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Structure of Pentaamminechlororuthenium(III) Sesquichloride Hemi(tetrafluoroborate)

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Abstract. $[RuCl(NH_3)_5]_2(BF_4)Cl_3$, $M_r = 636{\cdot}52$, orthorhombic, *Ibam*, $a = 9{\cdot}2995$ (5), $b = 20{\cdot}984$ (1), $c = 10{\cdot}7336$ (5) Å, $V = 2094{\cdot}6$ (2) Å^3, $Z = 4$, $D_x = 2{\cdot}018$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 20{\cdot}34$ cm^{-1}, $F(000) = 1256$, $T = 294$ K. Final $R = 0{\cdot}019$ for 1760 observed reflections. Five ammine ligands and one chloro ligand are coordinated to the Ru^{III} atom in an octahedral arrangement. The average Ru—N bond length, 2·108 Å, and the Ru—Cl bond length, 2·343 (1) Å, are not significantly different from values reported previously for the chloride salt [Hambley & Lay (1986). *Inorg. Chem.* **25**, 4553–4558].

Introduction. We have recently reported a detailed analysis of π-bonding and hydrogen-bonding trends in pentaammine- and pentakis(methylamine)chlorometal(III) complexes (Hambley & Lay, 1986, 1987). Also, we have used variations in bond lengths observed between these two series to rationalize variations in the rate constants of spontaneous aquation (Hambley & Lay, 1987; Lay, 1986, 1987). These studies have relied on relatively small, but significant, changes in bond lengths (0·003–0·028 Å) and consequently they have been questioned on the basis that the experimental values of the bond lengths may have been affected by crystal packing and hydrogen-bonding effects (Monsted & Monsted, 1989). In response, we have undertaken a precise determination of a different salt of one of the compounds, namely $[RuCl(NH_3)_5]_2(BF_4)Cl_3$, since the only other structure containing the $[RuCl(NH_3)_5]^{2+}$ cation was performed in 1962 (Prout & Powell, 1962) and is not sufficiently precise for meaningful comparison. Our choice of salt was limited by the need to obtain very high quality crystals.

Experimental. $NaBF_4$ (3 equivalents) in water was added to an aqueous solution of $[RuCl(NH_3)_5]Cl_2$. The solution was cooled and crystals of $[RuCl(NH_3)_5]_2(BF_4)Cl_3$ formed as small yellow prisms. A crystal was mounted on a glass fibre with epoxy resin. Data were collected using an Enraf–Nonius CAD-4 automatic diffractometer, graphite-monochromated Mo $K\alpha$ radiation. 25 independent reflections with $20 \le 2\theta \le 25°$ were used for least-squares determination of cell constants. Intensities of three reflections were monitored, and indicated less than 1·5% decomposition. The structure was solved by Patterson methods. All non-H atoms were refined with anisotropic thermal parameters. H atoms were located and refined with individual isotropic thermal parameters. Full-matrix least-squares refinement converged with all shifts less than $0{\cdot}02\sigma$. Maximum excursions in a final difference map were 0·5 and $-0{\cdot}9$ e Å^{-3}.

Data reduction and application of absorption corrections were carried out using the Enraf–Nonius *SDP* structure determination package (Enraf–Nonius, 1985). All other calculations were performed using the *SHELX76* system of programs (Sheldrick, 1976). Drawings were produced using the *ORTEP* program (Johnson, 1965). Scattering factors (neutral Ru for Ru^{III}) and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Data collection and refinement parameters are collected in Table 1. Final positional parameters and bond lengths and angles are listed in

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Table 1. *Summary of data collection and processing parameters*

Crystal dimensions (mm)	0·20 × 0·15 × 0·15
Crystal faces	(100), $(1\bar{2}\bar{1})$, (121), $(\bar{1}\bar{2}\bar{1})$, $(12\bar{1})$, $(0\bar{1}3)$, $(\bar{1}2\bar{1})$, $(1\bar{2}2)$
Data collection range (°)	$2 \leq 2\theta \leq 60$
Scan width (°)	$(1·00 + 0·34\tan\theta)$
Horizontal counter aperture (mm)	$(2·70 + 1·05\tan\theta)$
Scan type	ω–θ
Absorption correction*	
Number of sampling points	10 × 10 × 10
Maximum correction	1·590
Minimum correction	1·385
Range of *hkl*	$\pm h,\ +k,\ +l$
Total data collected	4084
Unique data	1940
$R_{\rm int}$	0·021
Data with $I \geq 2·5\sigma(I)$	1760
Total variables	109
R	0·019
wR	0·022
Weighting constants†	$g = 2·7$, $k = 0·000095$

* Gaussian method.

† Weight $w = g/[\sigma^2(F_o) + kF_o^2]$, *g* and *k* refined.

Table 2. *Final atomic coordinates, with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters B_{eq} (Å^2)*

$$B_{\rm eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$B_{\rm eq}$
Ru(1)	−0·19891 (2)	0·13348 (1)	0·0000	1·65
Cl(1)	0·05286 (6)	0·13740 (2)	0·0000	2·51
N(1)	−0·2067 (3)	0·23436 (10)	0·0000	2·79
N(2)	−0·1972 (2)	0·13407 (7)	0·1964 (1)	2·52
N(3)	−0·1921 (2)	0·03336 (9)	0·0000	2·33
N(4)	−0·4253 (2)	0·13190 (10)	0·0000	2·60
Cl(2)	0·0000	0·0000	0·2500	2·35
Cl(3)	0·5000	0·22320 (3)	0·2500	2·62
B(1)	0·0000	0·5000	0·2500	2·74
F(1)†	0·4150 (4)	0·0377 (2)	0·1823 (4)	6·98
F(2)	0·0000	0·5000	0·1118 (6)	7·01
F(3)	0·5000	0·0629 (4)	0·2500	10·52
F(4)	0·3584 (8)	0·0000	0·2500	11·67

† Partial occupancies: F(1) 0·5, F(2)–F(4) 0·1667.

Table 3. *Bond lengths* (Å) *and angles* (°)

Cl(1)—Ru(1)	2·343 (1)	N(1)—Ru(1)	2·118 (2)
N(2)—Ru(1)	2·108 (2)	N(3)—Ru(1)	2·102 (2)
N(4)—Ru(1)	2·105 (2)	F(1)—B(1)	1·334 (4)
F(2)—B(1)	1·484 (6)	F(3)—B(1)	1·319 (6)
F(4)—B(1)	1·317 (6)		
N(1)—Ru(1)—Cl(1)	90·0 (1)	N(2)—Ru(1)—Cl(1)	89·6 (1)
N(2)—Ru(1)—N(1)	89·7 (1)	N(3)—Ru(1)—Cl(1)	90·3 (1)
N(3)—Ru(1)—N(1)	179·7 (1)	N(3)—Ru(1)—N(2)	90·3 (1)
N(4)—Ru(1)—Cl(1)	178·9 (1)	N(4)—Ru(1)—N(1)	88·9 (1)
N(4)—Ru(1)—N(2)	90·4 (1)	N(4)—Ru(1)—N(3)	90·8 (1)
N(2)—Ru(1)—N(2$^{\rm i}$)	180·0 (1)		

Symmetry code: (i) *x*, *y*, −*z*.

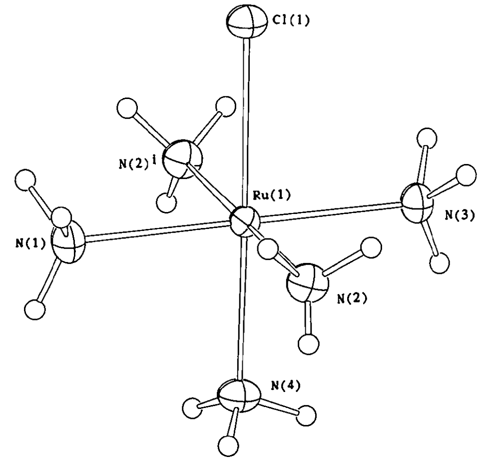

Fig. 1. The $[RuCl(NH_3)_5]^{2+}$ cation showing atomic labels. The superscript denotes the symmetry operation as defined in Table 3.

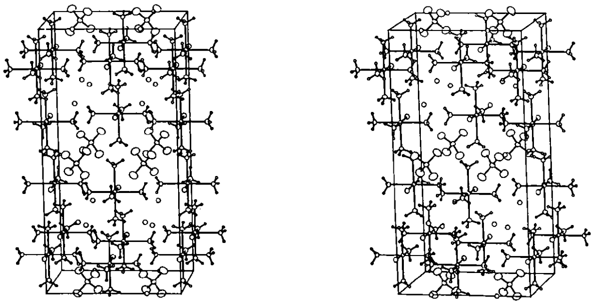

Fig. 2. Unit cell of $[RuCl(NH_3)_5]_2(BF_4)Cl_3$. Origin at bottom left, $0 \leq x \leq a$ away from reader, $0 \leq y \leq b$ up the page, $0 \leq z \leq c$ horizontal.

Tables 2 and 3.* Fig. 1 shows the $[RuCl(NH_3)_5]^{2+}$ cation with the atomic labelling and Fig. 2 is a stereoview of the unit cell.

Discussion. The structure consists of the dipositive complex cation lying on a mirror plane at $z = 0$, two Cl^- anions, one at $0,0,\frac{1}{4}$, a site with 222 symmetry, and the other on a twofold rotation axis, and a BF_4^- anion at $0,\frac{1}{2},\frac{1}{4}$, a site with 222 symmetry. The BF_4^- anion is disordered; one contributor adheres to the site symmetry and accounts for 50% of the density and three other contributors to the F atoms lie on twofold axes and account for the remaining 50%. There are weak hydrogen bonds between H(ammine) atoms and all Cl^- anions and all F-atom sites. There is one hydrogen bond involving the coordinated Cl atom with an N···Cl distance of 3·498 (3) Å. This distance is similar to equivalent distances in $[RuCl(NH_3)_5]Cl_2$ of 3·417 and 3·536 Å (Hambley &

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* Structure amplitudes, anisotropic thermal parameters of non-H atoms, positional and thermal parameters of H atoms and close contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53715 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Lay, 1986). Likewise the average of the other N···Cl⁻ distances (3·414 Å) is similar to that in the chloride salt (3·457 Å).

The motivation for determining the present structure was to obtain a comparison with $[Ru(NH_3)_5Cl]Cl_2$. The precisely determined Ru—Cl bond lengths are not significantly different, 2·343 (1) and 2·346 (1) Å. Likewise the average Ru—N bond lengths are very similar, 2·108 and 2·103 Å. Thus, the present results are contrary to arguments that analyses of trends in M—X bond distances must be qualified because these distances may be significantly affected by crystal-packing and hydrogen-bonding effects (Monsted & Monsted, 1989). In the present structure, the coordinated Cl atom is involved in one hydrogen bond only and in $[RuCl(NH_3)_5]Cl_2$ it is involved in two, yet the bond lengths are indistinguishable. The ammine groups are hydrogen bonded to Cl^- and BF_4^- anions in the present structure and only to Cl^- in $[RuCl(NH_3)_5]Cl_2$, yet again the bond lengths do not appear to be significantly affected. We believe that such results may be quite general if structural comparisons are only made between precisely determined structures.

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Structure of a Five-Coordinate Copper(II) Monocomplex with the Rigid Tridentate Ligand *N*-(6-Methyl-2-pyridylmethylene)-2-(2-pyridyl)ethylamine: $[CuBr_2(C_{14}H_{15}N_3)]$

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Abstract. Dibromo[*N*-(6-methyl-2-pyridylmethylene)-2-(2-pyridyl)ethylamine]copper(II), $M_r = 448{\cdot}3$, monoclinic, $P2_1/c$, $a = 8{\cdot}636\ (3)$, $b = 12{\cdot}165\ (1)$, $c = 15{\cdot}021\ (4)$ Å, $\beta = 92{\cdot}72\ (2)°$, $V = 1576\ (2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}9\ (1)$, $D_x = 1{\cdot}89\ \text{g cm}^{-3}$, $\lambda(\text{Cu}\ K\alpha_1) = 1{\cdot}54059$ Å, $\mu(\text{Cu}\ K\alpha) = 85{\cdot}06\ \text{cm}^{-1}$, $F(000) = 868$, $T = 294$ K, final $R = 0{\cdot}036$ for 1137 observed reflections. The structure consists of monomeric $[C(pymep)Br_2]$ molecules. The pymep ($C_{14}H_{15}N_3$) tridentate ligand and the bromine ions coordinate to the copper(II) ion to form a distorted trigonal bipyramid. Both reflectance and ESR spectra are in good agreement with the molecular structure.

Introduction. The study of the title compound is a continuation of the investigation of copper(II) complexes with tridentate ligands. The copper(II) ion forms two types of metallic complexes when it reacts with one tridentate ligand, L_{III}. The biscomplexes, $[Cu(L_{\text{III}})_2](Y)_2$ ($Y = PF_6^-$, NO_3^-), corresponding to a ratio of metal to L_{III} of 1:2, are always discrete molecules in which the metallic cation is hexacoordinated by two molecules of the tridentate ligand (Allman, Henke & Reinen, 1978; Arriortua, Rojo, Amigó, Germain & Declercq, 1982). The monocomplexes $[Cu(L_{\text{III}})X_2]$ (X = halide), ratio of metal to L_{III} 1:1, are five-coordinate discrete molecules, with a geometry around the copper(II) ion near to that of a regular square pyramid (Henke, Kramer & Reinen, 1983; Rojo, Vlasse & Beltrán, 1983); however, the rigidity of the tridentate ligand or packing effects in the unit cell may lead towards an unusual C_{2v} symmetry (Arriortua, Mesa, Rojo, Debaerdemaeker, Beltrán, Stratemeier & Reinen, 1988).

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