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[1,4-Bis(pyridyl-2-ylmethyl)-1,4-diazacycloheptane]chlorocobalt(II) perchlorate

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The crystal structure of a Co^{II} complex with 1,4-diazacycloheptane (DACH) functionalized by two additional pyridine donor pendants, $[CoCl(L)](ClO_4)$, where L = 1,4-bis(pyridyl-2-ylmethyl)-DACH ($C_{17}H_{22}N_4$), has been determined by X-ray diffraction analysis. In the mononuclear complex, the Co^{II} center is pentacoordinated by the four nitrogen donors of the ligand and one axial chloride anion, resulting in a coordination sphere intermediate between ideal square-pyramidal and trigonal bipyramidal. It forms a one-dimensional linear structure through intermolecular C—H···Cl and C—H···O hydrogen-bonding interactions.

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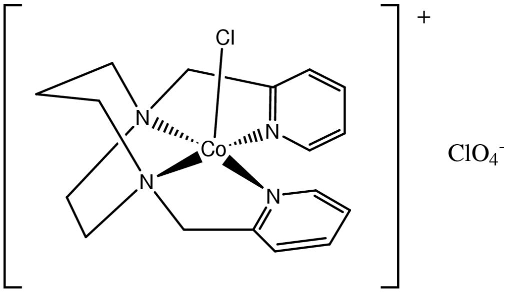
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.049
wR factor = 0.091
Data-to-parameter ratio = 14.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Diazamesocyclic ligands occupy an important role in the coordination chemistry involving acyclic and macrocyclic polyamine ligands, due to their stronger ligand fields and further functionalizations (Mills *et al.*, 1990; Musker, 1992). 1,5-Diazacyclooctane (DACO) and 1,4-diazacycloheptane (DACH) are the most typical examples of diazamesocyclic ligands. So far, some derivatives of diazamesocyclic ligands bearing donor pendants and their metal complexes have been reported (West & Legg, 1976; Lai *et al.*, 1999), and the Ni^{II} complexes with such functionalized ligands were shown to have very interesting properties and functions (Grapperhaus & Darensbourg, 1998).



(I)

In our efforts to investigate systematically the control of the structures and properties, as well as the coordination chemistry of diazamesocyclic ligands by modification of their backbone, we have reported a variation of the coordination modes and magnetic properties of Cu^{II} (Bu *et al.*, 2000) and Ni^{II} (Bu *et al.*, 2001) complexes by altering the donor pendants. However, reports of the Co^{II} complexes of such ligands are still quite rare. To the best of our knowledge, only three structures of these complexes have been reported (Du *et al.*, 2001; Guo *et al.*, 2002). As a continuation of our efforts, we report here the crystal structure of a Co^{II} complex of 1,4-

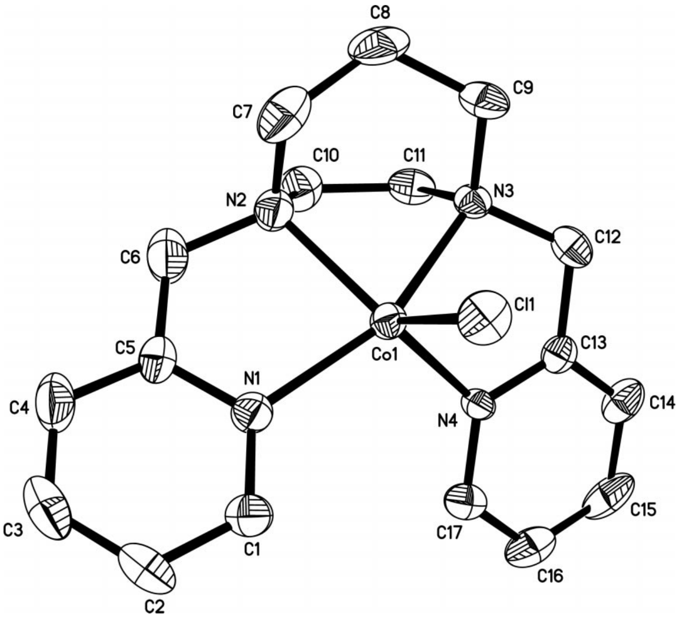


Figure 1
*ORTEP*II view (Johnson, 1976) of the $[\mathrm{CoCl}(L)]^+$ cation in the title complex, shown with 30% probability displacement ellipsoids

bis(pyridyl-2-ylmethyl)-DACH, denoted as $[\mathrm{CoCl}(L)](\mathrm{ClO_4})$, (I).

The structure of (I) consists of a discrete $[\mathrm{CoCl}(L)]^+$ cation and a perchlorate counter-anion. The central $\mathrm{Co^{II}}$ atom is pentacoordinated by two N atoms of the DACH ring, two nitrogen donors of the pyridine pendants and a chloride anion, as shown in Fig. 1. The coordination geometry around the $\mathrm{Co^{II}}$ center can be best described as a distorted square-pyramid or trigonal bipyramid, with a τ value of 0.5 ($\tau = 0$ for an ideal square-pyramid and $\tau = 1$ for an ideal trigonal bipyramid; Addison *et al.*, 1984). The two N atoms of the pendant pyridine groups and the other two N atoms of the DACH ring are in *cis* positions in the coordination polyhedron and the $\mathrm{Co^{II}}$ ion deviates from the least-squares N1/N2/N3/N4 basal plane by 0.58 (5) Å. In the complex cation, the DACH ring takes the normal boat configuration and the dihedral angle between the two pyridine rings is 46.5 (6)°. The ligand gives rise, with the $\mathrm{Co^{II}}$ center, to two five-membered chelate rings (N1/C5/C6/N2/Co1 and N3/C12/C13/N4/Co1), forming an N2—Co1—N1 angle of 82.45 (18)° and an N3—Co1—N4 angle of 78.82 (16)°. The Co—N bond distances are in the range 2.048 (4)–2.136 (4) Å. The distances of the two $\mathrm{Co{-}N_{DACH}}$ bonds are longer than those of the $\mathrm{Co{-}N_{pyridine}}$ bonds, which indicates the weaker donor character.

A notable feature of (I) is the formation of a one-dimensional linear arrangement along the *b* direction, linked through intermolecular C12—H12B···Cl1$^{\mathrm{i}}$ [symmetry code: (i) $x, y+1, z$] interactions, as depicted in Fig. 2, and the adjacent Co···Co separation in this chain is 7.300 Å. There also exists an intermolecular C17—H17*A*···O4$^{\mathrm{ii}}$ [symmetry code: (ii) $-x+1, -\frac{1}{2}+y, \frac{1}{2}-z$] bond between the $[\mathrm{CoCl}(L)]^+$ cation and the perchlorate anion, which may further stabilize the crystal structure.

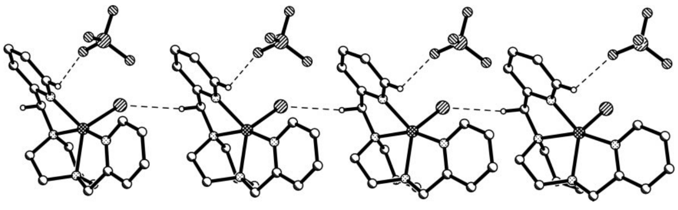


Figure 2
View of the one-dimensional arrangement along the *b* direction (irrelevant H atoms have been omitted for clarity).

Experimental

The title complex was prepared by mixing equimolar amounts of $\mathrm{Co(ClO_4)_2{\cdot}6H_2O}$ and 1,4-bis(pyridyl-2-ylmethyl)-1,4-diazacycloheptane in methanol/water. The pH value of this solution was adjusted with dilute KOH aqueous solution to *ca* 7. The reaction mixture was filtered and left to stand at room temperature. Purple crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent.

Crystal data

$[\mathrm{CoCl(C_{17}H_{22}N_4)}](\mathrm{ClO_4})$
$M_r = 476.22$
Monoclinic, $P2_1/c$
$a = 12.286$ (4) Å
$b = 7.300$ (2) Å
$c = 22.573$ (7) Å
$\beta = 95.731$ (6)°
$V = 2014.5$ (10) Å^3
$Z = 4$
$D_x = 1.570$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8012 reflections
$\theta = 1.7$–25.0°
$\mu = 1.15$ mm^{-1}
$T = 293$ (2) K
Prism, purple
0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART 1000 diffractometer
ω scans
Absorption correction: multi-scan [*SAINT* (Bruker, 1998) and *SADABS* (Bruker, 1998)]
$T_{\min} = 0.725$, $T_{\max} = 0.803$
8055 measured reflections
3555 independent reflections
1824 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.084$
$\theta_{\max} = 25.0°$
$h = -13 \rightarrow 14$
$k = -7 \rightarrow 8$
$l = -19 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.091$
$S = 0.98$
3555 reflections
253 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0188P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.52$ e Å^{-3}
$\Delta\rho_{\min} = -0.51$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—N4	2.048 (4)	Co1—N3	2.137 (4)
Co1—N1	2.070 (4)	Co1—Cl1	2.253 (2)
Co1—N2	2.102 (4)		
N4—Co1—N1	109.30 (17)	N2—Co1—N3	75.50 (17)
N4—Co1—N2	126.72 (18)	N4—Co1—Cl1	105.86 (11)
N1—Co1—N2	82.45 (17)	N1—Co1—Cl1	100.36 (13)
N4—Co1—N3	78.79 (16)	N2—Co1—Cl1	123.36 (15)
N1—Co1—N3	156.62 (17)	N3—Co1—Cl1	98.21 (12)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C12—H12$B\cdots$Cl1^{i}	0.97	2.78	3.664 (5)	151
C17—H17$A\cdots$O4^{ii}	0.93	2.49	3.164 (9)	129

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

The C-bonded H atoms were placed in geometrically calculated positions and included in the final refinement in the riding-model approximation with displacement parameters derived from those of the atoms to which they were bonded.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 1998); software used to prepare material for publication: *SHELXL*97.

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