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A mononuclear cobalt(III) complex of the ligand *N*,*N*′-bis(pyridin-2-ylmethyl)pyrazine-2,3-dicarboxamide

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In the complex, bis[*N*,*N*′-bis(pyridin-2-ylmethyl)pyrazine-2,3-dicarboxamide]cobalt(III) tris(perchlorate) acetonitrile 3.5-solvate, $[Co(C_{18}H_{16}N_6O_2)_2](ClO_4)_3\cdot 3.5CH_3CN$, the result of the reaction of $Co(ClO_4)_2$ with the ligand *N*,*N*′-bis(pyridin-2-ylmethyl)pyrazine-2,3-dicarboxamide, the Co^{II} atom has been oxidized to Co^{III} and has a slightly distorted octahedral coordination geometry. In each ligand, one amide NH proton has been transferred to a non-coordinated pyridine ring, thereby producing a zwitterion. This proton is hydrogen bonded to the carbonyl O atom of the adjacent deprotonated (pyridin-2-ylmethyl)amide substiutent involved in coordination.

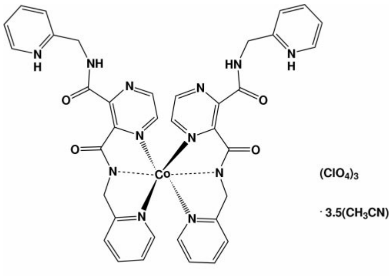
Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.009 Å
Disorder in solvent or counterion
R factor = 0.048
wR factor = 0.119
Data-to-parameter ratio = 12.1

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

Comment

Structures of both copper(II) (Hausmann *et al.*, 2003; Cati *et al.*, 2004) and nickel(II) (Cati *et al.*, 2004) complexes of the ligand pyrazine-2,3-dicarboxylic acid bis[(pyridin-2-ylmethyl)amide] (L), including [2 × 2] grids, have been described recently. Cati *et al.* (2004) also described the synthesis of L and the structure of its triclinic polymorph. The structure of the orthorhombic polymorph of L has also been described recently (Cati & Stoeckli-Evans, 2004).



(I)

The molecular structure of the title complex, (I), is illustrated in Fig. 1. The bond distances and angles are normal for such compounds, and selected geometrical parameters are given in Table 1. The complex cation has pseudo-twofold symmetry (Fig. 2), with the Co atom having a slightly distorted octahedral coordination geometry. The presence of three perchlorate anions per molecule of complex and the fact that, in each ligand, one amide NH proton has been transferred to a non-coordinated pyridine ring, thereby producing a zwitterion, indicates that the original cobalt(II) ion has been oxidized to cobalt(III). The pyridinium H atoms (H6N and H26N) are hydrogen bonded to the carbonyl O atoms, (O1 and O3, respectively) of the adjacent deprotonated (pyridin-2-ylmethyl)amide substituents involved in coordination. Details are given in Table 2 and Fig. 2. This situation is similar to that

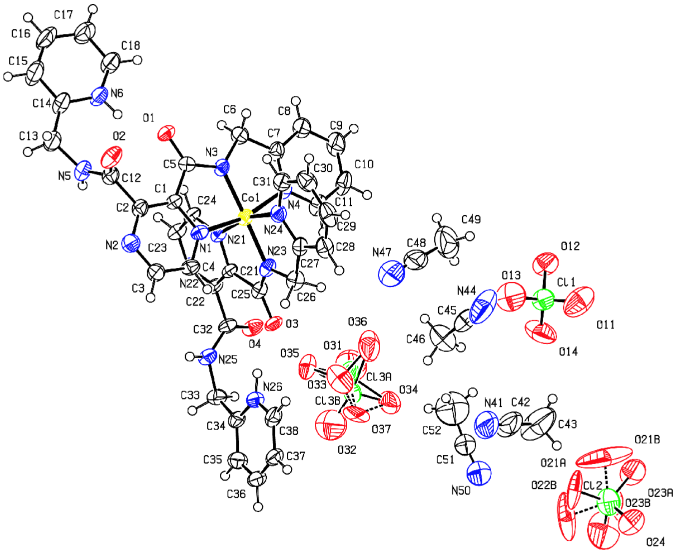


Figure 1
View of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

observed for a dimeric Cu$(BF_4)_2$ complex of *L*, reported by Hausmann *et al.* (2003).

The complex crystallizes as an acetonitrile solvate. One of the solvent molecules is disordered across a centre of symmetry and two of the perchlorate anions are partially disordered. In the crystal structure, molecules are linked by N5—H and N25—H···O(perchlorate) hydrogen bonds (Fig. 3 and Table 2). There are also a number of weaker C—H···N(acetonitrile) and C—H···O(perchlorate) intermolecular hydrogen bonds (details in the CIF).

Experimental

The synthetic and analytical details concerning the ligand, *L*, have been described elsewhere (Cati *et al.*, 2004). The complex was prepared by layering a dichloromethane solution of the ligand (0.156 mmol/6 ml CH_2Cl_2) with a methanol solution of $Co(ClO_4)_2 \cdot 6H_2O$ (0.078 mmol/5 ml CH_3OH), with a narrow buffer zone of methanol. After a few days, large dark-red block-like crystals suitable for X-ray analysis were obtained.

Crystal data

$[Co(C_{18}H_{16}N_6O_2)_2]$-
$(ClO_4)_3 \cdot 3.5C_2H_3N$
$M_r = 1197.71$
Triclinic, $P\bar{1}$
$a = 13.174$ (5) Å
$b = 14.061$ (5) Å
$c = 15.905$ (5) Å
$\alpha = 100.197$ (5)°
$\beta = 111.189$ (5)°
$\gamma = 99.505$ (5)°
$V = 2618.0$ (16) Å^3
$Z = 2$
$D_x = 1.519$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6268 reflections
$\theta = 1.9$–26.0°
$\mu = 0.56$ mm^{-1}
$T = 153$ (2) K
Rod, dark red
0.50 × 0.25 × 0.15 mm

Data collection

Stoe IPDS diffractometer
φ oscillation scans
Absorption correction: none
20558 measured reflections
9551 independent reflections
3742 reflections with $I > 2\sigma(I)$
$R_{int} = 0.087$
$\theta_{max} = 26.0°$
$h = -16 \rightarrow 16$
$k = -17 \rightarrow 17$
$l = -17 \rightarrow 19$

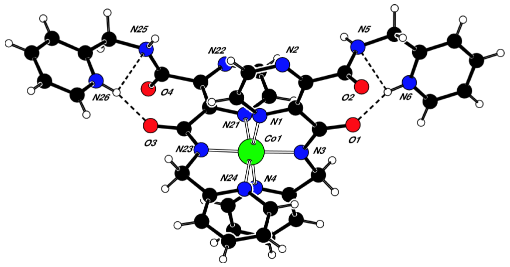


Figure 2
View of the intramolecular hydrogen bonds (dashed lines) in the cation.

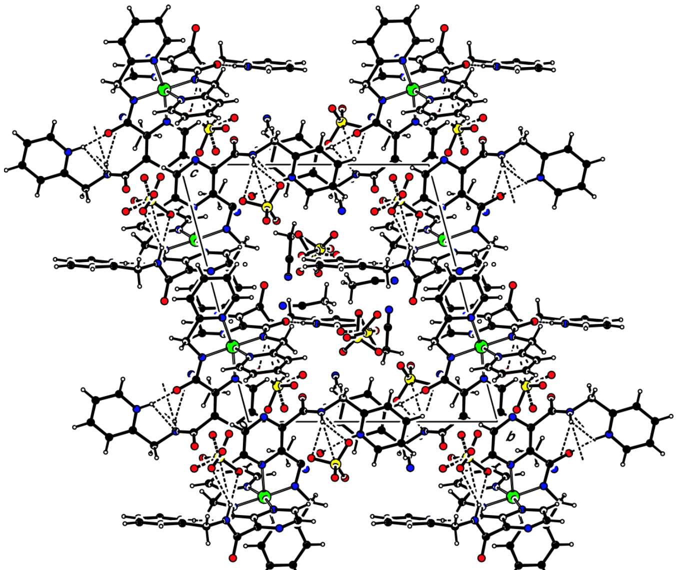


Figure 3
The molecular packing of the complex, viewed down the *a* axis. Hydrogen bonds are indicated by dashed lines.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.120$
$S = 0.99$
9551 reflections
787 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = [\exp\{3(\sin\theta/\lambda)^2\}]/[\sigma^2(F_o^2) + (0.032P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—N3	1.875 (4)	N3—C5	1.327 (5)
Co1—N23	1.875 (4)	N3—C6	1.447 (6)
Co1—N4	1.936 (4)	N5—C12	1.342 (7)
Co1—N24	1.939 (4)	N5—C13	1.448 (6)
Co1—N21	1.944 (4)	N23—C25	1.313 (6)
Co1—N1	1.956 (4)	N23—C26	1.454 (6)
O1—C5	1.264 (5)	N25—C32	1.337 (6)
O2—C12	1.223 (6)	N25—C33	1.449 (6)
O3—C25	1.266 (5)		
N3—Co1—N23	178.17 (19)	N4—Co1—N21	90.78 (17)
N3—Co1—N4	82.89 (16)	N24—Co1—N21	165.34 (15)
N23—Co1—N4	97.92 (16)	N3—Co1—N1	82.90 (15)
N3—Co1—N24	98.94 (17)	N23—Co1—N1	96.28 (16)
N23—Co1—N24	82.71 (17)	N4—Co1—N1	165.79 (15)
N4—Co1—N24	90.42 (17)	N24—Co1—N1	92.05 (16)
N3—Co1—N21	95.70 (16)	N21—Co1—N1	90.36 (16)
N23—Co1—N21	82.65 (17)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N5—H5N$\cdots$O21$A^{\rm i}$	0.90 (3)	2.41 (4)	3.104 (11)	134 (5)
N5—H5N$\cdots$O24$^{\rm i}$	0.90 (3)	2.13 (4)	2.963 (6)	155 (5)
N6—H6N$\cdots$O1	0.90 (6)	1.78 (7)	2.637 (7)	157 (6)
N6—H6N$\cdots$N5	0.90 (6)	2.37 (6)	2.750 (7)	105 (5)
N25—H25N$\cdots$O12$^{\rm ii}$	0.87 (7)	2.29 (6)	3.046 (7)	145 (6)
N25—H25N$\cdots$O14$^{\rm ii}$	0.87 (7)	2.32 (7)	3.075 (8)	145 (6)
N26—H26N$\cdots$O3	0.90 (4)	1.78 (4)	2.664 (6)	165 (4)
N26—H26N$\cdots$N25	0.90 (4)	2.44 (5)	2.749 (7)	101 (4)

Symmetry codes: (i) $x-1, 1+y, z$; (ii) $x-1, y, z$.

All of the H atoms of the complex, including the pyridinium NH H atoms, could be located in Fourier difference maps. However, in the final cycles of refinement the C—H H atoms were included in calculated positions and treated as riding atoms: C—H distances 0.95–0.99 Å, and $U_{\rm iso}$(H) = 1.2 or 1.5(for CH_3) times $U_{\rm eq}$(parent C atom). For the amide and pyridinium (NH) H atoms, the N—H distances were restrained to be 0.89 (2) Å and refined isotropically. The perchlorate anions and the solvent molecules of crystallization undergo considerable thermal motion. For two of the perchlorate anions, it was possible to split the O atoms. The partially occupied acetonotrile molecule is disordered about a centre of symmetry.

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 2000); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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