Bis{2-[3-(2-pyridyl)pyrazol-1-ylmethyl]pyridine}-nickel(II) bis(perchlorate) chloroform disolvate

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In the title compound, $[Ni(C_{14}H_{12}N_4)_2](ClO_4)_2 \cdot 2CHCl_3$, each of the two crystallographically independent nickel(II) complex molecules lies on a twofold axis. In each case, the Ni^{II} atom is coordinated by the six N atoms of two 2-[3-(2-pyridyl)pyrazol-1-ylmethyl]pyridine ligands in a distorted octahedral geometry. The Ni—$N_{pyrazole}$ bond lengths [1.977 (3)–1.997 (4) Å] are appreciably shorter than the Ni—$N_{pyridine}$ bond lengths [2.133 (4)–2.184 (4) Å].

Comment

Many new multinucleating ligands based on pyrazolyl–pyridine chelating units have been prepared and studied (Bell *et al.*, 2002; Ward *et al.*, 2001; Zou *et al.*, 2004). These ligands have proved to be a fertile source of interesting new metal complexes, which encompass a wide range of structural types, and which have made a significant contribution to coordination and supramolecular chemistry. Recently, we have prepared a non-planar flexible ligand, 2-[3-(2-pyridyl)pyrazol-1-ylmethyl]pyridine (*L*). In this paper, we present a nickel complex of this ligand, which crystallizes as the title solvate, $[Ni(L)_2](ClO_4)_2 \cdot 2CHCl_3$, (I).

(I)
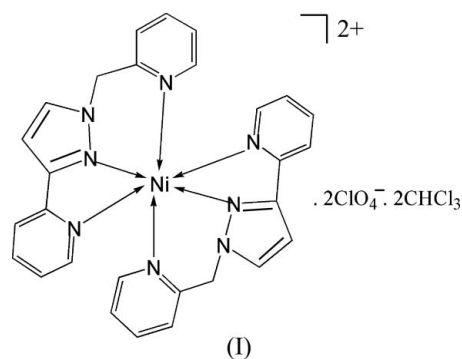
The asymmetric unit of (I) contains two half-cations, two ClO_4^- anions and two $CHCl_3$ molecules (Fig. 1). In both cations, the Ni^{II} atom, on a twofold axis, has a distorted MN_6 octahedral geometry defined by six N atoms of two ligands. All the Ni—N bond distances (Table 1) are within the range expected for such bonds (Singh *et al.*, 2003; Watson *et al.*, 1987). With the Ni^{II} atom, the coordinated tridentate ligand gives rise to one five- and one six-membered chelate rings. The distortions from ideal octahedral geometry are evident from the values presented in Table 1.

The Ni—$N_{pyrazole}$ bond lengths [1.977 (3)–1.997 (4) Å] are appreciably shorter than the Ni—$N_{pyridine}$ bond lengths [2.133 (4)–2.184 (4) Å]. A similar trend was observed in other Ni complexes (Singh *et al.*, 2003; Watson *et al.*, 1987).
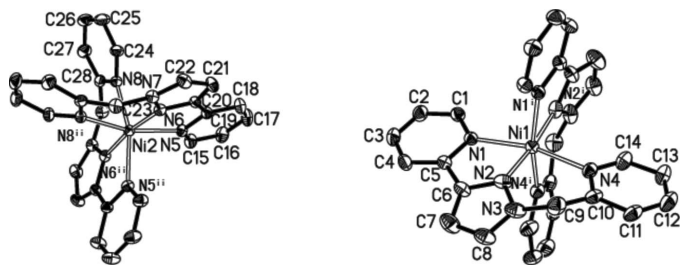
Figure 1
A perspective view of the two independent cations of (I), with 20% probability displacement ellipsoids and the atom-labelling scheme [symmetry code: (i) $-x, y, -z - \frac{1}{2}$; (ii) $1 - x, y, \frac{1}{2} - z$]. The perchlorate groups, chloroform molecules and H atoms have been omitted for clarity.

In the Ni1-containing cation (Fig. 1), the pyrazole ring N2/N3/C8/C7/C6 (A1) and the pyridine ring N1/C1–C5 (B1) are almost coplanar, with a dihedral angle A1/B1 of 4.0 (1)°. The dihedral angles A1/C1 and B1/C1, where C1 denotes the N4/C10–C14 pyridine ring, are 25.01 (1) and 16.6 (1)°, respectively. In the Ni2-containing cation, the corresponding dihedral angles A2/B2, A2/C2 and B2/C2 are 8.5 (1), 31.2 (2) and 35.0 (1)°, respectively (A2, B2 and C2 denote the N6/N7/C20–C22, N5/C15–C19 and N8/C24–C28 rings, respectively). Thus, the six-membered chelate rings exist in boat conformations. Similar chelate ring conformations were observed in the crystal structures of other compounds with this class of non-planar ligands (Mahapatra *et al.*, 1993; Manikandan *et al.*, 1996; Orrell *et al.*, 1997).

Experimental

The ligand 2-[3-(2-pyridyl)pyrazol-1-ylmethyl]pyridine was prepared by a general procedure reported in the literature (Singh *et al.*, 2003). The title complex was prepared by stirring together a solution of 2-[3-(2-pyridyl)pyrazol-1-ylmethyl]pyridine (94.3 mg, 0.4 mmol) in chloroform (20 ml) with a methanol solution (20 ml) of [Ni(H$_2$O)$_6$][ClO$_4$]$_2$ (73.2 mg, 0.20 mmol) for 5 h at room temperature and then filtering. Slow evaporation of the filtrate yielded block-shaped purple crystals suitable for X-ray analysis. Analysis found: C 37.31, H 2.75, N 11.58%; calculated for $C_{30}H_{26}Cl_8N_8NiO_8$: C 37.19, H, 2.70, N 11.57%.

Crystal data

[Ni(C$_{14}$H$_{12}$N$_4$)$_2$](ClO$_4$)$_2$·2CHCl$_3$	D_x = 1.571 Mg m^{-3}
M_r = 968.90	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 1006
a = 22.297 (6) Å	reflections
b = 17.257 (5) Å	θ = 3.0–22.6°
c = 23.801 (7) Å	μ = 1.05 mm^{-1}
β = 116.551 (4)°	T = 293 (2) K
V = 8192 (4) Å^3	Block, purple
Z = 8	0.36 × 0.30 × 0.30 mm

Data collection

Bruker SMART CCD area-detector diffractometer	8395 independent reflections
φ and ω scans	4749 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	R_{int} = 0.055
(*SADABS*; Sheldrick, 1996)	θ_{max} = 26.4°
T_{min} = 0.703, T_{max} = 0.743	h = −27 → 27
23272 measured reflections	k = −18 → 21
	l = −29 → 27

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0746P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.060	$+ 8.6393P]$
$wR(F^2)$ = 0.166	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.01	$(\Delta/\sigma)_{max}$ = 0.002
8395 reflections	$\Delta\rho_{max}$ = 0.62 e Å^{-3}
552 parameters	$\Delta\rho_{min}$ = −0.39 e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ni1—N2	1.997 (4)	Ni2—N6	1.977 (3)
Ni1—N1	2.133 (4)	Ni2—N5	2.143 (3)
Ni1—N4	2.184 (4)	Ni2—N8	2.173 (3)
N2—Ni1—N2^i	173.8 (3)	N6—Ni2—N6^{ii}	171.7 (2)
N2—Ni1—N1^i	98.32 (15)	N6—Ni2—N5^{ii}	97.35 (13)
N2—Ni1—N1	77.45 (16)	N6—Ni2—N5	77.21 (13)
N1^i—Ni1—N1	96.02 (19)	N5^{ii}—Ni2—N5	98.95 (19)
N2—Ni1—N4^i	97.70 (16)	N6—Ni2—N8^{ii}	87.29 (14)
N1—Ni1—N4^i	90.26 (14)	N6—Ni2—N8	98.89 (13)
N2—Ni1—N4	86.81 (17)	N5—Ni2—N8^{ii}	162.57 (13)
N1—Ni1—N4	163.72 (15)	N5—Ni2—N8	90.80 (13)
N4^i—Ni1—N4	87.7 (2)	N8^{ii}—Ni2—N8	83.70 (19)

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

H atoms were included in calculated positions and refined as riding, with C—H distances of 0.93 Å (aromatic H) and 0.97 Å (methylene H), and U_{iso}(H) = 1.2U_{eq}(C). One perchlorate ion is rotationally disordered, around the Cl2—O5 bond, between two positions with refined occupancies of 0.446 (12) and 0.554 (12) for atoms O6, O7 and O8, and atoms O6′, O7′ and O8′, respectively. The Cl—O distances were restrained to be equal to within 0.01 Å. The Cl atoms of one chloroform molecule (attached to C29) were also refined as disordered between two positions with occupancies of 0.446 (12) and 0.554 (12), and with restrained Cl—C bond lengths.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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