

# [1,5-Bis(1-methyl-1*H*-imidazol-2-ylmethyl- $\kappa$ N<sup>3</sup>)-1,5-diazacyclooctane-*N,N'*]chlorocobalt(II) perchlorate

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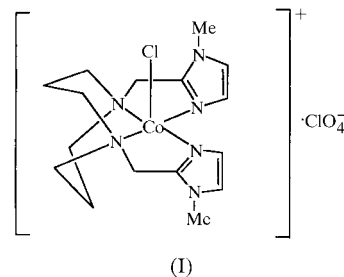
The crystal structure of the title compound,  $[\text{CoCl}(\text{C}_{16}\text{H}_{26}\text{N}_6)]\text{ClO}_4$ , consists of discrete  $[\text{CoCl}(\text{C}_{16}\text{H}_{26}\text{N}_6)]^+$  cations and perchlorate anions. The five-coordinate  $\text{Co}^{\text{II}}$  atom has four nitrogen donors from the new mesocyclic ligand 1,5-bis(1-methyl-1*H*-imidazol-2-ylmethyl)-1,5-diazacyclooctane  $[\text{Co}-\text{N} 2.046(3)-2.214(4) \text{ \AA}]$ , and a chloride anion at the apical site  $[\text{Co}-\text{Cl} 2.3184(13) \text{ \AA}]$ . The coordination geometry of the complex is essentially square pyramidal. The mesocyclic ligand takes a boat-chair configuration and the two imidazole pendants are not coplanar. The dihedral angle between the two imidazole planes is  $15.97^\circ$ . An H atom from the 1,5-diazacyclooctane group effectively blocks the axial coordination site opposite the Cl ligand.

## Comment

1,5-Diazacyclooctane (DACO) derivatives bearing two additional functional donor pendants can strongly coordinate to transitional metal centers, forming square-pyramidal five-coordinate or square-planar four-coordinate complexes (Grapperhaus & Darenbourg, 1998; Nielson *et al.*, 1971; Bu *et al.*, 1999).

The four donor atoms of such tetradentate ligands coordinate to the central metal ions nearly in a plane and the DACO backbone usually adopts a boat-chair configuration. This configuration will force a portion of the chelate framework across to the axial coordination position, and will sterically restrict further axial coordination to the metal center. Therefore, such DACO derivatives can be used as very good ligands for the construction of metal complexes with a square-planar or square-pyramidal configuration. The interesting chemistry of such DACO derivatives prompted us to create more such ligands by modifying DACO with heterocyclic donor pendants to obtain new complexes with functional properties. We synthesized a new mesocyclic ligand functionalized by two imidazole donor pendants, 1,5-bis(1-methyl-

1*H*-imidazol-2-ylmethyl)-1,5-diazacyclooctane and its cobalt(II) complex,  $[\text{CoCl}(\text{C}_{16}\text{H}_{26}\text{N}_6)]\text{ClO}_4$ , (I). We report herein the crystal structure of this new complex.



The structure of (I) comprises discrete  $[\text{CoCl}(\text{C}_{16}\text{H}_{26}\text{N}_6)]^+$  cations and perchlorate anions (Fig. 1). In the complex cation, the  $\text{Co}^{\text{II}}$  atom is five coordinate. 1,5-Bis(1-methyl-1*H*-imidazol-2-ylmethyl)-1,5-diazacyclooctane acts as a tetradentate ligand through one pair of nitrogen donors of the mesocyclic ring and the two N atoms of the imidazole pendants. The coordination geometry about the  $\text{Co}^{\text{II}}$  atom can be described as square pyramidal. The four nitrogen donors of the ligand coordinate to the central  $\text{Co}^{\text{II}}$  in one plane, with a chloride anion occupying an apical position. The  $\tau$  value used to describe the degree of trigonal distortion is 0.006 (Addison *et al.*, 1984), *i.e.* nearly zero, indicating that the distortion is very small. The Co atom is above the mean plane formed by atoms N1, N2, N3 and N5 by  $0.549 \text{ \AA}$  towards the apical Cl ligand. The two imidazole pendants are not coplanar, their planes forming an angle of  $15.97^\circ$ .

The six-membered  $\text{CoNCH}_2\text{CH}_2\text{CH}_2\text{N}$  rings in  $[\text{CoCl}(\text{C}_{16}\text{H}_{26}\text{N}_6)]\text{ClO}_4$  adopt boat-chair configurations. The boat-form ring causes one H atom (H5B on C5) to lie about  $2.509 \text{ \AA}$  from the metal, at the axial position. Thus, the Co atom is well shielded from axial interactions opposite the Cl ligand. All of the  $\text{Co}-\text{N}$  and the  $\text{Co}-\text{Cl}$  distances are normal. The

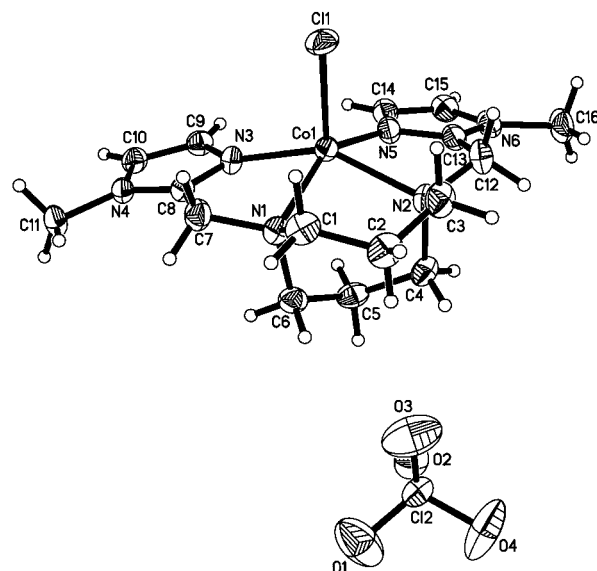


Figure 1

View of the title complex drawn with 30% probability ellipsoids.

conformation of the ligand restricts the placement of the N atoms in the coordination sphere, so the N1—Co1—N2 angle is reduced to 82.41 (14)°, whereas the N3—Co1—N5 angle is 103.38 (14)°.

## Experimental

The ligand 1,5-bis(1-methyl-1*H*-imidazol-2-ylmethyl)-1,5-diazacyclooctane dihydrochloride was prepared by the reaction of 1,5-diazacyclooctane hydrobromide and 1-methyl-2-chloromethylimidazole hydrochloride in ethanol solution in the presence of KOH (Buhle *et al.*, 1943; Billman & Dorman, 1962) and the details will be published elsewhere. A mixture of Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (370 mg, 1 mmol) and 1,5-bis(1-methyl-1*H*-imidazol-2-ylmethyl)-1,5-diazacyclooctane hydrochloride (340 mg, 1 mmol) was dissolved in methanol (30 ml, room temperature). The ligand was neutralized by slow addition of a KOH-methanol solution to the above mixture and the resulting solution was allowed to stand for *ca* 7 d. Purple block-shaped crystals were deposited slowly upon evaporation of the solvent. FT-IR data (KBr pellet, cm<sup>-1</sup>): 3127 (*w*), 2908 (*w*), 1628 (*m*), 1551 (*w*), 1501 (*m*), 1453 (*m*), 1082 (*s*), 762 (*m*), 624 (*m*).

### Crystal data

[CoCl(C <sub>16</sub> H <sub>26</sub> N <sub>6</sub> )]ClO <sub>4</sub>	<i>Z</i> = 2
<i>M<sub>r</sub></i> = 496.26	<i>D<sub>x</sub></i> = 1.576 Mg m <sup>-3</sup>
Triclinic, <i>P</i> 1̄	Mo <i>K</i> α radiation
<i>a</i> = 7.5865 (9) Å	Cell parameters from 2632 reflections
<i>b</i> = 11.8102 (14) Å	<i>θ</i> = 1.70–25.02°
<i>c</i> = 12.2307 (15) Å	<i>μ</i> = 1.112 mm <sup>-1</sup>
<i>α</i> = 78.612 (3)°	<i>T</i> = 293 (2) K
<i>β</i> = 84.519 (2)°	Rectangular, purple
<i>γ</i> = 77.170 (2)°	0.25 × 0.20 × 0.15 mm
<i>V</i> = 1045.9 (2) Å <sup>3</sup>	

**Table 1**

Selected geometric parameters (Å, °).

Co1—N3	2.046 (3)	Co1—N1	2.214 (4)
Co1—N5	2.071 (4)	Co1—Cl1	2.3184 (13)
Co1—N2	2.169 (4)		
N3—Co1—N5	103.38 (14)	N2—Co1—N1	82.41 (14)
N3—Co1—N2	148.09 (15)	N3—Co1—Cl1	107.04 (11)
N5—Co1—N2	79.71 (15)	N5—Co1—Cl1	107.92 (11)
N3—Co1—N1	78.80 (14)	N2—Co1—Cl1	101.91 (10)
N5—Co1—N1	147.75 (15)	N1—Co1—Cl1	101.89 (10)

### Data collection

Bruker SMART 1000 diffractometer	<i>R</i> <sub>int</sub> = 0.048
<i>ω</i> scans	<i>θ</i> <sub>max</sub> = 25.02°
Absorption correction: multi-scan (SADABS; Sheldrick, 1998)	<i>h</i> = -8 → 9
<i>T</i> <sub>min</sub> = 0.732, <i>T</i> <sub>max</sub> = 0.808	<i>k</i> = -14 → 11
4361 measured reflections	<i>l</i> = -11 → 14
3638 independent reflections	4 standard reflections
2856 reflections with <i>I</i> > 2σ( <i>I</i> )	every 400 reflections
	intensity decay: none

### Refinement

Refinement on <i>F</i> <sup>2</sup>	H-atom parameters constrained
<i>R</i> ( <i>F</i> ) = 0.064	<i>w</i> = 1/[σ <sup>2</sup> ( <i>F<sub>o</sub></i> <sup>2</sup> ) + (0.1000 <i>P</i> ) <sup>2</sup> ]
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.163	where <i>P</i> = ( <i>F<sub>o</sub></i> <sup>2</sup> + 2 <i>F<sub>c</sub></i> <sup>2</sup> )/3
<i>S</i> = 1.180	(Δ/σ) <sub>max</sub> = 0.012
3638 reflections	Δρ <sub>max</sub> = 0.87 e Å <sup>-3</sup>
263 parameters	Δρ <sub>min</sub> = -0.73 e Å <sup>-3</sup>

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1118). Services for accessing these data are described at the back of the journal.

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