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trans-Dibromotetra(3-*tert*-butylpyrazole-κ*N*)nickel(II)

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Key indicators

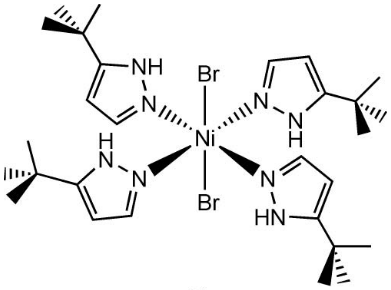
Single-crystal X-ray study
T = 223 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.045
wR factor = 0.125
Data-to-parameter ratio = 18.6

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

The title compound, $[NiBr_2(C_7H_{12}N_2)_4]$, is an octahedral Ni^{II} complex coordinated by four pyrazolyl rings and two Br$^-$ anions. In the crystal structure, there are two independent Ni complexes, each with inversion symmetry. The *tert*-butyl groups of the ligands show orientational disorder.

Comment

Late transition metal complexes with *N*-containing ligands have attracted recent interest for their potential use as catalysts for olefin polymerization (Johnson *et al.*, 1995) or magnetic devices (Reger *et al.*, 2002). In the course of our studies on the coordination chemistry of polypyrazolyl ligands with nickel, the synthesis of the title compound, (I), $(Py3^t Bu)_4NiBr_2$ ($Py3^t Bu$ is 3-*tert*-butylpyrazole) was undertaken in order to confirm the identity of a by-product of the reaction of tris(3-*tert*-butylpyrazolyl)methane with $NiBr_2$, and its structure is presented here.



(I)

In (I), there are two independent Ni^{II} complexes (Figs. 1 and 2). In both complexes, the Br$^-$ anions are *trans* to each other. The presence of an inversion center at each Ni means that the *tert*-butyl groups on *trans* pyrazole ligands are on opposite sides of the NiN_4 coordination plane. The Ni1 complex is almost perfectly octahedral, with *cis* angles within 1.8 (1)° of 90°, while the Ni2 complex seems to be more distorted, with N—Ni—N angles deviating by up to 4.4 (1)° from 90°. One other difference between the independent complexes is in the tilt angle of the pyrazolyl ring to the coordination plane. In the Ni1 complex, the pyrazolyl ring planes are almost perpendicular to the NiN_4 coordination plane [69.2 (2)° and 82.5 (2)°], whereas in the Ni2 complex, the pyrazolyl rings are more tilted [58.4 (2)° and 64.9 (2)°]. In both molecules, the *tert*-butyl groups exhibit a high level of disorder. The packing diagram seems to exclude any interaction between the independent complexes (Fig. 3).

Two related Ni^{II} complexes have previously been characterized by X-ray crystallography, namely dibromotetrapyrazolenickel(II) [$(Py)_4NiBr_2$; Mighell *et al.*, 1969] and

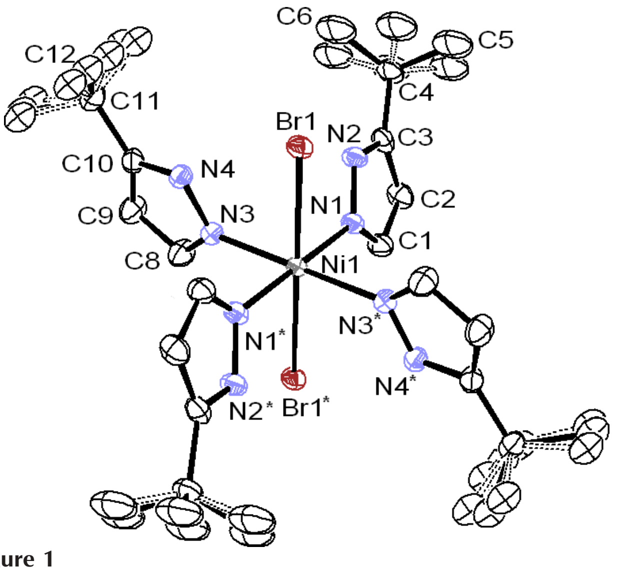


Figure 1

The structure of the Ni1 complex in (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity. Atoms labeled with an asterisk (*) are at the symmetry position ($1 - x, 2 - y, 1 - z$).

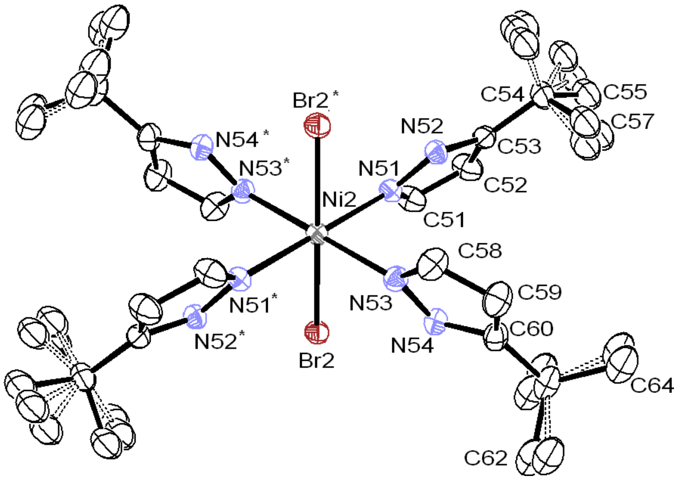


Figure 2

The structure of the Ni2 complex in (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity. Atoms labeled with an asterisk (*) are at the symmetry position ($-x, 2 - y, -z$). All disorder components are shown.

dibromotetra(3-methylpyrazole)nickel(II) [$(\mathrm{Py3Me})_4\mathrm{NiBr}_2$; Nelana *et al.*, 2004]. Both compounds have the same connectivity and similar bond lengths, but some notable differences exist. The average of 2.085 (2) Å for the Ni—pyrazole bond lengths in (I) is the shortest in all three compounds. Indeed, it seems that the greater donating capability of the *tert*-butylpyrazole ligand compensates for the steric bulk of the ligand. Also, the average Ni—Br bond length in (I) [2.6749 (6) Å] is between the average for $(\mathrm{Py})_4\mathrm{NiBr}_2$ [2.682 (1) Å] and $(\mathrm{Py3Me})_4\mathrm{NiBr}_2$ [2.6617 (2) Å].

Experimental

A boiling butanol solution of tris(3-*tert*-butylpyrazolyl)methane (10 ml) (290 mg, 0,758 mmol) was added to a hot stirred suspension of NiBr_2 (165 mg, 0,755 mmol) in butanol (30 ml). The resulting mixture was stirred at 383 K for 20 min until all the NiBr_2 was solubilized and the solution turned yellow. It was then cooled down to room temperature and hexane (40 ml) was added. The stirring was stopped and the solution kept at 298 K for 18 h. The solution was then heated again for 2 h to help solubilize the remaining NiBr_2, when the solution had turned green and was clear of any solid. The solvent mixture was then evaporated to give a green oil. The oil was solubilized in diethyl ether and purple crystals of (I) were grown by diffusion of pentane (yield < 5%).

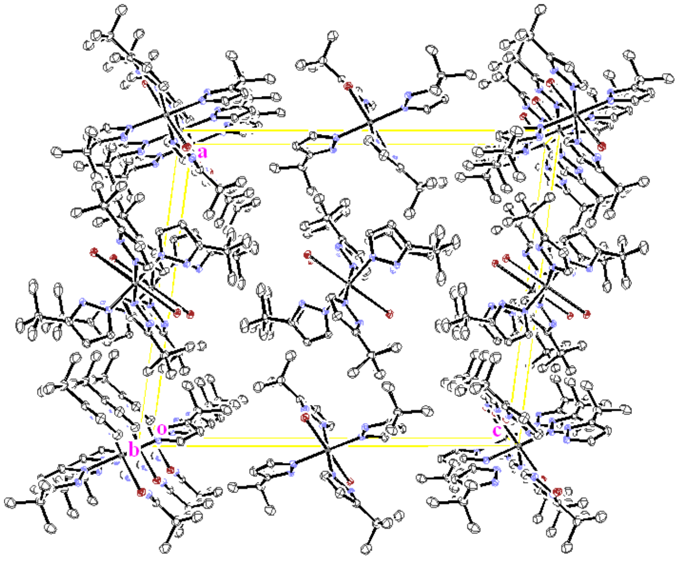


Figure 3

The crystal structure of (I), projected along the *b* axis. Ellipsoids are drawn at the 20% probability level. H atoms and all but one disorder component for each substituent have been omitted for clarity.

Crystal data

$[\mathrm{NiBr}_2(\mathrm{C}_7\mathrm{H}_{12}\mathrm{N}_2)_4]$
$M_r = 715.27$
Monoclinic, $P2_1/c$
$a = 17.822$ (4) Å
$b = 9.536$ (2) Å
$c = 21.256$ (5) Å
$\beta = 97.445$ (17)°
$V = 3582.1$ (14) Å^3
$Z = 4$
$D_x = 1.326$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 999 reflections
$\theta = 6.8$–72.1°
$\mu = 3.61$ mm^{-1}
$T = 223$ (2) K
Block, purple
0.60 × 0.30 × 0.30 mm

Data collection

Bruker SMART 2K/Platform diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.108$, $T_{\max} = 0.336$
42 742 measured reflections
7012 independent reflections
6687 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.058$
$\theta_{\max} = 72.8°$
$h = -22 \rightarrow 21$
$k = -11 \rightarrow 11$
$l = -25 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.125$
$S = 1.06$
7012 reflections
378 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.074P)^2 + 3.302P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 0.70$ e Å^{-3}
$\Delta\rho_{\min} = -0.56$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.00105 (9)

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Table 1
Selected geometric parameters (Å, °).

Ni1—N1	2.083 (2)	Ni2—N51	2.075 (3)
Ni1—N3	2.088 (2)	Ni2—N53	2.095 (2)
Ni1—Br1	2.6732 (7)	Ni2—Br2	2.6765 (6)
N1—Ni1—N3	88.2 (1)	N51—Ni2—N53	85.56 (10)
N1—Ni1—Br1	90.06 (7)	N51—Ni2—Br2	89.82 (7)
N3—Ni1—Br1	89.93 (7)	N53—Ni2—Br2	90.85 (7)
Br1—Ni1—N1—C1	171.3 (3)	Br2—Ni2—N51—C51	18.5 (3)
Br1—Ni1—N1—N2	−20.8 (2)	Br2—Ni2—N51—N52	−148.4 (2)
Br1—Ni1—N3—C8	166.3 (3)	Br2—Ni2—N53—C58	−176.3 (3)
Br1—Ni1—N3—N4	−7.5 (2)	Br2—Ni2—N53—N54	25.1 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*N*···Br1	0.91 (4)	2.46 (4)	3.198 (2)	139 (3)
N4—H4*N*···Br1	0.91 (4)	2.40 (4)	3.148 (2)	139 (3)
N52—H52*N*···Br2^{i}	0.84 (4)	2.62 (4)	3.257 (2)	133 (3)
N54—H54*N*···Br2	0.84 (4)	2.53 (4)	3.232 (2)	141 (3)

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

H atoms bonded to N atoms were located in difference Fourier maps and refined isotropically. H atoms bonded to C atoms were positioned geometrically and constrained to the parent site using a riding model, with C—H distances in the range 0.93–0.98 Å and with U_{iso}(H) = $1.2U_{eq}$(C), or $1.5U_{eq}$(C_{methyl}). The *tert*-butyl groups show orientational disorder. The occupancy factors were first refined using a free variable, then fixed to the closest logical values of occupancy. There are two or three possible sets of positions for the terminal C atoms: C5/C6/C7 (occupancy factor 74%) and C5*A*/C6*A*/C7*A* (26%), C12/C13/C14 (34%), C12*A*/C13*A*/C14*A* (33%) and C12*B*/C13*B*/C14*B* (33%), C55/C56/C57 (34%), C55*A*/C56*A*/C57*A* (33%) and C55*B*/C56*B*/C57*B* (33%), and C62/C63/C64 (50%) and C62*A*/C63*A*/C64*A* (50%). The interatomic distances were restrained and the atomic displacement parameters were constrained for the methyl groups on the same *tert*-butyl group.

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); software used to prepare material for publication: *UdMX* (Marris, 2003).

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