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cis-Dichloro(*C*-*rac*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane-*N*,*N'*,*N''*,*N'''*)-cobalt(III) Chloride, $[CoCl_2(C_{12}H_{28}N_4)]Cl$

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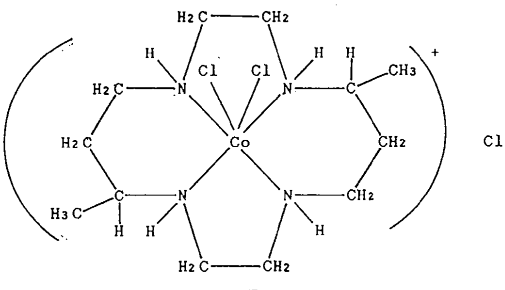
Abstract

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).



(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.

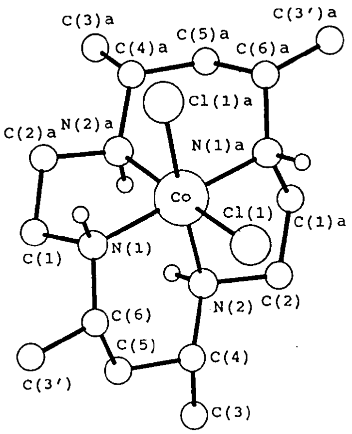


Fig. 1. A perspective view of the complex cation (*a* denotes symmetry transformation $1-x, y, \frac{1}{2}-z$).

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

$[CoCl_2(C_{12}H_{28}N_4)]Cl$	Mo $K\alpha$ radiation
$M_r = 393.67$	$\lambda = 0.71073$ Å

Monoclinic
$C2/c$
$a = 9.178$ (1) Å
$b = 11.722$ (2) Å
$c = 16.100$ (5) Å
$\beta = 90.96$ (2)°
$V = 1731.9$ (6) Å^3
$Z = 4$
$D_x = 1.510$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 7.42$–17.5°
$\mu = 1.45$ mm^{-1}
$T = 298$ (3) K
Parallelepiped
0.44 × 0.32 × 0.28 mm
Deep violet

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{\min} = 0.873$, $T_{\max} = 0.999$
2663 measured reflections
2521 independent reflections

2071 observed reflections $[I \geq 2.5(I)]$
$R_{\rm int} = 0.019$
$\theta_{\max} = 29.9$°
$h = 0 \rightarrow 12$
$k = -16 \rightarrow 16$
$l = -22 \rightarrow 22$
3 standard reflections
frequency: 60 min
intensity variation: ±0.5%

Refinement

Refinement on F
$R = 0.045$
$wR = 0.049$
$S = 1.78$
2071 reflections
118 parameters
Only H-atom U's refined
Unit weights applied
$(\Delta/\sigma)_{\max} = 0.059$

$\Delta\rho_{\max} = 0.53$ (8) e Å^{-3}
$\Delta\rho_{\min} = -0.40$ (8) e Å^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient: 0.21 (1) mm
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)

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

	Occupancy	x	y	z	$B_{\rm eq}$
Co	1.00	1/2	0.45528 (5)	1/4	2.695 (23)
Cl(1)	1.00	0.42314 (14)	0.59486 (8)	0.16271 (7)	5.15 (5)
Cl(2)	1.00	1/2	0.09937 (10)	1/4	5.17 (7)
N(1)	1.00	0.6964 (3)	0.44819 (25)	0.19995 (21)	3.87 (13)
N(2)	1.00	0.4246 (3)	0.34068 (24)	0.16897 (19)	3.78 (12)
C(1)	1.00	0.7764 (4)	0.3512 (3)	0.2369 (3)	4.75 (20)
C(2)	1.00	0.2627 (5)	0.3440 (4)	0.1740 (3)	5.11 (20)
C(3)	0.35	0.4366 (19)	0.2540 (14)	0.0292 (8)	6.3 (7)
C(3′)	0.65	0.8539 (9)	0.4486 (8)	0.0700 (5)	6.7 (4)
C(4)	1.00	0.4677 (6)	0.3464 (4)	0.0802 (3)	5.47 (22)
C(5)	1.00	0.6285 (7)	0.3475 (4)	0.0689 (3)	6.3 (3)
C(6)	1.00	0.7095 (6)	0.4483 (4)	0.1077 (3)	5.87 (22)

Table 2. *Selected geometric parameters* (Å, °)

Co—Cl(1)	2.262 (1)	N(2)—C(4)	1.492 (6)
Co—N(1)	1.989 (3)	C(1)—C(2$^{\rm i}$)	1.488 (7)
Co—N(2)	1.989 (3)	C(3)—C(4)	1.39 (1)
N(1)—C(1)	1.473 (5)	C(3′)—C(6)	1.468 (9)
N(1)—C(6)	1.491 (6)	C(4)—C(5)	1.490 (8)
N(2)—C(2)	1.490 (5)	C(5)—C(6)	1.525 (8)
Cl(1)—Co—Cl(1$^{\rm i}$)	87.34 (5)	Co—N(2)—C(2)	106.5 (3)
Cl(1)—Co—N(1)	93.1 (1)	Co—N(2)—C(4)	120.2 (3)
Cl(1)—Co—N(1$^{\rm i}$)	90.4 (1)	C(2)—N(2)—C(4)	109.4 (3)
Cl(1)—Co—N(2)	88.83 (9)	N(1)—C(1)—C(2$^{\rm i}$)	107.9 (3)
Cl(1)—Co—N(2$^{\rm i}$)	176.05 (9)	N(2)—C(2)—C(1$^{\rm i}$)	108.1 (3)
N(1)—Co—N(1$^{\rm i}$)	175.2 (1)	N(2)—C(4)—C(3)	118.5 (7)
N(1)—Co—N(2)	90.8 (1)	N(2)—C(4)—C(5)	113.3 (4)
N(1)—Co—N(2$^{\rm i}$)	86.0 (1)	C(3)—C(4)—C(5)	97.4 (9)
N(2)—Co—N(2$^{\rm i}$)	95.0 (1)	C(4)—C(5)—C(6)	115.7 (4)
Co—N(1)—C(1)	108.5 (2)	N(1)—C(6)—C(5)	111.1 (4)
Co—N(1)—C(6)	119.5 (3)	N(1)—C(6)—C(3′)	120.0 (6)
C(1)—N(1)—C(6)	110.8 (3)	C(3′)—C(6)—C(5)	105.6 (5)

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

The structure was solved by direct and Fourier methods, and refined using least-squares techniques. H atoms were located by difference Fourier synthesis and theoretical calculations. All computation was performed using the *NRCVAX* system of programs (Gabe, Le Page, White & Lee, 1987).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: AS1107). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dipyridiniomethane Chloropentafluoroosmate(IV), $[(C_5H_5N)_2CH_2][OsF_5Cl]$

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Abstract

The sublattice of the mixed-ligand complex anions, $[OsF_5Cl]^{2-}$, of the title compound [*N*,*N*-methylenepyridinium chloropentafluoroosmate(IV)] is completely ordered. Due to the mutual *trans* influence in the asymmetric Cl—Os—F axis, the Os—F distance of

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