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Key indicators

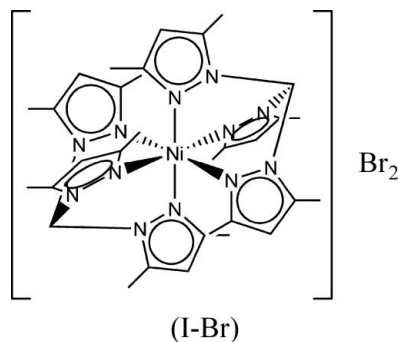
Single-crystal X-ray study
 $T = 298$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.040
 wR factor = 0.108
Data-to-parameter ratio = 15.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis[tris(3,5-dimethylpyrazolyl)methane]nickel(II)
dibromide

In the title complex, $[\text{Ni}(\text{C}_{16}\text{H}_{22}\text{N}_6)_2]\text{Br}_2$, the Ni atom is in a slightly distorted octahedral coordination environment, having crystallographic $2/m$ symmetry. The Ni atom is coordinated by the six pyrazolyl rings of the two tridentate tris(3,5-dimethylpyrazolyl)methane ligands, with Ni–N distances in the range 2.0753 (17)–2.110 (3) Å.

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Comment

Polypyrazolylmethane late-transition-metal complexes of the first row have shown great potential for the construction of magnetic devices. In the course of our studies of the coordination chemistry of these ligands with nickel, the synthesis of $\{\text{Ni}[\text{HC}(3,5\text{-Me}_2\text{pz})_3]_2\}\text{Br}_2$, (I-Br), has been carried out [$\text{HC}(3,5\text{-Me}_2\text{pz})_3$ is tris(3,5-dimethylpyrazolyl)methane].



The title compound (Fig. 1) is similar to that reported previously by Reger *et al.* (2002) using $\text{Ni}(\text{BF}_4)_2 \cdot 3\text{H}_2\text{O}$ as precursor. The main differences between the crystallographic studies of $\{\text{Ni}[\text{HC}(3,5\text{-Me}_2\text{pz})_3]_2\}(\text{BF}_4)_2$, (I- BF_4), and (I-Br) are the counter-ion and the data collection temperature [220 K for (I- BF_4)].

Both complexes crystallize in the monoclinic system with C -centered unit cells, but (I-Br) does not possess a glide plane ($C2/m$), whereas (I- BF_4) does ($C2/c$). The cation in (I-Br) has crystallographic $2/m$ symmetry, giving only two unique Ni–N bond distances (see Table 1).

In both cases, the Ni^{II} cations adopt a slightly distorted octahedral geometry. The *cis* N–Ni–N angles within each tridentate ligand of (I-Br) are essentially equivalent [85.65 (11) and 86.53 (7)°] and are comparable with those found in (I- BF_4) [85.30 (9)–86.26 (9)°]; the average value of these angles in each compound is the same within experimental error [86.2 (3)° for (I-Br), compared with 85.9 (3)° for (I- BF_4)]. The average of the Ni–N bond lengths in (I-Br) is the same for both complexes (2.09 Å), even though the range of Ni–N distances varies slightly [2.0754 (17)–2.110 (3) Å for (I-Br), compared with 2.076 (2)–2.096 (2) Å for (I- BF_4)].

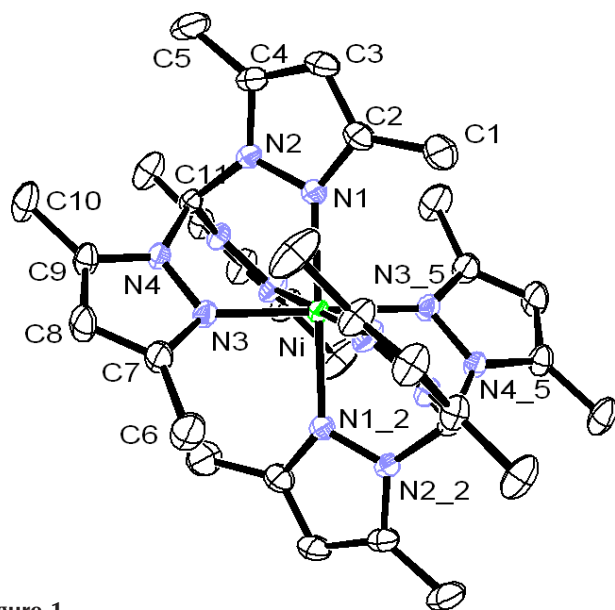


Figure 1

A view of the title cation, showing 30% probability displacement ellipsoids and the atom-numbering scheme. Atoms labelled with the suffixes ‘_2’ and ‘_5’ are related by the symmetry codes $(-x, y, -z)$ and $(-x, -y, -z)$, respectively.

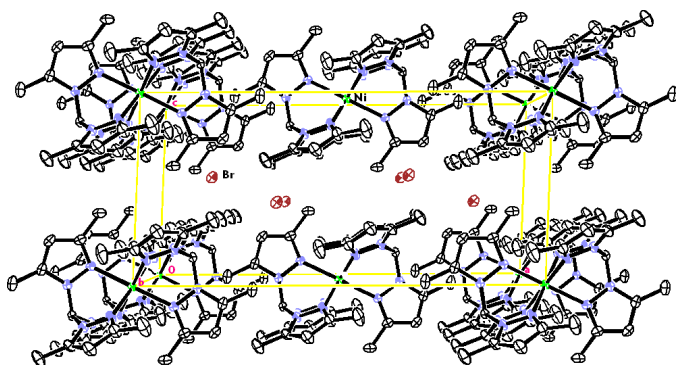


Figure 2

A view of the unit-cell contents. Ellipsoids are drawn at the 30% probability level. H atoms have been omitted.

Apart from some long C—H...N (> 2.5 Å) and C—H...Br (> 2.8 Å) contacts, there are no chemically significant interactions between the Br⁻ anions and the complex cations (Fig. 2).

Experimental

A solution of HC(3,5-Me₂pz)₃ (1.07 g, 3.58 mmol) in boiling butanol was added to a suspension of NiBr₂ (360 mg, 1.65 mmol) in boiling butanol. The reaction mixture was stirred until all the solid suspension had dissolved and a deep blue solid precipitated. The solution was cooled to room temperature and the resulting solid filtered off. Subsequent washing with cold butanol and cold diethyl ether afforded the analytically pure title compound (yield 776 mg, 58%). Diffusion of diethyl ether into a solution of the title compound in methanol afforded X-ray quality crystals. Analysis calculated for C₃₂H₄₄N₁₂Br₂Ni: C 47.14, H 5.44, N 20.62%; found: C 47.05, H 5.56, N 20.74%. ¹H NMR (CD₃CN, δ, p.p.m.): 55.61, -0.50, -2.93, -10.23; IR (KOH, ν, cm⁻¹): 3413 (br), 3117–2947 (m), 1670 (w), 1562 (s), 1459–

1387 (s), 1306 (s), 1256 (s), 1175–1125 (w), 1114 (m), 1042 (s), 987 (m), 908 (m), 859 (s), 703 (s), 631 (w), 492 (w); UV-vis [CH₃CN, λ (nm), ε (mol l⁻¹)⁻¹ cm⁻¹]: (367, 426), (387, 322), (610, 97), (650, 124), (706, 104), (753, 72). M.p. > 593 K. $\mu_{\text{eff}} = 3.95$.

Crystal data

[Ni(C₁₆H₂₂N₆)₂]Br₂
 $M_r = 815.32$
 Monoclinic, $C2/m$
 $a = 18.9240$ (2) Å
 $b = 10.996$ (1) Å
 $c = 8.8821$ (1) Å
 $\beta = 92.580$ (1)°
 $V = 1846.39$ (17) Å³
 $Z = 2$

$D_x = 1.467$ Mg m⁻³
 Cu $K\alpha$ radiation
 Cell parameters from 8952 reflections
 $\theta = 4.7$ – 72.9°
 $\mu = 3.61$ mm⁻¹
 $T = 298$ (2) K
 Block, pale pink
 $0.18 \times 0.15 \times 0.10$ mm

Data collection

Bruker SMART 2K/Platform diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.447$, $T_{\text{max}} = 0.697$
 11 178 measured reflections

1907 independent reflections
 1702 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.125$
 $\theta_{\text{max}} = 72.9^\circ$
 $h = -23 \rightarrow 23$
 $k = -13 \rightarrow 13$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.108$
 $S = 1.07$
 1907 reflections
 126 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0739P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.60$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.60$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni—N3	2.0754 (17)	C3—C4	1.366 (5)
Ni—N1	2.110 (3)	C4—C5	1.493 (5)
C11—N2	1.438 (4)	N3—C7	1.332 (3)
C11—N4	1.445 (2)	N3—N4	1.370 (2)
N1—C2	1.314 (4)	N4—C9	1.358 (3)
N1—N2	1.372 (3)	C6—C7	1.496 (4)
N2—C4	1.363 (4)	C7—C8	1.399 (3)
C1—C2	1.509 (6)	C8—C9	1.357 (3)
C2—C3	1.395 (5)	C9—C10	1.482 (3)
N3 ⁱ —Ni—N3	85.65 (11)	N3—Ni—N1	86.53 (7)
N3 ⁱ —Ni—N3 ⁱⁱ	180.0	N3 ⁱⁱ —Ni—N1	93.47 (7)
N3—Ni—N3 ⁱⁱ	94.35 (11)	N1—Ni—N1 ⁱⁱⁱ	180.0

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

H atoms were constrained to the parent site using a riding-model approximation, with C—H distances in the range 0.93–0.98 Å and with $U_{\text{iso}}(\text{H}) = 1.5$ (methyl) or 1.2 (others) times U_{eq} of the parent site. The H atoms on the methyl groups where the C atom is on a crystallographic mirror plane are distributed over six positions and therefore have 0.5 occupancy. A final verification of possible voids was performed using the VOID routine of the PLATON program (Spek, 2003).

Data collection: SMART (Bruker, 1999); 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: ORTEPIII (Burnett & Johnson, 1996) and SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXL97.

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