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Bis(9-methylhypoxanthinium) Oxonium Hexachlororuthenate(III) Trihydrate

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Abstract

The unit cell of the title compound, $2(C_6H_7N_4O)(H_3O)[RuCl_6].3H_2O$, contains the octahedral $[RuCl_6]^{3-}$ ion lying on an inversion centre. Its charge is balanced by one H_3O^+ and two N7-protonated 9-methyl-hypoxanthinium cations (9-methyl-6-oxo-1,9-dihydro-$7H^+$-purinium). The H_3O^+ ion and three water molecules form a disordered hydrogen-bonded chain parallel to the *a* axis.

Comment

The title compound was obtained as a by-product of a reaction between $RuCl_3$ and 9-methylhypoxanthine. An activated solution was first made by refluxing commercial hydrated $RuCl_3$ (0.4 mmol) in a mixture of ethanol (5 ml) and 1*M* aqueous HCl (5 ml) for 2 h. The solution was cooled to room temperature and three equivalents of 9-methylhypoxanthine dissolved in 1*M* HCl (5 ml) were added. After stirring vigorously for 15 min, two thirds of the solution was evaporated and an orange powder, subsequently identified as $RuCl_3(H_2O)_2$(9-methylhypoxanthine), was removed by filtration. Red crystals, first believed to be the latter complex, appeared after several days at room temperature. The unit cell was found to contain the $[RuCl_6]^{3-}$ anion with two protonated 9-methylhypoxanthinium and one H_3O^+ counter-ions. The UV-VIS spectrum of the crystals in 12 *M* HCl is in agreement with that reported by James & McMillan (1975) for $K_3[RuCl_6]$, thereby confirming the Ru^{III} oxidation state.
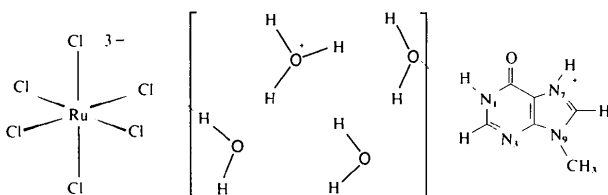
The $[RuCl_6]^{3-}$ anion (Fig. 1*a*) lies on a crystallographic inversion centre and its angles correspond to the ideal octahedral values to within ±2.6° (Table 2). The mean Ru—Cl distance (2.376 Å) is close to those of the $[Al(H_2O)_6]^{3+}$ salt (Hopkins, Zalkin, Templeton & Adamson, 1969). A small tetragonal distortion makes the Ru—Cl(2) bonds [2.364 (1) Å] slightly shorter than Ru—Cl(1) and Ru—Cl(3) [2.382 (1) Å].

The geometry of the 9-methylhypoxanthinium unit (Fig. 1*b* and Table 2) confirms its protonation state. The C(5)—N(7)—C(8) angle of 108.2 (2)°, definitely greater than in the neutral molecule (~104°), is clear evi-
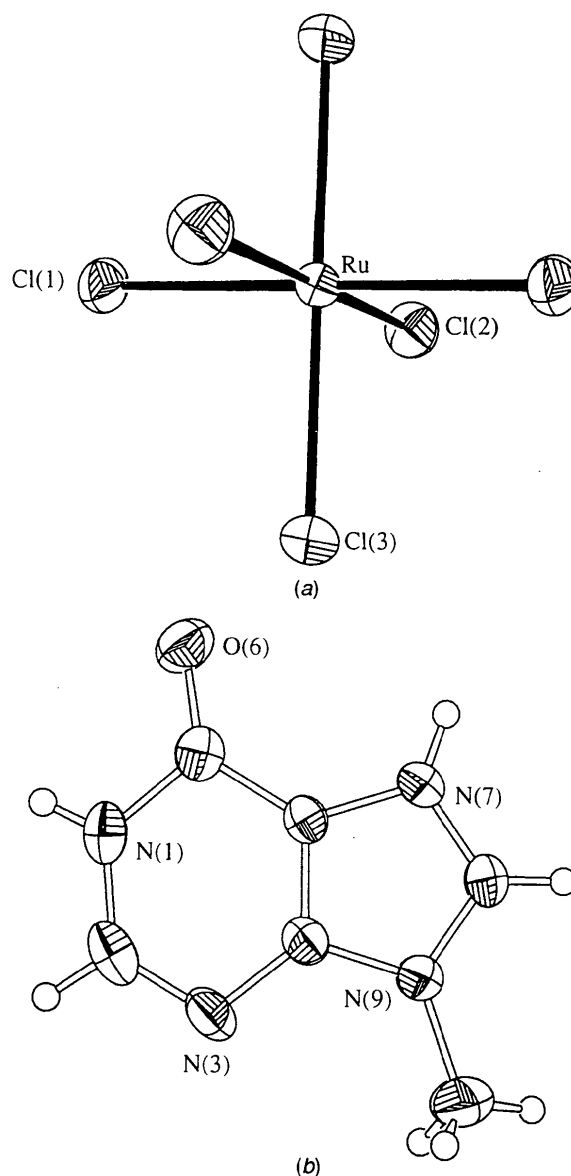

(*a*)

(*b*)

Fig. 1. *ORTEP* (Johnson, 1965) drawings of (*a*) the $[RuCl_6]^{3-}$ anion and (*b*) the 9-methylhypoxanthinium cation. Ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary size.

dence for protonation at N(7) (Bélanger-Gariépy & Beauchamp, 1981; Rosenstein, Oberding, Hyde, Zubieta, Karlin & Seeman, 1982; Taylor & Kennard, 1982). On the other hand, the C(2)—N(1)—C(6) and C(2)—N(3)—C(4) angles [126.0 (2) and 111.8 (2)°, respectively] are similar to those of neutral 9-methylhypoxanthine, confirming that N(1) has retained its proton and that N(3) is not protonated (Bélanger-Gariépy & Beauchamp, 1981; Rosenstein *et al.*, 1982; Sletten & Kaale, 1977). The ring remains planar within 0.012 Å (4σ) but the substituents show large displacements from this plane [O(6) 0.039 (3), C(9) 0.095 (5) Å].

The [RuCl₆]³⁻ units on the cell corners and parallel 9-methylhypoxanthinium ions at $z \simeq \frac{1}{2}$ form layers in the *ac* face (Fig. 2) in which both acidic protons form N—H⋯Cl bonds (Table 2). The unit cell also contains a disordered hydrogen-bonded chain which includes three water molecules for each H₃O⁺ ion, running along the *a* direction at $y \simeq \frac{1}{2}$ in the *ab* face. The positions fully and half occupied by the H atoms are consistent with the superposition of two individual chains; this is represented schematically in Fig. 3. These chains are related by the inversion centres indicated by arrows and they are equally populated. One O(1) site is filled by H₃O⁺ whereas the remaining O(1) and both O(2) positions are occupied by water molecules. For clarity, the acidic proton H(O1A) is represented arbitrarily on two sites (grey

spheres), slightly off its average unresolved position on the inversion centre. The remaining H-atom sites, half occupied in the disordered structure, are shown as open spheres; the dark spheres represent sites of full occupancy in which the two disordered positions are not resolved. The O(1)⋯O(1) separation [2.590 (5) Å], which corresponds to an H₂O–H₃O⁺ interaction, is comparable with those found previously for such systems (Gustafsson, 1987; Krebs, Bonmann & Erpenstein, 1991; Lundgren, 1978; Taesler & Lundgren, 1978). Since the water molecule O(2) interacts with an O(1) site occupied by either H₂O or H₃O⁺, the refined coordinates of O(2) are the average of the unresolved disordered O atoms. As a result, the O⋯O distances (mean 2.63 Å) calculated from these average positions are slightly greater than for O(1)⋯O(1) but less than expected for H₂O–H₂O interactions in similar systems (~ 2.78 Å) (Taesler & Lundgren, 1978; Krebs *et al.*, 1991). The H₂O–H₃O⁺ chain is anchored *via* donor hydrogen-bonding interactions to the Cl atoms of [RuCl₆]³⁻ and to N(3) and O(6) of the 9-methylhypoxanthinium cation (Fig. 3 and Table 2).
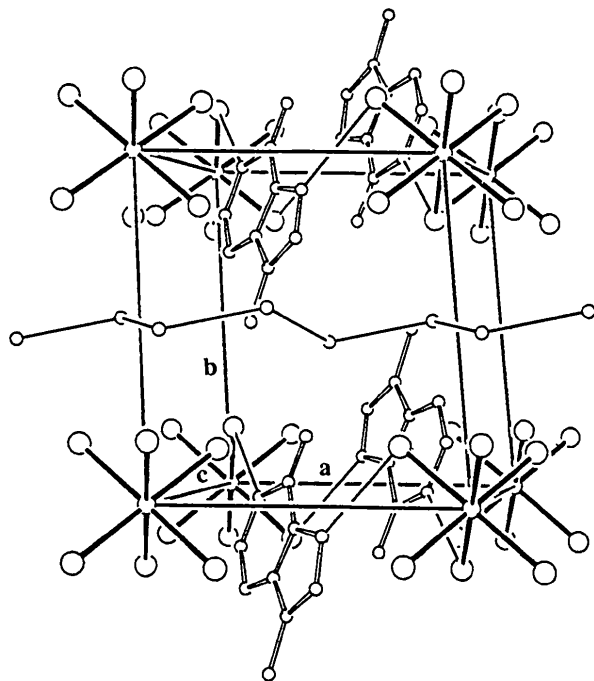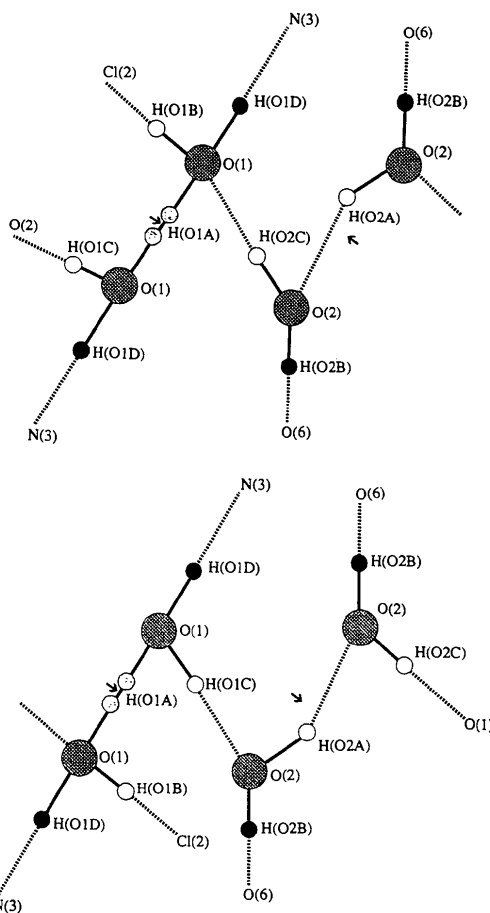

Fig. 2. View of the unit cell down the *c* axis. Atoms can be identified by comparison with Fig. 1. Hydrogen bonds are shown as thin lines and H atoms are omitted. The hydrogen-bonded H₂O–H₃O⁺ chain runs parallel to the *a* axis at $y \simeq \frac{1}{2}$ in the *ab* face.
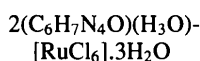

Fig. 3. Schematic representation of the two oxonium–water patterns corresponding to the disordered chain. These equally populated patterns are related by the inversion centres indicated by arrows.

Experimental

Crystal data

2($C_6H_7N_4O$)(H_3O)-
[$RuCl_6$].$3H_2O$
M_r = 689.15
Triclinic
$P\bar{1}$
a = 7.745 (5) Å
b = 9.048 (3) Å
c = 9.547 (2) Å
α = 109.20 (2)°
β = 98.51 (4)°
γ = 94.51 (4)°
V = 619.0 (5) Å^3
Z = 1
D_x = 1.849 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 24 reflections
θ = 10.0–11.0°
μ = 1.32 mm^{-1}
T = 273 K
Prism
0.57 × 0.42 × 0.39 mm
Red

Data collection

Enraf–Nonius diffractometer
$\omega/2\theta$ scans
Absorption correction:
none
4363 measured reflections
2182 independent reflections
2057 observed reflections
$[I \geq 3\sigma(I)]$

R_{int} = 0.010
θ_{max} = 25°
h = -9 → 9
k = -10 → 10
l = -11 → 10
4 standard reflections
frequency: 60 min
intensity variation: 2.0%

Refinement

Refinement on F
R = 0.020
wR = 0.027
S = 2.46
2057 reflections
192 parameters
$w = 1/[\sigma^2(F) + 0.00005F^2]$
$(\Delta/\sigma)_{max}$ = 0.605
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = -0.32 e Å^{-3}

Extinction correction:
secondary
(Zachariasen, 1967)
Extinction coefficient:
0.199 (9)
Atomic scattering factors
from International Tables
for X-ray Crystallography
(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ru	0	0	0	0.0173 (1)
Cl(1)	0.21407 (7)	-0.16356 (6)	0.04144 (7)	0.0255 (2)
Cl(2)	0.20678 (7)	0.15043 (6)	-0.07579 (7)	0.0265 (2)
Cl(3)	0.08426 (8)	0.18406 (6)	0.25069 (6)	0.0271 (2)
O(1)	0.0939 (3)	0.4845 (2)	0.1171 (3)	0.0548 (12)
O(2)	0.4324 (4)	0.5472 (2)	0.1242 (3)	0.0707 (14)
O(6)	0.4203 (2)	0.1753 (2)	0.6361 (2)	0.0354 (9)
N(1)	0.2126 (3)	-0.0126 (2)	0.4581 (2)	0.0315 (10)
N(3)	0.1487 (3)	-0.2767 (2)	0.4406 (2)	0.0320 (9)
N(7)	0.4811 (2)	-0.0980 (2)	0.7618 (2)	0.0250 (8)
N(9)	0.3274 (3)	-0.3290 (2)	0.6459 (2)	0.0280 (9)
C(2)	0.1261 (3)	-0.1608 (3)	0.3919 (3)	0.0345 (13)
C(4)	0.2725 (3)	-0.2324 (3)	0.5681 (3)	0.0241 (9)
C(5)	0.3682 (3)	-0.0869 (3)	0.6410 (2)	0.0221 (10)
C(6)	0.3432 (3)	0.0401 (3)	0.5872 (3)	0.0261 (10)
C(8)	0.4527 (3)	-0.2426 (3)	0.7621 (3)	0.0285 (10)
C(9)	0.2530 (5)	-0.4921 (3)	0.6140 (4)	0.0578 (17)

Table 2. *Bond lengths* (Å), *angles* (°) *and hydrogen-bonding geometry* (Å, °)

Ru—Cl(1)	2.382 (1)	C(4)—N(9)	1.374 (3)
Ru—Cl(2)	2.364 (1)	C(5)—C(6)	1.420 (3)
Ru—Cl(3)	2.382 (1)	C(5)—N(7)	1.378 (3)
N(1)—C(2)	1.350 (4)	C(6)—O(6)	1.224 (3)
N(1)—C(6)	1.392 (3)	N(7)—C(8)	1.311 (3)
C(2)—N(3)	1.293 (4)	C(8)—N(9)	1.333 (3)
N(3)—C(4)	1.354 (3)	N(9)—C(9)	1.456 (3)
C(4)—C(5)	1.363 (3)		
Cl(1)—Ru—Cl(2)	90.83 (4)	C(4)—C(5)—C(6)	121.2 (2)
Cl(1)—Ru—Cl(2^i)	89.17 (4)	C(4)—C(5)—N(7)	106.7 (2)
Cl(1)—Ru—Cl(3)	92.57 (5)	C(6)—C(5)—N(7)	132.1 (2)
Cl(1)—Ru—Cl(3^i)	87.43 (5)	N(1)—C(6)—C(5)	108.8 (2)
Cl(2)—Ru—Cl(3)	88.70 (5)	N(1)—C(6)—O(6)	121.7 (2)
Cl(2)—Ru—Cl(3^i)	91.30 (5)	C(5)—C(6)—O(6)	129.5 (2)
C(2)—N(1)—C(6)	126.0 (2)	C(5)—N(7)—C(8)	108.2 (2)
N(1)—C(2)—N(3)	125.2 (2)	N(7)—C(8)—N(9)	110.4 (2)
C(2)—N(3)—C(4)	111.8 (2)	C(4)—N(9)—C(8)	107.3 (2)
N(3)—C(4)—C(5)	127.0 (2)	C(4)—N(9)—C(9)	126.3 (2)
N(3)—C(4)—N(9)	125.6 (2)	C(8)—N(9)—C(9)	126.3 (2)
C(5)—C(4)—N(9)	107.4 (2)		

D—H$\cdots A$	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N(1)—H(1)$\cdots$Cl(3)	2.41 (3)	3.176 (2)	164 (3)
N(7)—H(7)$\cdots$Cl(1^{ii})	2.26 (2)	3.096 (3)	172 (2)
O(1)—H(O1A)$\cdots$O(1^v)	1.30	2.590 (5)	180
O(1)—H(O1B)$\cdots$Cl(1^i)	2.57 (6)	3.371 (3)	127 (4)
O(1)—H(O1B)$\cdots$Cl(2)	2.48 (6)	3.244 (2)	124 (4)
O(1)—H(O1B)$\cdots$Cl(3)	2.44 (6)	3.361 (2)	138 (4)
O(1)—H(O1C)$\cdots$O(2)	2.11 (7)	2.624 (4)	122 (6)
O(1)—H(O1D)$\cdots$N(3^{iv})	2.48 (3)	3.077 (3)	153 (3)
O(2)—H(O2A)$\cdots$O(2^{vi})	2.09 (6)	2.645 (6)	138 (6)
O(2)—H(O2B)$\cdots$O(6^{iii})	2.11 (3)	2.800 (3)	162 (3)
O(2)—H(O2C)$\cdots$O(1)	1.67	2.624 (4)	179

Symmetry codes: (i) $-x, -y, -z$; (ii) $1 - x, -y, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $x, 1 + y, z$; (v) $-x, 1 - y, -z$; (vi) $1 - x, 1 - y, -z$.

The unit cell was checked with axial photographs. The structure was solved by the heavy-atom method and it refined normally in $P\bar{1}$. Attempts to reduce the symmetry to $P1$ failed. The non-H atoms were refined anisotropically by full-matrix least-squares procedures. All H-atom positions were found in the ΔF map. The H-atom positions and U_{iso} of the hypoxanthine unit were refined. For the remaining atoms, positions were refined with U_{iso} fixed to 0.075 Å^2, except for H(O2C), which showed instability and was fixed at an idealized position.

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(I)

Two molecules of different conformations occupy the same position. The only difference is in the disposition of the methyl group, as shown in Fig. 1: one at C(3) with 35% probability and the other at C(3′) with 65% probability. Both molecules contain a twofold axis passing through Co as well as through the uncoordinated Cl⁻ ion. The Co^{III} ion is six coordinate with a distorted octahedral geometry. The quadridentate macrocyclic ligand is in a *cis*-folded conformation with both five-membered rings in skew formations and both six-membered rings in chair forms. The four chiral N-atom centres are 1*SR*, 4*SR*, 8*SR* and 11*SR*, and the chiral C-atom centres are 5*RS* and 12*SR*. The hydrogen bonds between the NH groups and the Cl⁻ ion help stabilize the crystal structure.

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cis-Dichloro(C-rac-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane-N,N',N'',N''')-cobalt(III) Chloride, [CoCl2(C12H28N4)]Cl

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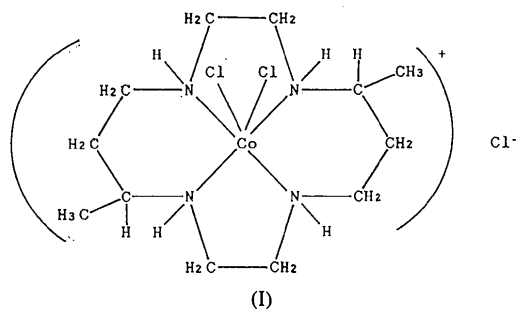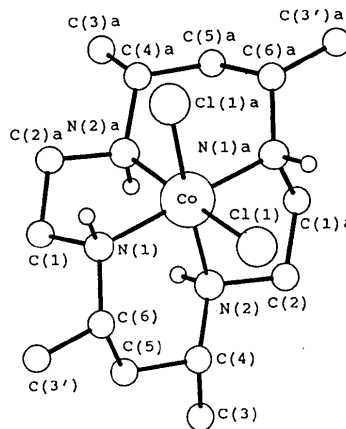*Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300*

Abstract

The Co^{III} ion is six coordinate with a distorted octahedral geometry. The quadridentate macrocyclic ligand is in a *cis*-folded conformation. This complex ion contains a twofold axis which passes through Co and has a 1*SR*, 4*SR*, 8*SR* and 11*SR* configuration at the chiral N-atom centres and a 5*RS* and 12*SR* configuration at the chiral C-atom centres. The two five-membered rings are in skew formations and the two six-membered rings have chair forms. Hydrogen bonds between the NH groups and the uncoordinated Cl ion help stabilize the crystal structure.

Comment

Transition metal–polyazacycloalkane complexes have been the subject of numerous investigations because of their particular stereochemistry (Bosnich, Poon & Tobe, 1965; Lindoy, 1989). In this paper, we report the crystal structure of cis-dichloro(C-rac-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane-N,N',N'',N''')cobalt(III) chloride, (I).

Fig. 1. A perspective view of the complex cation (*a* denotes symmetry transformation $1-x, y, \frac{1}{2}-z$).

Experimental

The ligand C-rac-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane and the title compound were prepared according to the literature method (Hay & Piplani, 1977; Hay, Bembi & House, 1984). The deep violet crystals obtained were recrystallized from 6 *N* HCl solution.

Crystal data

[CoCl2(C12H28N4)]Cl	Mo $K\alpha$ radiation
$M_r = 393.67$	$\lambda = 0.71073$ Å