no other near distances appropriate for ordinary hydrogen bonds. If its hydrogen atoms are approximately tetrahedral with respect to the hydrogen bonds to O(3) and O(4), then one is in the geometry of the bifurcated bond with respect to the pair of chlorine atoms Cl(1)
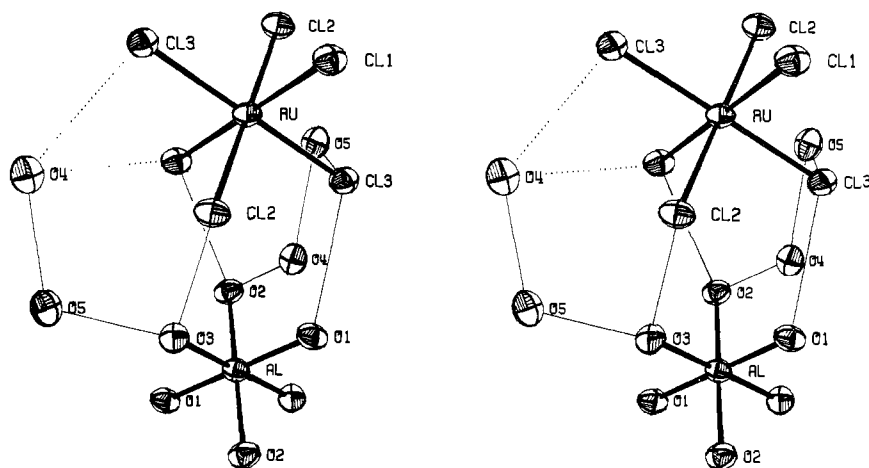
Figure 2.—Stereographic view of the environment around the metal atoms. Hydrogen bonding is indicated by the thin and dotted (for bifurcated) lines.

TABLE IV

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

Atoms	Dist, Å	Atoms	Dist, Å	Atoms	Dist, Å
Al–2O(1)	1.883 (3)	O(1)–O(4)	2.676 (5)[b]	O(4)–Cl(3)	3.266 (4)[c]
Al–2O(2)	1.884 (4)	O(1)–Cl(3)	3.068 (4)[b]	O(5)–Cl(1)	3.369 (4)[c]
Al–2O(3)	1.873 (4)	O(2)–O(3)	2.632 (5)[a]	O(5)–Cl(2)	3.295 (4)[c]
Ru–2Cl(1)	2.372 (2)	O(2)–O(3)	2.681 (5)[a]	O(5)–Cl(3)	3.229 (5)[b]
Ru–2Cl(2)	2.370 (2)	O(2)–O(4)	2.687 (5)[b]	Cl(1)–Cl(2)	3.342 (2)[d]
Ru–2Cl(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 $Al(H_2O)_6RuCl_6 \cdot 4H_2O$

Octahedral angles	Value, deg	Angles involving hydrogen bonds	Value, deg
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.

and Cl(2), and one points to the Cl(3) atom. The difference function shows peaks of about 0.5 and 0.4 $e^-/Å^3$, which rank as the 13th and 27th peaks in magnitude in the maps and are near the calculated locations shown in Table III.

In summary, the structure consists of $Al(H_2O)_6$ and $RuCl_6$ 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 the type O–H$\cdots$O, three are in bonds of the type O–H$\cdots$Cl, and three are not in simple hydrogen bonds.