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A redetermination of chlorido[hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borato]nickel(II)

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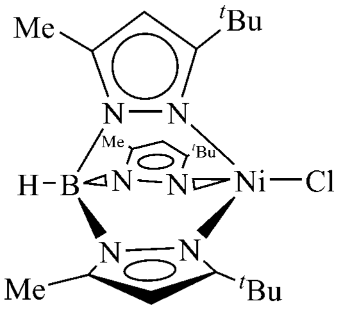
Key indicators: single-crystal X-ray study; T = 193 K; mean σ(C–C) = 0.003 Å; R factor = 0.018; wR factor = 0.045; data-to-parameter ratio = 14.0.

In the title complex, $[\mathrm{NiCl(C_{24}H_{40}BN_6)}]$, the Ni atom is coordinated by three N atoms, with the typical facial arrangement imposed by trispyrazolylborate ligands, and a chloride ligand in a distorted tetrahedral geometry. A structure of the title complex was previously reported in a lower symmetry space group [Santi, Romano, Sommazzi, Grande, Bianchini & Mantovani (2005). *J. Mol. Catal. A: Chem.* **229**, 191–197].

Related literature

A previously reported structure of the title complex was refined in the space group $R3$ (Santi *et al.*, 2005). Checking this structure's CCDC deposited .cif with *PLATON*'s (Spek, 2003) ADDSYM suggests $R3m$ to be a better choice of space group. This is consistent with the $R3m$ assignment of our structure; however, without processing the prior structure's data, at room temperature a polymorph cannot be absolutely ruled out. For related literature, see: Allen (2002); Alsfasser *et al.* (1991); Belderrain *et al.* (2002); Desrochers *et al.* (2003); Han & Parkin (1992); Kunrath *et al.* (2003); Shirasawa *et al.* (2001); Thyagarajan *et al.* (2003); Trofimenko (1999 and references therein, 2004); Trofimenko *et al.* (1987); Uehara *et al.* (2002).



Experimental

Crystal data

$[\mathrm{NiCl(C_{24}H_{40}BN_6)}]$
M_r = 517.59
Trigonal, $R3m$
a = 15.8900 (4) Å
c = 9.4584 (5) Å
V = 2068.22 (13) Å^3
Z = 3
Mo $K\alpha$ radiation
μ = 0.82 mm^{-1}
T = 193 (2) K
0.66 × 0.4 × 0.31 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan *SADABS* (Sheldrick, 1996)
$T_{\min}$ = 0.682, $T_{\max}$ = 0.785
4349 measured reflections
964 independent reflections
964 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.045
S = 1.08
964 reflections
69 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.23 e Å^{-3}
$\Delta\rho_{\min}$ = −0.14 e Å^{-3}
Absolute structure: Flack (1983), with 444 Friedel pairs
Flack parameter: 0.033 (11)

Table 1
Selected geometric parameters (Å, °).

Cl—Ni	2.2077 (9)	N11—N12	1.374 (2)
Ni—N12	2.0084 (15)	N11—B	1.552 (2)
N12$^{\mathrm{i}}$—Ni—N12	93.26 (6)	N12—Ni—Cl	122.93 (5)

Symmetry code: (i) $-x + y + 1, -x + 1, z$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *publCIF* (Westrip, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FI2040).

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supplementary materials

Acta Cryst. (2007). E**63**, m2520-m2521 [**doi:10.1107/S1600536807043814**]

A redetermination of chlorido[hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borato]nickel(II)

A. D. Beitelman and **G. M. Ferrence**

Comment

The chemistry of scorpionate supported transition-metal complexes has been the subject of intense research with in excess of 2000 papers published on polypyrazolylborate complexes spanning over seventy elements of the periodic table (Trofimenko, 2004; Trofimenko, 1999). The Cambridge Structural Database includes data for over 2800 crystal structures of trispyrazolylborate (Tp) metal complexes, many with bulky derivatives, including 54 incorporating the tris(3-*tert*-butyl-5-methylpyrazolyl)borate ligand, $Tp^{tBu,Me}$ (Allen, 2002). The coordination number of Tp coordinated metals is heavily controlled by the steric properties of the substituents attached to the 3-pyrazolyl carbon atoms. Sterically demanding Tp ligands have been found to be well suited for the isolation of low coordinate metal complexes; those with *tert*-butyl groups attached to the pyrazolyl 3-positions have been referred to as tetrahedral enforcers (Trofimenko *et al.* 1987). The title complex, $(Tp^{tBu,Me})NiCl$ is consistent with this generalization.

The molecular structure of (I) is shown in Fig. 1. All bond distances and angles are indistinguishable from those previously reported. (Santi *et al.*, 2005). The core geometry of (I) is indistinguishable, with few bond distances or angles differing more than within error, from those of the related complexes, including, $(Tp^{tBu})NiCl$ (Belderrain *et al.*, 2002), $(Tp^{iPr,iPr})NiCl$ (Shirasawa *et al.*, 2001), $(Tp^{Mes})NiCl$ (Kunrath *et al.*, 2003), $(Tp^{Ph,Me})NiCl$ (Uehara *et al.*, 2002), and $(Tp^{Me,Me})NiCl$ (Desrochers *et al.*, 2003). The Ni atom is coordinated by three N atoms, arranged with the typical facial arrangement imposed by trispyrazolylborato ligands, and a chloride ligand in a distorted tetrahedral geometry.

Arguably the most interesting feature of the structure is that the title compound preserves its highest possible, C_{3v}, point group symmetry in the solid state by residing upon appropriate crystallographic symmetry elements. Specifically, the H—B—Ni—Cl axis lies along a crystallographic threefold axis, and the pyrazolyl ring planes reside on crystallographic mirror planes. About 600 of the over 2800 crystallographically characterized trispyrazolylborate complexes have atomic connectivity capable of idealized C_{3v} point group symmetry. Of these, less than 65 have a Tp ligand with an H—B axis coincident with a crystallographic threefold axis, and only $(Tp^{tBu})BeH$ (Han & Parkin, 1992), $(Tp^{tBu,Me})CoNO$ (Thyagarajan *et al.*, 2003), and $(Tp^{tBu,Me})ZnOH$ (Alsfasser *et al.*, 1991) additionally lie on the necessary crystallographic mirror planes to display true C_{3v} symmetry in the solid state. Curiously, these three examples, like the title compound, contain Tp ligands with *tert*-butyl groups on the 3-pyrazolyl positions.

Experimental

Synthesis of $(Tp^{tBu,Me})NiCl$ was carried out according to the procedure previously reported for $(Tp^{tBu})NiCl$, substituting $KTp^{tBu,Me}$ for KTp^{tBu} (Trofimenko *et al.* 1987). An X-ray quality crystal was selected from crystals grown by slow evaporation of a mixture (2:1 ratio) of methylene chloride and acetonitrile).

Refinement

The H atom attached to the B atom was identified through difference Fourier synthesis and refined with an isotropic displacement parameter. All other H atoms were included in the refinement in the riding-model approximation, with respective isotropic aromatic and methyl displacement parameters fixed at 1.2Ueq and 1.5Ueq of the parent atom (C–H = 0.95 and 0.98 Å). Atom C16 was refined as an idealized disordered methyl group with H atoms included using the HFIX 123 instruction in *SHELXL97*.

Figures

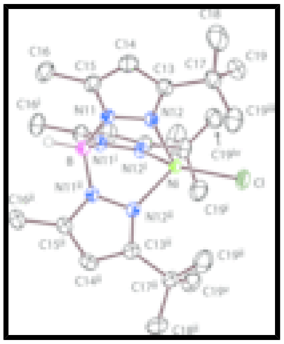


Fig. 1. The molecular structure of compound (I), with the atomic numbering scheme [symmetry codes: (i) 1 − *y*, *x*-*y*, *z*; (ii) *x*, *x*-*y*, *z*; (iii) 1 − *x* + *y*, *y*, *z*; (iv) 1 − *y*, 1 − *x*, *z*; (v) *x*, *x*-*y*, *z*]. H atoms except H1 are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Unlabeled atoms are related to the respective atoms C13, C14, C15, C17, and C18 of the asymmetric unit by 1 − *y*, *x*-*y*, *z*.

chlorido[hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borato]nickel(II)

Crystal data

$[NiCl(C_{24}H_{40}BN_6)]$

$M_r = 517.59$

Trigonal, *R*3*m*

Hall symbol: R 3 -2"

$a = 15.8900\ (4)$ Å

$b = 15.8900\ (4)$ Å

$c = 9.4584\ (5)$ Å

$\alpha = 90°$

$\beta = 90°$

$\gamma = 120°$

$V = 2068.22\ (13)$ Å^3

$Z = 3$

$F_{000} = 828$

$D_x = 1.247$ Mg m^{-3}

Mo *K*α radiation
$\lambda = 0.71073$ Å

Cell parameters from 5297 reflections

$\theta = 2.6–26.3°$

$\mu = 0.82$ mm^{-1}

$T = 193\ (2)$ K

Prism, violet

0.66 × 0.4 × 0.31 mm

Data collection

CCD area detector
diffractometer

$T = 193(2)$ K

φ and ω scans

Absorption correction: multi-scan
SADABS (Sheldrick, 1996)

964 reflections with $I >> 2\sigma(I)$

$R_{int} = 0.020$

$\theta_{max} = 26.3°$

$\theta_{min} = 3.7°$

$T_{\min} = 0.682$, $T_{\max} = 0.785$	$h = -19 \rightarrow 19$
4349 measured reflections	$k = -19 \rightarrow 19$
964 independent reflections	$l = -11 \rightarrow 10$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0143P)^2 + 0.6826P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.018$	$(\Delta/\sigma)_{\max} = <0.001$
$wR(F^2) = 0.045$	$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$S = 1.08$	$\Delta\rho_{\min} = -0.14$ e Å^{-3}
964 reflections	Extinction correction: none
69 parameters	Absolute structure: Flack (1983), 444 Friedel pairs
1 restraint	Flack parameter: 0.033 (11)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$	Occ. (<1)
Cl	0.6667	0.3333	0.42261 (9)	0.0350 (2)	
Ni	0.6667	0.3333	0.65602 (2)	0.01925 (10)	
N11	0.71951 (5)	0.43902 (11)	0.91467 (16)	0.0216 (3)	
N12	0.72792 (5)	0.45584 (11)	0.77144 (18)	0.0220 (3)	
B	0.6667	0.3333	0.9718 (4)	0.0219 (7)	
C13	0.77645 (7)	0.55289 (13)	0.7537 (2)	0.0266 (4)	
C14	0.79873 (7)	0.59746 (13)	0.8855 (3)	0.0329 (4)	
H14	0.8327	0.6654	0.9035	0.039*	
C15	0.76206 (7)	0.52412 (14)	0.9853 (2)	0.0272 (4)	
C16	0.76527 (8)	0.53054 (16)	1.1429 (2)	0.0381 (5)	
H16A	0.7324	0.4649	1.1831	0.057*	0.5
H16B	0.7324	0.5655	1.1745	0.057*	0.25
H16C	0.8331	0.5654	1.1745	0.057*	0.25
H16D	0.7995	0.599	1.1716	0.057*	0.5
H16E	0.7996	0.4984	1.1803	0.057*	0.25
H16F	0.6989	0.4985	1.1803	0.057*	0.25
C17	0.80046 (7)	0.60092 (14)	0.6087 (2)	0.0333 (4)	
C18	0.85597 (9)	0.71194 (17)	0.6292 (3)	0.0613 (8)	
H18A	0.8719	0.7439	0.5367	0.092*	
H18B	0.916	0.7313	0.6819	0.092*	0.5
H18C	0.8153	0.7312	0.6822	0.092*	0.5

C19	0.70656 (13)	0.57256 (12)	0.52716 (18)	0.0420 (4)
H19A	0.7227	0.604	0.4342	0.063*
H19B	0.6674	0.5937	0.5802	0.063*
H19C	0.6696	0.5019	0.515	0.063*
H1	0.6667	0.3333	1.090 (4)	0.023 (9)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl	0.0435 (3)	0.0435 (3)	0.0179 (4)	0.02173 (16)	0	0
Ni	0.02115 (12)	0.02115 (12)	0.01547 (18)	0.01057 (6)	0	0
N11	0.0241 (5)	0.0220 (7)	0.0181 (8)	0.0110 (3)	−0.0006 (3)	−0.0012 (6)
N12	0.0254 (5)	0.0219 (7)	0.0176 (7)	0.0110 (3)	0.0005 (3)	0.0011 (6)
B	0.0238 (10)	0.0238 (10)	0.0181 (18)	0.0119 (5)	0	0
C13	0.0279 (6)	0.0237 (8)	0.0268 (10)	0.0118 (4)	0.0010 (4)	0.0020 (7)
C14	0.0403 (8)	0.0192 (8)	0.0321 (11)	0.0096 (4)	−0.0022 (4)	−0.0043 (8)
C15	0.0297 (7)	0.0252 (8)	0.0251 (10)	0.0126 (4)	−0.0021 (4)	−0.0041 (7)
C16	0.0498 (9)	0.0322 (10)	0.0263 (11)	0.0161 (5)	−0.0037 (4)	−0.0073 (8)
C17	0.0434 (8)	0.0236 (9)	0.0263 (11)	0.0118 (5)	0.0024 (4)	0.0047 (8)
C18	0.0949 (18)	0.0235 (10)	0.0418 (15)	0.0117 (5)	0.0036 (5)	0.0072 (10)
C19	0.0557 (9)	0.0446 (8)	0.0340 (9)	0.0314 (7)	−0.0017 (8)	0.0066 (7)

Geometric parameters (Å, °)

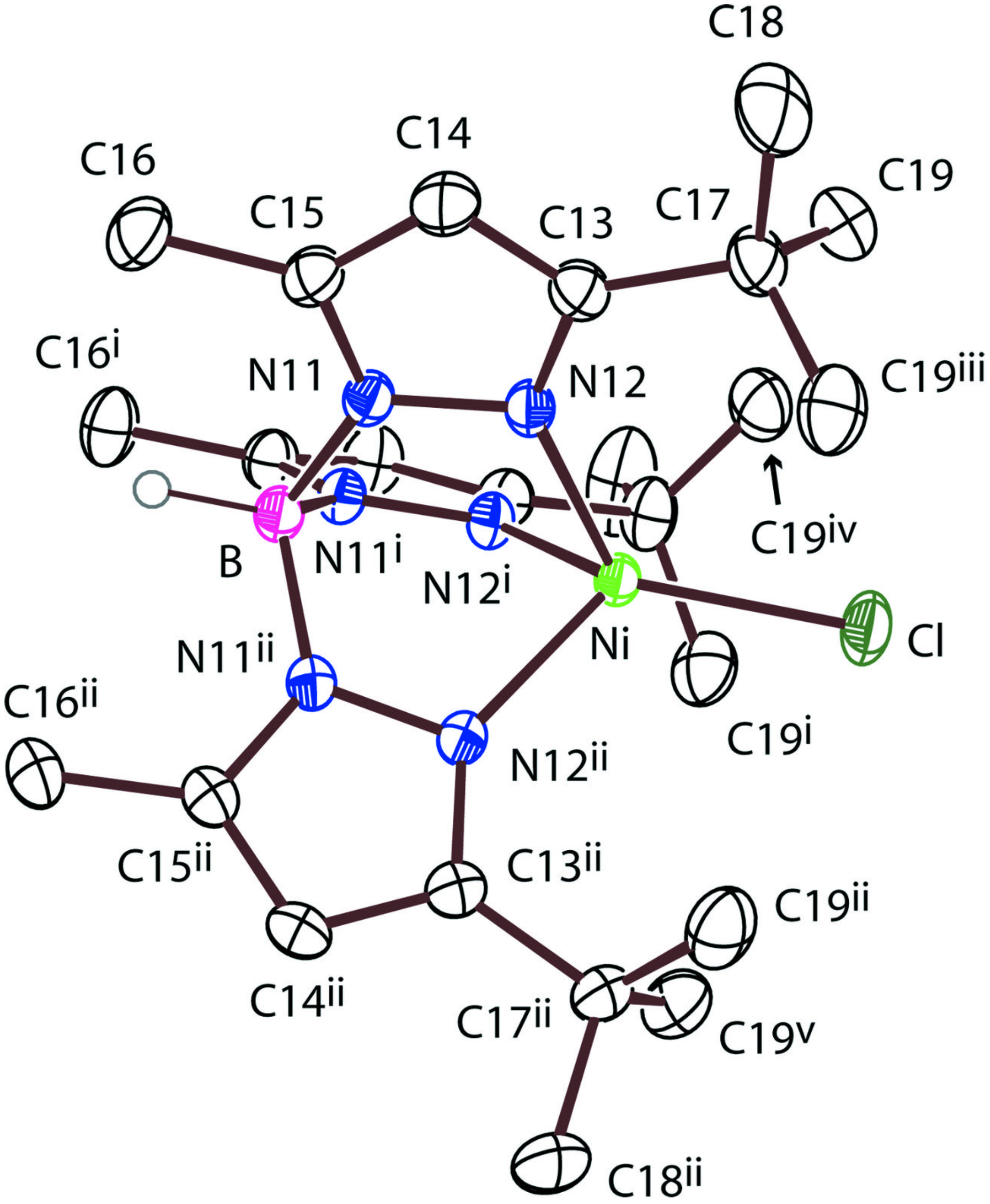
Cl—Ni	2.2077 (9)	C16—H16B	0.98
Ni—N12	2.0084 (15)	C16—H16C	0.98
N11—C15	1.348 (2)	C16—H16D	0.98
N11—N12	1.374 (2)	C16—H16E	0.98
N11—B	1.552 (2)	C16—H16F	0.98
N12—C13	1.346 (2)	C17—C19	1.534 (2)
B—H1	1.12 (4)	C17—C18	1.540 (3)
C13—C14	1.389 (3)	C18—H18A	0.98
C13—C17	1.522 (3)	C18—H18B	0.98
C14—C15	1.382 (3)	C18—H18C	0.98
C14—H14	0.95	C19—H19A	0.98
C15—C16	1.493 (3)	C19—H19B	0.98
C16—H16A	0.98	C19—H19C	0.98
N12^{i}—Ni—N12	93.26 (6)	C15—C16—H16D	109.5
N12—Ni—Cl	122.93 (5)	C15—C16—H16E	109.5
C15—N11—N12	110.02 (15)	H16C—C16—H16E	56.3
C15—N11—B	129.89 (19)	H16D—C16—H16E	109.5
N12—N11—B	120.08 (18)	C15—C16—H16F	109.5
C13—N12—N11	106.84 (15)	H16C—C16—H16F	141.1
C13—N12—Ni	139.93 (14)	H16D—C16—H16F	109.5
N11—N12—Ni	113.23 (11)	H16E—C16—H16F	109.5
N11^{i}—B—N11	108.53 (15)	C13—C17—C19	110.04 (11)
N11—B—H1	110.40 (14)	C19—C17—C19^{ii}	111.36 (19)
N12—C13—C14	109.06 (18)	C13—C17—C18	108.5 (2)

N12—C13—C17	122.88 (18)	C19—C17—C18	108.41 (12)
C14—C13—C17	128.06 (18)	C17—C18—H18A	109.5
C15—C14—C13	106.89 (17)	C17—C18—H18B	109.5
C15—C14—H14	126.6	H18A—C18—H18B	109.5
C13—C14—H14	126.6	C17—C18—H18C	109.5
N11—C15—C14	107.18 (17)	H18A—C18—H18C	109.5
N11—C15—C16	123.11 (18)	H18B—C18—H18C	109.5
C14—C15—C16	129.71 (19)	C17—C19—H19A	109.5
C15—C16—H16A	109.5	C17—C19—H19B	109.5
C15—C16—H16B	109.5	H19A—C19—H19B	109.5
H16A—C16—H16B	109.5	C17—C19—H19C	109.5
C15—C16—H16C	109.5	H19A—C19—H19C	109.5
H16A—C16—H16C	109.5	H19B—C19—H19C	109.5
H16B—C16—H16C	109.5		

C15—N11—N12—C13	0	Ni—N12—C13—C17	0.0000 (10)
B—N11—N12—C13	180	N12—C13—C14—C15	0
C15—N11—N12—Ni	180	C17—C13—C14—C15	180
B—N11—N12—Ni	0	N12—N11—C15—C14	0
N12^{i}—Ni—N12—C13	133.27 (4)	B—N11—C15—C14	180
Cl—Ni—N12—C13	0	N12—N11—C15—C16	180
N12^{i}—Ni—N12—N11	−46.73 (4)	B—N11—C15—C16	0.0000 (10)
Cl—Ni—N12—N11	180	C13—C14—C15—N11	0
C15—N11—B—N11^{i}	−121.12 (18)	C13—C14—C15—C16	180.0000 (10)
N12—N11—B—N11^{i}	58.88 (18)	N12—C13—C17—C19	61.54 (12)
N11—N12—C13—C14	0	C14—C13—C17—C19	−118.46 (12)
Ni—N12—C13—C14	180	N12—C13—C17—C18	180.0000 (10)
N11—N12—C13—C17	180	C14—C13—C17—C18	0.0000 (10)

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

Fig. 1


C18
C14
C16
C19
C15
C13
C17
C16i
N11
N12
C19iii
C19iv
B
N11i
N12i
Ni
Cl
N11ii
C16ii
C19i
N12ii
C15ii
C13ii
C19ii
C14ii
C17ii
C19v
C18ii