

(12-Hydroxymethyl-5,5,7,12,14-pentamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetato-*N,N',N'',N'''*,-*O,O'*)cobalt(III) chloride perchlorate monohydrateKaliyamoorthy Panneerselvam,^a Tian-Huey Lu,^{a*} Ta-Yung Chi,^b Shu-Fang Tung^c and Chung-Sun Chung^b^aDepartment of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China, ^bDepartment of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China, and ^cSouthern Instrument Center, National Cheng Kung University, Tainan, Taiwan 701, Republic of China

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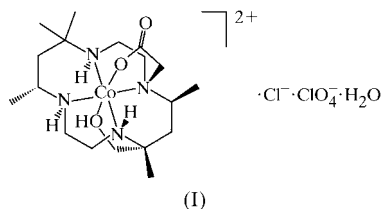
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In the title compound, $[\text{Co}(\text{C}_{18}\text{H}_{37}\text{N}_4\text{O}_3)](\text{ClO}_4)\text{Cl}\cdot\text{H}_2\text{O}$, the Co^{III} ion has a distorted octahedral geometry, with four N atoms and two O atoms constituting the coordination sphere. The crystal structure is stabilized by a three-dimensional network of hydrogen bonds.

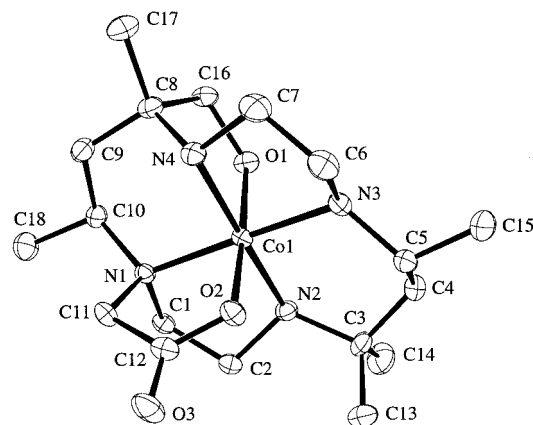
Comment

There is much interest in modification of ligand reactivity on complex formation, particularly in the oxidation and reduction of coordinated ligands (Constable, 1990; Chen *et al.*, 1994). In the presence of suitable reagents, a complex in which a metal ion has an atypical oxidation number can undergo an intramolecular reaction that generates a complex with an oxidized form of the ligand. We describe here the crystal structure of the title compound, (I), in which one of the methyl groups in the starting ligand *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetic acid has been oxidized to a hydroxymethyl group.



The coordination around the Co^{III} ion is six-coordinate in a distorted octahedral geometry, with the four N atoms of the macrocyclic ligand in equatorial positions and two O atoms in axial positions. This macrocyclic ligand is hexadentate whereas

the unoxidized ligand is pentadentate (Xu *et al.*, 1988; Panneerselvam *et al.*, 1998). The additional ligating $-\text{CH}_2\text{OH}$ group arises by oxidation of the original. House *et al.* (1984) found that direct O_2 oxidation of *trans*- $[\text{CoCl}_2(\text{C-meso-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane})]\text{ClO}_4$ in refluxing methanol containing triethylamine resulted in the oxidation of one of the geminal dimethyl groups to form a pentadentate N_4O ligand with a coordinated $-\text{CH}_2\text{OH}$ group. The present complex is similar. The macrocyclic ligand adopts the usual stable conformation with the two six-membered rings in the chair form and the two five-membered rings in the *gauche* form. The four chiral N atoms are *1RS*, *4RS*, *8SR* and *11SR*, and the methyl C atoms are *7RS*, *12RS* and *14SR*. The configuration of the four chiral N atoms in the complex cation corresponds to that of the *trans*-III diastereomer of planar $[\text{Ni}(1,4,8,11\text{-tetraazacyclotetradecane})]^{2+}$ (Bosnich *et al.*, 1965).

**Figure 1**

The structure of the cation in (I) showing 30% probability displacement ellipsoids. The chloride anion, uncoordinated water, perchlorate anion and H atoms have been excluded for clarity.

The average $\text{Co}-\text{N}$ distance [1.985 (3) Å] is similar to that in the *trans*-dichloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) cation [1.978 (4) Å; Sosa-Torres & Toscano, 1997], but longer than that in the [1,4-*N,N'*-bis(carboxymethyl)-1,4,8,11-tetraazacyclotetradecane]cobalt(III) cation [1.969 (4) Å; Ware *et al.*, 1996]; it is shorter than that in the *trans*-dichloro-(2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(III) cation [2.011 (7) Å; Bembi *et al.*, 1991]. The $\text{Co}-\text{O}(\text{carboxyl})$ distance [1.867 (2) Å] is shorter than that found in the [1,4-*N,N'*-bis(carboxymethyl)-1,4,8,11-tetraazacyclotetradecane]cobalt(III) cation [1.887 (3) and 1.892 (3) Å; Ware *et al.*, 1996]. The $\text{Co}-\text{O}(\text{hydroxy})$ distance [1.925 (2) Å] is shorter than that found in the chloro(5-hydroxymethyl-5,7,12,12,14-pentamethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(III) cation (1.963 Å; House *et al.*, 1984). Hydrogen bonds (Table 2) between the imino groups, the chloride anion, the disordered perchlorate anion and the water molecule help stabilize the crystal structure.

Experimental

Samples of $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$ and the ligand, *i.e.* *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetic acid, were prepared according to literature methods (Bauer & Drinkard, 1960; Xu *et al.*, 1988). $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$ (1.0 g) and the ligand (1.0 g) were suspended in water (50 ml). The mixture was heated on a water bath for 2 h. An aliquot of aqueous HCl (4 ml, 12 M) was added dropwise to the solution. The solution was heated for another 30 min, NaClO_4 (4.0 g) was added and the solution was cooled. The green powder obtained was filtered off, the filtrate left to stand in air and purple crystals were obtained. Crystals suitable for X-ray analysis were obtained from 0.1 M HCl by slow evaporation.

Crystal data

$[\text{Co}(\text{C}_{18}\text{H}_{37}\text{N}_4\text{O}_3)](\text{ClO}_4)\text{Cl} \cdot \text{H}_2\text{O}$	$D_x = 1.521 \text{ Mg m}^{-3}$
$M_r = 569.36$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 10.789$ (3) Å	$\theta = 5.97\text{--}15.75^\circ$
$b = 8.918$ (2) Å	$\mu = 0.955 \text{ mm}^{-1}$
$c = 25.847$ (4) Å	$T = 293$ (2) K
$\beta = 91.79$ (2)°	Pillar, purple
$V = 2485.6$ (8) Å ³	$0.25 \times 0.22 \times 0.16 \text{ mm}$
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.047$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 25^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -12 \rightarrow 12$
$T_{\text{min}} = 0.795$, $T_{\text{max}} = 0.858$	$k = 0 \rightarrow 10$
4613 measured reflections	$l = 0 \rightarrow 30$
4361 independent reflections	3 standard reflections every 100 reflections
2981 reflections with $I > 2\sigma(I)$	intensity decay: 1%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2]$
$wR(F^2) = 0.109$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.013$	$(\Delta/\sigma)_{\text{max}} = 0.001$
4361 reflections	$\Delta\rho_{\text{max}} = 0.51 \text{ e \AA}^{-3}$
339 parameters	$\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$

Table 1

Selected bond lengths (Å).

Co1—O2	1.867 (2)	Co1—N4	1.967 (3)
Co1—O1	1.925 (2)	Co1—N2	1.997 (3)
Co1—N3	1.966 (3)	Co1—N1	2.011 (3)

The maximum 2θ for data collection is 50.0° and the data collection would not go beyond this limit because of the crystal quality. The H atoms were fixed geometrically, but H atoms of the water molecule and the hydroxy group were located from the difference Fourier map. All H atoms were refined with constraints.

Table 2

Hydrogen-bonding geometry (Å, °).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
O1—H1O1 \cdots Cl2	0.99	1.88	2.865 (2)	175
N2—H1N2 \cdots Cl2	0.91	2.46	3.350 (3)	167
N3—H1N3 \cdots Cl2 ⁱ	0.91	2.40	3.304 (3)	173
N4—H1N4 \cdots OW1 ⁱⁱ	0.91	1.98	2.854 (4)	160
OW1—H1OW \cdots O3	0.84	2.08	2.840 (4)	150
OW1—H2OW \cdots O4 ⁱⁱⁱ	0.88	2.23	2.918 (12)	135
OW1—H2OW \cdots O5 ⁱⁱⁱ	0.88	2.21	2.975 (14)	145

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $1 - x, -y, -z$; (iii) $x, y - 1, z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *NRCVAX*; software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1092). Services for accessing these data are described at the back of the journal.

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