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Diazido[bis(2-pyridyl)amine-*N*,*N*′]cobalt(III) perchlorate

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Key indicators

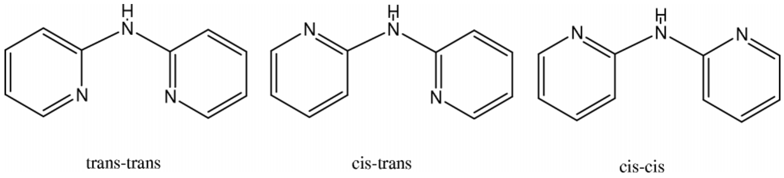
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.006 Å
R factor = 0.045
wR factor = 0.120
Data-to-parameter ratio = 12.3

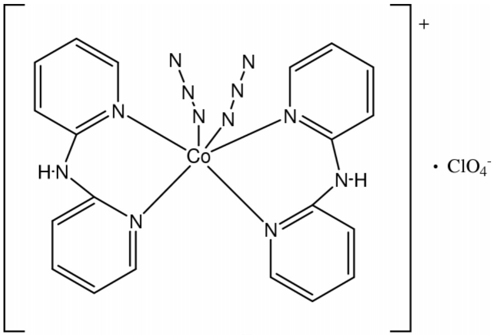
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title complex, $[Co(C_{10}H_9N_3)_2(N_3)_2]ClO_4$, consists of discrete cations and anions. The central Co^{III} ion has an approximate octahedral geometry, coordinated with four N atoms of the pyridine rings of the bis(2-pyridyl)amine ligands in a *trans–trans* mode, and with two terminal N atoms of the azide anions. The crystal structure is stabilized by N—H···O hydrogen bonds between the amino groups and the perchlorate anions.

Comment

Ligands containing aromatic nitrogen heterocycles play a leading role in the molecular self-assembling processes that lead to supramolecular architectures (Jones, 1998; Fujita, 1998). In recent years, bis(2-pyridyl)amine has attracted great interest in the formation of directly bonded linear chains of metal centers (Cotton, Daniels, Jordan & Murillo, 1997; Cotton, Daniels, Murillo & Pascual, 1997; Cotton *et al.*, 1998), and three different coordination modes were found for this feasible ligand (see Scheme below). In order to systematically study the coordination behavior of this ligand, we report herein the crystal structure of the first Co^{III} complex of bis(2-pyridyl)amine with azide co-ligands, namely diazido[bis(2-pyridyl)amine-*N*,*N*′]cobalt(III) perchlorate, (I).





(I)

The structure of (I) comprises a discrete $[Co(C_{10}H_9N_3)_2(N_3)_2]^+$ cation and a ClO_4^- anion. The central Co^{III} ion is six-coordinated by four N-donors of the pyridine rings, and two

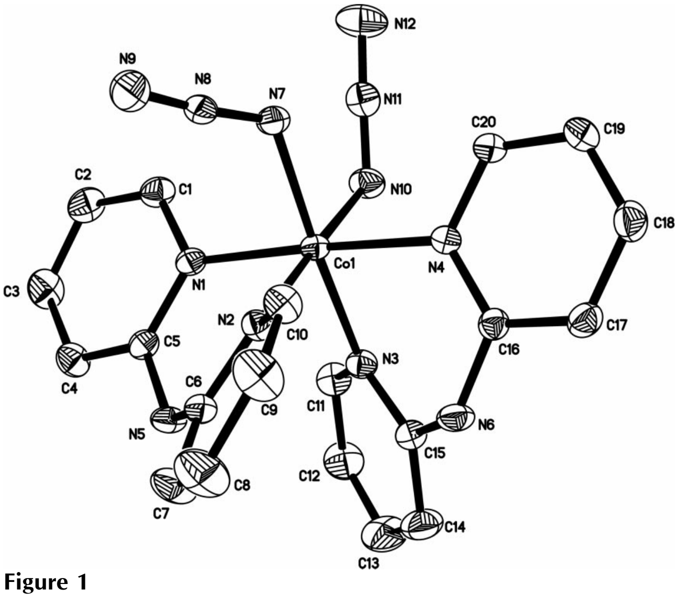


Figure 1
View (*XP* in *SHELXTL*; Bruker, 1998) of the cation in (I) with 30% probability displacement ellipsoids.

terminal N-donors of the azide anions, as shown in Fig. 1.

In the complex cation, the Co^{III} center lies essentially in the least-squares plane defined by N1, N3, N4 and N7, deviating by only 0.0087 (4) Å from this plane. All the bond angles within the plane are very close to 90° (Table 1), and the sum of these bond angles is 360.2°. The N2—Co1—N10 bond angle deviates from linearity (180°) by only 2.39° in this complex, which can be defined as the apex of the octahedron. The six Co—N bond distances are in the range 1.934 (3)–1.980 (3) Å (the mean bond length is 1.957 Å).

The bidentate ligands chelate the Co^{III} atom to form two six-membered coordination rings N1—C5—N5—C6—N2—Co1 and N3—C15—N6—C16—N4—Co1. The pyridine rings in the same ligand are in the normal *trans–trans* mode (Gornitzka & Stalke, 1998) and the dihedral angles are 39.9 (2) and 35.5 (3)°, respectively. Both azide anions are almost linear, with bond angles of 175.1 (4) and 175.9 (4)° for N9—N8—N7 and N12—N11—N10, respectively. The N—N bond lengths in the azide anions are approximately equal to each other, and the longer bonds involve the N atom linking to the metal center. The amino groups of the ligand form N—H···O hydrogen bonds with perchlorate anions, as shown in Fig. 2 (Table 2).

Experimental

A mixture of Co(ClO$_4$)$_2$·6H$_2$O (0.37 g, 1.0 mmol) and bis(2-pyridyl)amine (0.34 g, 2.0 mmol) was dissolved in methanol (40 ml). Then an excess of NaN$_3$ (0.20 g, 3.0 mmol) was added to the above solution under reflux. The resulting red solution was allowed to stand at room temperature for several days and red block-shaped crystals were deposited slowly with the evaporation of the solvent. Yield: 0.23 g (40%). FT–IR data (KBr pellet, cm^{-1}): 3448 (*b*), 3299 (*m*), 2921 (*w*), 2030 (*vs*), 1631 (*vs*), 1586 (*vs*), 1524 (*m*), 1473 (*vs*), 1104 (*s*), 1069 (*s*), 775 (*s*), 625 (*s*). Analysis calculated for the title complex: C 41.07, H 3.10, N 28.75%; found: C 40.88, H 3.34, N 28.66%.

Crystal data

[Co(C$_{10}$H$_9$N$_3$)$_2$(N$_3$)$_2$]ClO$_4$
M_r = 584.84
Triclinic, $P\overline{1}$
a = 8.554 (3) Å
b = 9.201 (3) Å
c = 17.036 (5) Å
α = 74.903 (5)°
β = 78.792 (5)°
γ = 69.739 (5)°
V = 1206.5 (6) Å^3

Z = 2
D_x = 1.610 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5012 reflections
θ = 1.3–25.0°
μ = 0.88 mm^{-1}
T = 298 (2) K
Prism, red
0.25 × 0.20 × 0.20 mm

Data collection

Bruker SMART 1000 diffractometer
ω scans
Absorption correction: multi-scan [*SAINT* (Bruker, 1998) and *SADABS* (Sheldrick, 1997)]
$T_{\min}$ = 0.810, $T_{\max}$ = 0.844
5057 measured reflections

4235 independent reflections
3065 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.025
$\theta_{\max}$ = 25.0°
$h = -9 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -20 \rightarrow 19$

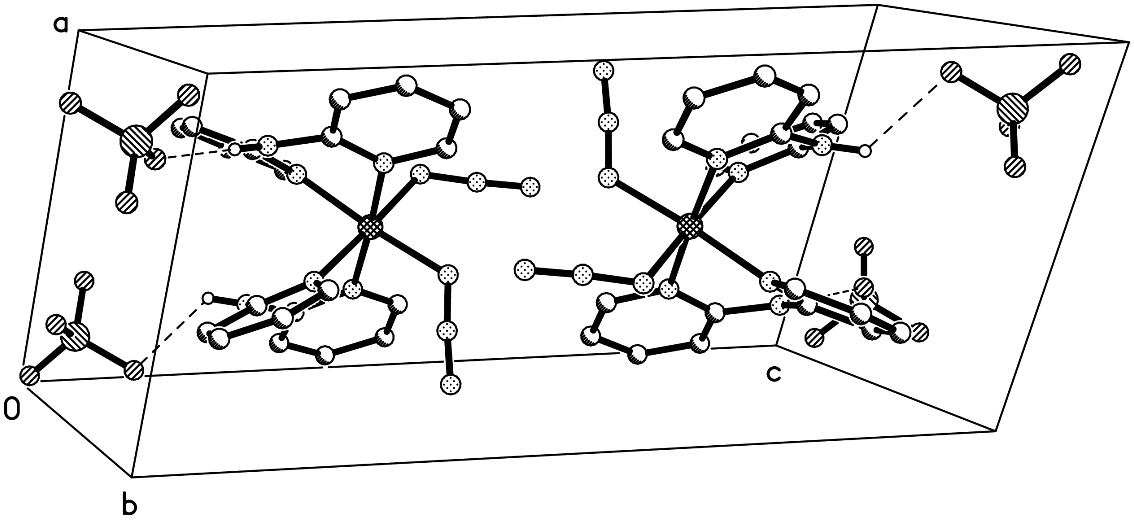


Figure 2
Packing diagram of (I). Bloken lines (or dashed lines) show hydrogen bonds.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.121$
$S = 1.01$
4235 reflections
343 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0594P)^2 + 0.3837P]$ $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.59$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—N7	1.934 (3)	Co1—N2	1.980 (3)
Co1—N10	1.952 (3)	N7—N8	1.206 (4)
Co1—N1	1.953 (3)	N8—N9	1.149 (4)
Co1—N4	1.953 (3)	N10—N11	1.213 (4)
Co1—N3	1.970 (3)	N11—N12	1.154 (5)
N7—Co1—N10	90.59 (13)	N4—Co1—N3	87.34 (12)
N7—Co1—N1	90.33 (13)	N7—Co1—N2	91.77 (13)
N10—Co1—N1	92.46 (13)	N10—Co1—N2	177.61 (13)
N7—Co1—N4	91.45 (13)	N1—Co1—N2	87.10 (12)
N10—Co1—N4	90.41 (13)	N4—Co1—N2	89.95 (12)
N1—Co1—N4	176.60 (12)	N3—Co1—N2	92.23 (12)
N7—Co1—N3	175.82 (13)	N8—N7—Co1	122.8 (2)
N10—Co1—N3	85.42 (13)	N11—N10—Co1	120.3 (3)
N1—Co1—N3	91.08 (12)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*A*···O1	0.86	2.30	2.922 (5)	130
N6—H6*A*···O3$^{\mathrm{i}}$	0.86	2.03	2.888 (5)	179

Symmetry code: (i) $1 - x, 1 - y, 2 - z$.

H atoms were located by geometry and included in the structure-factor calculations.

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* in *SHELXTL* (Bruker, 1998).

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