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trans-Dichloro[(2*RS*,5*RS*,9*SR*,12*RS*)-2,5,9,12-tetraazatridecane]cobalt(III) Perchlorate, $[CoCl_2(C_9H_{24}N_4)]ClO_4$

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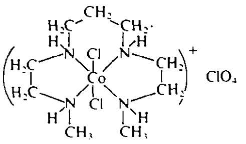
Abstract

The coordination geometry about Co^{III} is slightly distorted octahedral. The four donor N atoms of the tetraamine form the equatorial plane of the coordination octahedron and two Cl ligands occupy the apices. The alternate five-, six- and five-membered chelate rings have stable skew, chair and skew conformations, respectively. The perchlorate group binds the tetraamine groups through weak hydrogen bonds.

Comment

Previous studies indicate that the chelate ring sizes of the cobalt(III) complexes of tetraamines have significant effects on their structures; *cis* isomers (*cis*-α and *cis*-β) are more stable than *trans* isomers for the dichloro(triethylenetetraamine)cobalt(III) ion (Basolo, 1948) and the dinitro(1,4,7,10-tetraazacyclododecane)cobalt(III) ion (Iitaka, Shina & Kimura, 1974). On the other hand, the dichloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) ion (Bosnich, Poon & Tobe, 1965) and the dichloro(1,10-diamino-4,7-diazadecane)cobalt(III) ion (Payne, 1973) exhibit *trans* configurations.

The ligand 2,5,9,12-tetraazatridecane (α,ω-N-Me_2-2,3,2-tet) was prepared by the procedure described by Clay, Corr, Micheloni & Paoletti (1985). An aqueous solution of α,ω-N-Me_2-2,3,2-tet.4HCl (1.0 g) was passed through an anion-exchange column (Amberlite IR400, OH^- form) directly into an aqueous solution of $Na_3[Co(CO_3)_3].3H_2O$ (1.08 g) (Bauer & Drinkard, 1960). The resulting solution was heated to 373 K with stirring. A small amount of HCl was added, cooled to room temperature and a few drops of $HClO_4$ added. The precipitate was filtered and washed with ethanol. Green single crystals of the title complex (I) were obtained by slow evaporation from aqueous solution.



(I)

The crystal is comprised of discrete ions, linked by weak hydrogen bonds between the perchlorate ion and the amine groups of the complex ion. The coordination geometry about Co^{III} is slightly distorted octahedral. The four donor N atoms of the tetraamine in the equatorial plane are coplanar within ±0.06 (2) Å. The four Co—N distances are in a relatively large range of 1.93 (1)–2.03 (1) Å. The two *trans* Cl atoms occupy the apices, with a mean Co—Cl distance of 2.250 (2) Å, which agrees well with the mean Co—Cl distance of 2.255 (8) Å found in the *trans*-dichloro(1,10-diamino-4,7-diazadecane)cobalt(III) cation (Payne, 1973).

The complex has 2*RS*, 5*RS*, 9*SR*, 12*RS* configurations at the chiral N centres. The alternate five-, six- and five-membered chelate rings have the stable skew, chair and skew conformations, respectively. Consequently, the four donor N atoms in this complex nearly match the symmetry properties of the Co^{III} orbitals; a very stable *trans* complex is found.

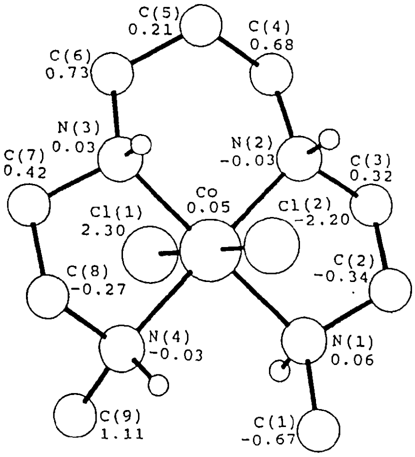


Fig. 1. A perspective view of the complex cation. The displacements from the best plane formed by atoms N(1), N(2), N(3) and N(4) are indicated.

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Experimental

Crystal data

$[CoCl_2(C_9H_{24}N_4)]ClO_4$
M_r = 417.60
Orthorhombic
$Pbc2_1$
a = 6.366 (2) Å
b = 15.052 (2) Å
c = 17.574 (3) Å
V = 1683.9 (6) Å^3
Z = 4
D_x = 1.647 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8.7–18.6°
μ = 1.51 mm^{-1}
T = 298 K
Rectangular pillar
0.34 × 0.16 × 0.13 mm
Green

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
T_{min} = 0.82, T_{max} = 0.99
2933 measured reflections
2524 independent reflections

1703 observed reflections [$I > 2.5\sigma(I)$]
R_{int} = 0.022
θ_{max} = 29.9°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 24$
3 standard reflections
frequency: 60 min
intensity variation: ±1%

Refinement

Refinement on F
R = 0.056
wR = 0.054
S = 0.80
1703 reflections
209 parameters
Only H-atom U's refined
Unit weights applied

$(\Delta/\sigma)_{max}$ = 0.250
$\Delta\rho_{max}$ = 0.68 (5) e Å^{-3}
$\Delta\rho_{min}$ = −0.55 (5) e Å^{-3}
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)

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

	x	y	z	B_{eq}
Co	0.75064 (16)	0.40604 (6)	0.32300	0.0225 (3)
Cl(1)	0.4809 (3)	0.50179 (15)	0.3145 (3)	0.0313 (9)
Cl(2)	1.0203 (3)	0.30954 (13)	0.3312 (3)	0.0348 (11)
Cl(3)	0.0844 (4)	0.2507 (4)	0.0693 (3)	0.0485 (12)
O(1)†	0.230 (3)	0.1788 (12)	0.0559 (11)	0.075 (4)
O(11)†	0.101 (8)	0.213 (3)	0.006 (3)	0.079 (11)
O(2)†	−0.121 (4)	0.2139 (19)	0.0567 (18)	0.102 (7)
O(21)†	−0.083 (7)	0.300 (3)	0.029 (3)	0.103 (11)
O(3)†	0.208 (3)	0.3263 (12)	0.0403 (10)	0.073 (4)
O(31)†	−0.093 (8)	0.235 (4)	0.123 (3)	0.085 (12)
O(4)†	0.075 (3)	0.2555 (11)	0.1503 (9)	0.061 (4)
O(41)†	0.131 (6)	0.3221 (23)	0.1176 (20)	0.057 (7)
N(1)	0.5457 (10)	0.3071 (4)	0.3284 (11)	0.039 (4)
N(2)	0.7439 (16)	0.3841 (7)	0.2147 (7)	0.040 (5)
N(3)	0.9558 (10)	0.5032 (4)	0.3143 (7)	0.024 (3)
N(4)	0.7773 (17)	0.4224 (7)	0.4373 (8)	0.039 (4)
C(1)	0.552 (3)	0.2425 (10)	0.3924 (12)	0.053 (8)
C(2)	0.548 (3)	0.2610 (10)	0.2559 (12)	0.054 (8)
C(3)	0.5547 (20)	0.3255 (10)	0.1975 (9)	0.052 (6)
C(4)	0.755 (3)	0.4563 (9)	0.1603 (7)	0.050 (6)
C(5)	0.962 (3)	0.5110 (11)	0.1772 (10)	0.055 (7)
C(6)	0.944 (3)	0.5625 (11)	0.2482 (9)	0.038 (6)
C(7)	0.962 (3)	0.5534 (10)	0.3877 (8)	0.033 (5)
C(8)	0.954 (3)	0.4858 (10)	0.4507 (9)	0.045 (6)
C(9)	0.599 (3)	0.4547 (12)	0.4833 (9)	0.057 (7)

† The occupancy factors of O(1), O(11), O(2), O(21), O(3), O(31), O(4) and O(41) are 0.7, 0.3, 0.6, 0.4, 0.7, 0.3, 0.7 and 0.3, respectively.

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

Co—Cl(1)	2.2467 (22)	N(2)—C(4)	1.449 (18)
Co—Cl(2)	2.2532 (22)	N(3)—C(6)	1.466 (18)
Co—N(1)	1.982 (6)	N(3)—C(7)	1.495 (18)
Co—N(2)	1.933 (13)	N(4)—C(8)	1.491 (19)
Co—N(3)	1.967 (7)	N(4)—C(9)	1.477 (18)
Co—N(4)	2.031 (13)	C(2)—C(3)	1.41 (3)
N(1)—C(1)	1.488 (24)	C(4)—C(5)	1.580 (25)
N(1)—C(2)	1.45 (3)	C(5)—C(6)	1.47 (3)
N(2)—C(3)	1.523 (17)	C(7)—C(8)	1.505 (22)
Cl(1)—Co—Cl(2)	179.72 (13)	C(1)—N(1)—C(2)	110.5 (11)
Cl(1)—Co—N(1)	88.97 (21)	Co—N(2)—C(3)	108.1 (9)
Cl(1)—Co—N(2)	91.5 (3)	Co—N(2)—C(4)	121.3 (8)
Cl(1)—Co—N(3)	91.44 (20)	C(3)—N(2)—C(4)	110.1 (12)
Cl(1)—Co—N(4)	93.0 (3)	Co—N(3)—C(6)	118.6 (9)
Cl(2)—Co—N(1)	90.81 (21)	Co—N(3)—C(7)	109.0 (8)
Cl(2)—Co—N(2)	88.3 (3)	C(6)—N(3)—C(7)	112.2 (10)
Cl(2)—Co—N(3)	88.78 (20)	Co—N(4)—C(8)	107.3 (9)
Cl(2)—Co—N(4)	87.2 (3)	Co—N(4)—C(9)	121.1 (10)
N(1)—Co—N(2)	84.5 (7)	C(8)—N(4)—C(9)	106.4 (12)
N(1)—Co—N(3)	178.2 (6)	N(1)—C(2)—C(3)	108.0 (12)
N(1)—Co—N(4)	95.7 (6)	N(2)—C(3)—C(2)	106.0 (12)
N(2)—Co—N(3)	93.7 (5)	N(2)—C(4)—C(5)	108.0 (12)
N(2)—Co—N(4)	175.5 (4)	C(4)—C(5)—C(6)	111.6 (13)
N(3)—Co—N(4)	86.0 (5)	N(3)—C(6)—C(5)	110.3 (13)
Co—N(1)—C(1)	120.6 (11)	N(3)—C(7)—C(8)	107.0 (11)
Co—N(1)—C(2)	108.0 (11)	N(4)—C(8)—C(7)	110.0 (12)

The structure was solved using the Patterson function. Refinement was by full-matrix least squares using anisotropic temperature factors. The H atoms were found by theoretical calculations. Calculations were performed using *NRCVAX* (Gabe, Le Page, White & Lee, 1987). The high value of the R factor seems to be due to the disordered perchlorate group.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71478 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1032]

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