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Bis[hydrotris(4-chloro-3,5-dimethylpyrazolyl)borato]nickel(II)

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Key indicators

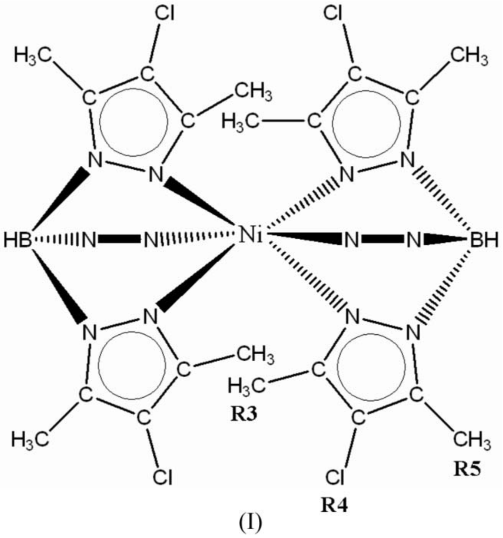
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.007 Å
R factor = 0.049
wR factor = 0.119
Data-to-parameter ratio = 19.2

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

The title compound, $[Ni(C_{15}H_{19}BCl_3N_6)_2]$ or $Ni(Tp^{*Cl})_2$, adds to the list of structurally characterized bis(tris-pyrazolyl)borate–nickel(II) complexes. The two facially coordinating N-donor Tp^{*Cl} ligands impose pseudo-octahedral coordination on the nickel(II) center. The asymmetric unit consists of two half molecules, primarily differing in the torsion angles of the coordinated pyrazole rings relative to the central B—Ni—B axis of the molecules; each molecule is centrosymmetric. An average overall Ni—N distance of 2.104 (15) Å is observed, typical of octahedral NiN_6 coordination spheres and this class of compound. The title compound readily forms good quality crystals, while its 4-H analog, $Ni(Tp^*)_2$, does not. This characteristic is attributed to close contacts between the pyrazole 4-chloro-substituents on adjacent molecules.

Comment

Tris(pyrazolyl)borates encompass a diverse class of facially coordinating tridentate N-donor ligands, originally developed and thoroughly reviewed by Trofimenko (1999). The title complex, (I), was prepared as a sterically equivalent but electronically modified relative of $Ni(Tp^*)_2$. In the scheme, R_3, R_4 and R_5 refer to the pyrazole-ring positions used in the ligand abbreviations (Trofimenko, 1999); two pyrazole rings are shown edge-on, normal to the plane of the paper. The TpX ligand abbreviations used in this discussion are as follows. For Tp, R_3 = R_4 = R_5 = H; for Tp*, R_3 = R_5 = CH_3, R_4 = H; for Tp^{*Cl}, R_3 = R_5 = CH_3, R_4 = Cl; for Tp^{Me}, R_3 = CH_3, R_4 = R_5 = H; for Tp^{Ph}, R_3 = Ph, R_4 = R_5 = H.



(I)

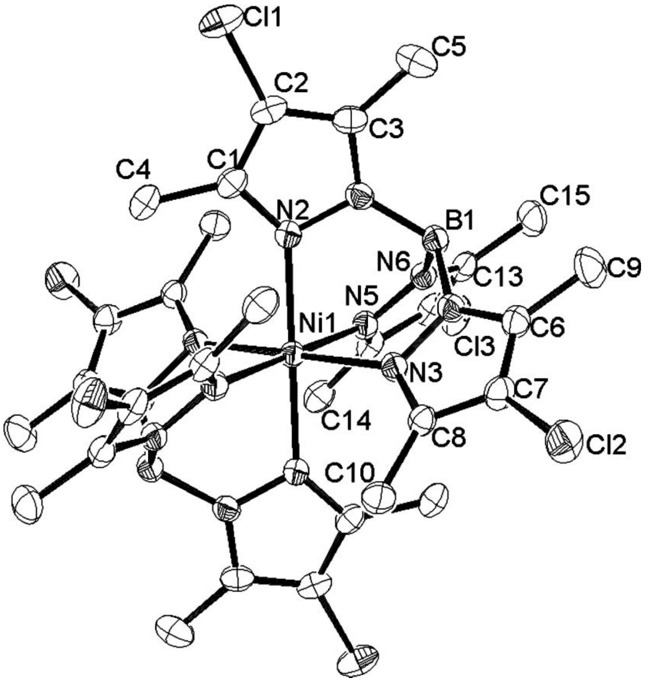


Figure 1
A diagram of molecule 1 of (I), with 50% probability displacement ellipsoids. H atoms have been omitted for clarity. Unlabeled atoms are related to labeled atoms by $(2 - x, 1 - y, 1 - z)$.

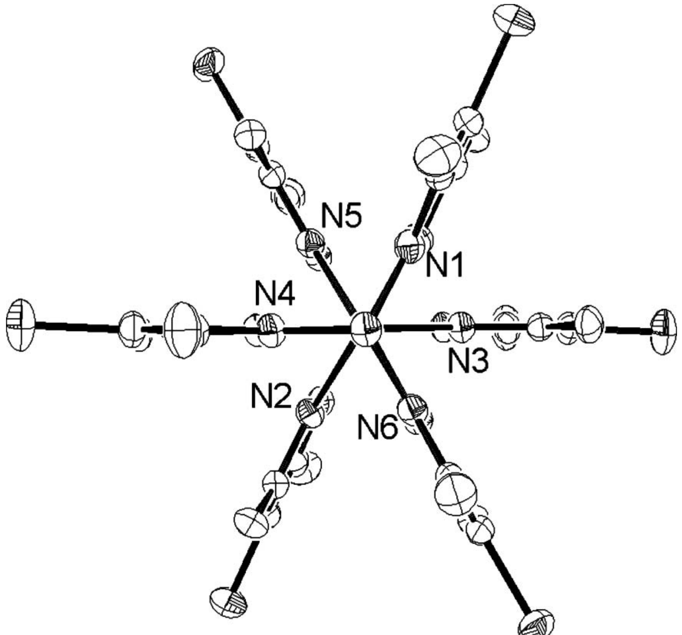


Figure 2
A view down the pseudo-threefold B—Ni—B axis of (I) (molecule 1). H atoms have been omitted.

Tp^X ligands can stabilize pseudo-tetrahedral four-coordinate geometries for nickel(II), so that a variety of $C_{3\mathrm{v}}$ $\mathrm{Tp}^X\mathrm{Ni}Y$ complexes are known (Calabrese & Trofimenko, 1992; Calabrese *et al.*, 1990; Trofimenko *et al.*, 1989, 1987) and a few have been structurally characterized (Desrochers *et al.*, 2003; Trofimenko *et al.*, 1992). Alterations in the pyrazole-ring substituents influence the electronic stability of adducts formed by the $\mathrm{Tp}^X\mathrm{Ni}^+$ Lewis acid center with S- and Se-donating amino acids (Desrochers *et al.*, 2002). Substitution at the pyrazole ring 4-position is the preferred method of controlling the electronic characteristics of the ligand without altering the steric demands imposed by the 3- and 5-position substituents. The direct synthesis of $\mathrm{Ni(Tp^{*Cl})_2}$, (I), is reported here. The compound also results as a thermodynamic product from reaction mixtures of the kinetically less stable five-coordinate $\mathrm{Tp^{*Cl}NiCysEt}$ complex (CysEt = cysteine ethyl ester).

The asymmetric unit of (I) consists of two distinct half molecules, each molecule lying on an inversion centre (Fig. 1). The average Ni—N distance of 2.104 (15) Å in $\mathrm{Ni(Tp^{*Cl})_2}$ is statistically identical to the combined average Ni—N distance observed for $\mathrm{Ni(Tp)_2}$ and $\mathrm{Ni(Tp^{Me})_2}$ [2.100 (14) Å; Cecchi *et al.*, 1994; Bandoli *et al.* 1979]. Very similar Ni—N distances have been observed over a wide variety of six-coordinate $\mathrm{NiN_6}$ systems, *e.g.* $\mathrm{Ni(tracn)_2}^{+2}$ [2.105 (9) Å; tracn = 1,4,7-triazacyclononane; Zompa & Margulis, 1978], $\mathrm{Ni(phen)_3}^{+2}$ [2.090 (11) Å; phen = 1,10-phenanthroline; Frenz & Ibers, 1972] and $\mathrm{Ni(bipy)_3}^{+2}$ [2.089 (4) and 2.107 (15) Å; bipy = 2,2′-bipyridine; Szalda *et al.*, 1984].

Several late transition metal $M(\mathrm{Tp}^X)_2$ complexes have been structurally characterized by single-crystal X-ray diffraction, and all exhibit pseudo-octahedral coordination geometries. The only other first-row transition metal complex of $\mathrm{Tp^{*Cl}}$ with a structure reported to date is the copper(II) derivative, $\mathrm{Cu(Tp^{*Cl})_2}$ (Santini *et al.*, 1999). This complex is nearly isostructural with $\mathrm{Ni(Tp^{*Cl})_2}$. The structures of comparative copper complexes are complicated by Jahn–Teller-induced tetragonal distortions; accordingly, (averaged) short and long Cu—N distances of 2.11 and 2.26 Å for $\mathrm{Cu(Tp^{*Cl})_2}$ (Santini *et al.*, 1999), 2.01 and 2.53 Å for $\mathrm{Cu(Tp)_2}$ (Murphy *et al.*, 1979), and 2.08 and 2.28 Å for $\mathrm{Cu(Tp^*)_2}$ (Marsh, 1989) have been reported.

Comparisons with related M—N distances in the series $\mathrm{Fe(Tp)_2}$ (Oliver *et al.*, 1980), $\mathrm{Fe(Tp^*)_2}$ (Oliver *et al.*, 1980) and $\mathrm{Fe(Tp^{Ph})_2}$ (Eichorn & Armstrong, 1990) are complicated by high-spin/low-spin transitions for the iron(II) complexes, which alter the Fe—N bond distance by as much as 0.2 Å. Nickel(II) in these environments invariably has an $S = 1$ spin state, consistent with an $e_g{}^2t_{2g}{}^6$ electron configuration. A longer average Co—N length of 2.129 (7) Å was observed in high-spin $\mathrm{Co(Tp)_2}$ (Churchill *et al.*, 1970). The closest high-spin iron(II) analog to $\mathrm{Ni(Tp^{*Cl})_2}$ is $\mathrm{Fe(Tp^*)_2}$, with an average Fe—N distance of 2.17 (2) Å. The longer M—N distances in these molecules reflect the larger atomic radii of Fe and Co compared with Ni.

A view down the pseudo-threefold B—Ni—B axis of the two $\mathrm{Ni(Tp^{*Cl})_2}$ molecules of (I) indicates distortions from perfect threefold symmetry (Fig. 2). The torsion angles between the pyrazole planes, defined by B—N—N—Ni, deviate more from an idealized angle of 0° for molecule 2 [0.5 (1)–10.1 (1)°] than for molecule 1 [0.1 (1)–6.5 (1)°]. Similar torsional ruffling behavior has been reported in the structure of the potassium salt, $\mathrm{KTp^{*Cl}}$ (Joshi *et al.* 2004), and for $\mathrm{Cu(Tp^{*Cl})_2}$ (Santini *et al.*, 1999). In the copper(II) system,

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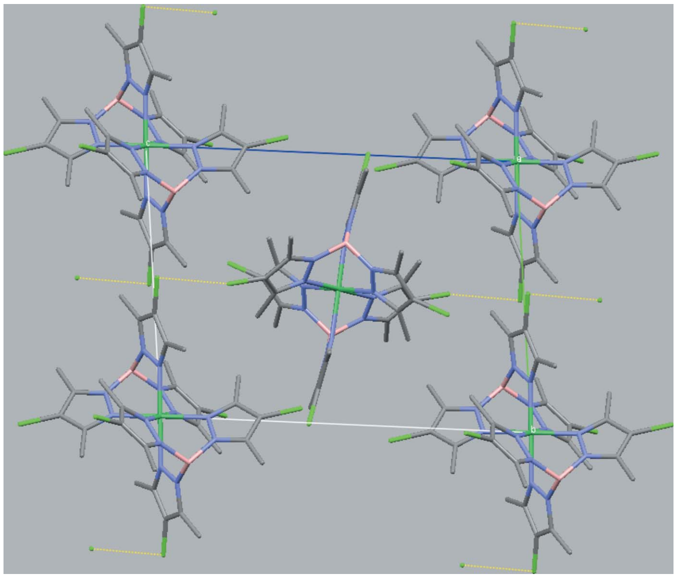

Figure 3
The unit-cell packing of (I), viewed along the *a* axis, showing the close Cl$\cdots$Cl intermolecular contacts. The dotted lines indicate Cl$\cdots$Cl contacts of 3.48 Å, less than twice the van der Waals radius of Cl.

these torsion angles range from 18 to 26°. The N—N—B angles in the potassium complex are about 2° larger, in order to accomodate complexation of the much larger K^+ ion compared with the Ni^{II} ion in $Ni(Tp^{*Cl})_2$.

Ni$\cdots$B non-bonded distances of 3.13 (3) and 3.14 (3) Å are observed for molecules 1 and 2, respectively. These are longer than the corresponding distances in Tp^*NiBH_4 (3.04 Å) and Tp*NiCl (3.00 Å), reflecting the greater steric repulsion of two opposing Tp^{*Cl} ligands *versus* the single Tp* opposite the smaller Cl^- and borohydride ligands in these two molecules. The comparable distance in the less sterically crowded Tp_2Ni complex is 3.17 Å, somewhat longer than in $Ni(Tp^{*Cl})_2$, despite the greater crowding of the 3-methyl substituents in the latter complex. This feature has been attributed to a compression of the Ni—N distance caused by repulsion of the 5-methyl substituents (Trofimenko, 1999).

The closest intermolecular contacts in the solid involve the Cl-atom ring substituents (Fig. 3). Some of these Cl$\cdots$Cl contacts are within the sum of the van der Waals radii for Cl. $Ni(Tp^*)_2$ shows little crystallinity, a fact that has precluded its structure determination by X-ray crystallography for nearly 40 years. In contrast, $Ni(Tp^{*Cl})_2$ is a nicely crystalline solid, a characteristic that may result from these close Cl$\cdots$Cl contacts, which are absent in $Ni(Tp^*)_2$. Similar observations of improved crystallinity with 4-bromo-substituted pyrazoles were noted for $KTp^{iPr,4Br}$ and $TlTp^{iPr,4Br}$ (Trofimenko *et al.*, 1989).

Experimental

A green aqueous solution of nickel(II) nitrate hexahydrate (0.112 g, 0.39 mmol, in 5 ml; Aldrich) was added dropwise to a colorless methanolic solution of KTp^{*Cl} (0.338 g, 0.77 mmol, in 20 ml). KTp^{*Cl} was prepared according to the method described by Trofimenko (1999). All solvents were obtained from Fisher Scientific. The product formed immediately as a finely divided lavender precipitate. After stirring for 15 min, the mixture was filtered and the solid washed with water to remove unreacted nickel nitrate, followed by ethanol and diethyl ether, and dried on the frit. This solid was purified using column chromatography, column dimension = 3 cm × 9 cm using 70–270 mesh, 60 Å silica-gel stationary phase (Aldrich) and chloroform mobile phase. The lavender-colored band moved down the column very rapidly, while a less-visible band remained near the top and did not elute from the column. Evaporation of this lavender solution yielded 250 mg of violet-colored solid. Elemental analysis (Atlantic Microlab, Norcross, GA) found (theoretical): C 42.17% (41.91%), H 4.60% (4.46%). Crystals of (I) suitable for X-ray diffraction measurements were obtained by slow evaporation of a chloroform solution of the compound.

Crystal data

$[Ni(C_{15}H_{19}BCl_3N_6)_2]$
$M_r = 859.84$
Triclinic, $P\bar{1}$
$a = 11.10$ (4) Å
$b = 12.38$ (3) Å
$c = 15.88$ (4) Å
$\alpha = 90.08$ (5)°
$\beta = 102.24$ (5)°
$\gamma = 113.59$ (6)°
$V = 1945$ (10) Å^3

$Z = 2$
$D_x = 1.468$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 360 reflections
$\theta = 1.8$–35.0°
$\mu = 0.95$ mm^{-1}
$T = 173$ (2) K
Prism, violet
0.50 × 0.35 × 0.10 mm

Data collection

Rigaku AFC-8 Mercury diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{min} = 0.656$, $T_{max} = 0.909$
26891 measured reflections

9313 independent reflections
7698 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 28.0°$
$h = -14 \rightarrow 14$
$k = -16 \rightarrow 16$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.119$
$S = 1.10$
9313 reflections
484 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 1.2406P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

H atoms were included as riding atoms, with C—H distances of 0.98 Å and with $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *DIRDIF99* (Beurskens *et al.*, 1999), *CRYSTALS* (Betteridge *et al.*, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *MERCURY* (Bruno *et al.*, 2002) and *ORTEP-3* (Version 1.076; Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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