Structure of a Tetrahedral Pyrazolylboratocobalt(II) Complex, Co[HB(3-iPr,4-Brpz)3]Cl*

BY MICHAEL D. OLSON, STEVEN J. RETTIG, ALAN STORR AND JAMES TROTTER

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1

AND S. TROFIMENKO

Du Pont Electronics Department, Experimental Station 336/205, Wilmington, DE 19898, USA

Abstract. $C_{18}H_{25}BBr_3ClCoN_6$, $M_r = 670.36$, orthorhombic, $Cmc2_1$, $a = 14.575$ (1), $b = 10.853$ (1), $c = 15.731$ (1) Å, $V = 2488.4$ (4) Å^3, $Z = 4$, $D_x = 1.789$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0.70930$ Å, $\mu = 55.9$ cm^{-1}, $F(000) = 1316$, $T = 294$ K, $R = 0.028$ for 970 reflections [$I > 3\sigma(I)$]. The molecule has crystallographic mirror and approximate C_{3v} symmetry with pseudo-tetrahedral coordination about the Co atom (mean Cl—Co—N = 122.1, N—Co—N = 94.4°) and principal bond lengths: Co—Cl = 2.207 (3), Co—N = 2.039 (6) and 2.057 (9) Å. The Co—N distances compare well with those in another complex of the same ligand, but are about 0.08 Å longer than those in complexes with less bulky ligands.

Experimental. Crystal dimensions $0.13 \times 0.18 \times 0.30$ mm. Nonius CAD-4F diffractometer, monochromatized Mo $K\alpha$ radiation, lattice parameters from 25 reflections with $\theta = 17$–$20°$. Intensities for $\theta \le 30°$, *hkl*: 0 to 20, 0 to 15, 0 to 22, ω–2θ scan, ω scan width $(0.80 + 0.35\tan\theta)°$ at 1.2–$10°$ min^{-1}, extended 25% on each side for background measurement, three standard reflections showed no significant variation, Lp and absorption corrections [transmission factors 0.36–0.53, analytical method (de Meulenaer & Tompa, 1965)]. 1935 unique reflections, 970 (50.1%) with $I \ge 3\sigma(I)$. Structure solved by Patterson and Fourier methods, refined by full-matrix least-squares procedures, H atoms in calculated positions, not refined. Refinement on F, with $w = 1/\sigma^2(F)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + (0.04I)^2$, S = scan, B_1 and B_2 = background counts, scattering factors (with anomalous-dispersion corrections) from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–102, 149), locally written, or locally modified versions of standard computer programs.

* Chlorotris[4-bromo-3-(2-methylethyl)pyrazolyl]hydroboratocobalt(II).

Table 1. *Positional (fractional) and equivalent isotropic thermal parameters* [$U_{eq} = \frac{1}{3} \times$ (*trace of diagonalized U matrix*), Å$^2 \times 10^3$]

|	x	y	z	U_{eq}
Br(1)	0	0.56130 (10)	0.33034	45
Br(2)	0.32108 (5)	−0.02959 (9)	−0.00027 (10)	57
Co	0	0.01747 (13)	0.24225 (13)	30
Cl	0	−0.1125 (2)	0.3501 (2)	43
N(1)	0	0.2622 (7)	0.1794 (5)	32
N(2)	0	0.2056 (8)	0.2583 (6)	37
N(3)	0.0861 (4)	0.1070 (5)	0.0927 (4)	33
N(4)	0.1031 (4)	0.0196 (5)	0.1546 (4)	36
C(1)	0	0.3858 (9)	0.1927 (7)	33
C(2)	0	0.4065 (8)	0.2774 (7)	26
C(3)	0	0.2912 (8)	0.3169 (7)	32
C(4)	0.1535 (5)	0.1046 (7)	0.0355 (5)	35
C(5)	0.2138 (5)	0.0148 (7)	0.0581 (5)	35
C(6)	0.1821 (5)	−0.0365 (7)	0.1328 (5)	37
C(7)	0	0.2621 (10)	0.4115 (8)	44
C(8)	0.0855 (7)	0.1926 (8)	0.4375 (5)	59
C(9)	0.2249 (6)	−0.1374 (8)	0.1857 (6)	61
C(10)	0.1623 (8)	−0.2522 (8)	0.1852 (7)	78
C(11)	0.2455 (7)	−0.0964 (11)	0.2765 (7)	76
B	0	0.1889 (9)	0.0975 (7)	29
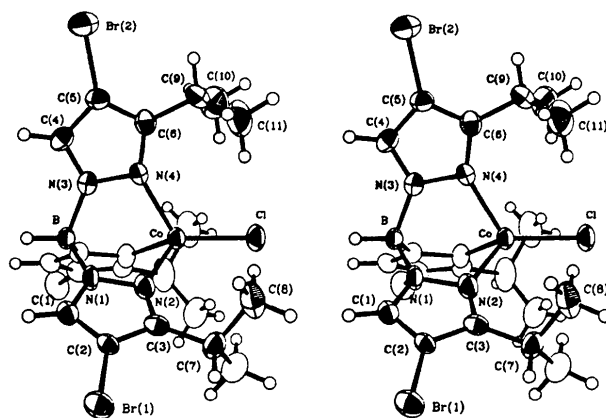
Fig. 1. Stereoview of the molecule; 50% ellipsoids for the non-H atoms.

Final $R = 0.028$, $wR = 0.032$ for 150 parameters, 970 reflections with $I > 3\sigma(I)$ (significantly poorer agreement for the opposite polarity, R and wR ratios

Table 2. *Bond lengths (Å) and angles (°), with e.s.d.'s in parentheses*

Br(1)—C(2)	1·874 (10)	N(3)—B	1·540 (8)
Br(2)—C(5)	1·876 (7)	N(4)—C(6)	1·347 (9)
Co—Cl	2·207 (3)	C(1)—C(2)	1·352 (15)
Co—N(2)	2·057 (9)	C(2)—C(3)	1·397 (13)
Co—N(4)	2·039 (6)	C(3)—C(7)	1·52 (2)
N(1)—N(2)	1·385 (11)	C(4)—C(5)	1·360 (10)
N(1)—C(1)	1·358 (12)	C(5)—C(6)	1·381 (11)
N(1)—B	1·514 (13)	C(6)—C(9)	1·510 (10)
N(2)—C(3)	1·309 (13)	C(7)—C(8)	1·513 (11)
N(3)—N(4)	1·383 (8)	C(9)—C(10)	1·544 (14)
N(3)—C(4)	1·332 (8)	C(9)—C(11)	1·525 (15)

Cl—Co—N(2)	122·7 (3)	C(1)—C(2)—C(3)	106·8 (9)
Cl—Co—N(4)	121·8 (2)	N(2)—C(3)—C(2)	108·9 (9)
Cl—Co—N(4')	121·8 (2)	N(2)—C(3)—C(7)	122·8 (9)
N(2)—Co—N(4)	94·1 (2)	C(2)—C(3)—C(7)	128·3 (9)
N(2)—Co—N(4')	94·1 (2)	N(3)—C(4)—C(5)	108·3 (6)
N(4)—Co—N(4')	94·9 (3)	Br(2)—C(5)—C(4)	126·5 (6)
N(2)—N(1)—C(1)	107·5 (9)	Br(2)—C(5)—C(6)	126·3 (5)
N(2)—N(1)—B	121·9 (7)	C(4)—C(5)—C(6)	107·2 (6)
C(1)—N(1)—B	130·6 (9)	N(4)—C(6)—C(5)	108·7 (6)
Co—N(2)—N(1)	109·3 (6)	N(4)—C(6)—C(9)	122·7 (7)
Co—N(2)—C(3)	142·3 (7)	C(5)—C(6)—C(9)	128·6 (7)
N(1)—N(2)—C(3)	108·4 (8)	C(3)—C(7)—C(8)	111·6 (6)
N(4)—N(3)—C(4)	109·3 (5)	C(3)—C(7)—C(8')	111·6 (6)
N(4)—N(3)—B	120·5 (6)	C(8)—C(7)—C(8')	110·9 (10)
C(4)—N(3)—B	130·2 (6)	C(6)—C(9)—C(10)	109·8 (8)
Co—N(4)—N(3)	110·6 (4)	C(6)—C(9)—C(11)	112·7 (8)
Co—N(4)—C(6)	142·8 (5)	C(10)—C(9)—C(11)	110·9 (8)
N(3)—N(4)—C(6)	106·5 (6)	N(1)—B—N(3)	110·2 (5)
N(1)—C(1)—C(2)	108·4 (9)	N(1)—B—N(3')	110·2 (5)
Br(1)—C(2)—C(1)	125·9 (7)	N(3)—B—N(3')	109·2 (7)
Br(1)—C(2)—C(3)	127·3 (8)		

Primed atoms are related to unprimed atoms by the mirror plane: $-x, y, z$.

$1\cdot14$ and $1\cdot18$), $S = 1\cdot06$, Δ/σ (maximum) $= 0\cdot07$, $\Delta\rho = 0\cdot69$ e Å^{-3}. Positional parameters are in Table 1, bond lengths and angles in Table 2, and a view of the molecule is in Fig. 1.*

Related literature. Guggenberger, Prewitt, Meakin, Trofimenko & Jesson (1973); Trofimenko, Calabrese, Domaille & Thompson (1989); Gorell & Parkin (1990).

References

GORELL, I. B. & PARKIN, G. (1990). *Inorg. Chem.* **29**, 2452–2456.
GUGGENBERGER, L. J., PREWITT, C. T., MEAKIN, P., TROFIMENKO, S. & JESSON, J. P. (1973). *Inorg. Chem.* **12**, 508–515.
MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.
TROFIMENKO, S., CALABRESE, J. C., DOMAILLE, P. J. & THOMPSON, J. S. (1989). *Inorg. Chem.* **28**, 1091–1101.

Structure of an Octahedral Pyrazolylboratonickel Complex, Ni[HB(3-^{i}Pr,4-Brpz)$_3$][HB(3,5-Me$_2$pz)$_3$]*

BY MICHAEL D. OLSON, STEVEN J. RETTIG, ALAN STORR AND JAMES TROTTER

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1

AND S. TROFIMENKO

Du Pont Electronics Department, Experimental Station 336/205, Wilmington, DE 19898, USA

Abstract. C$_{33}$H$_{47}$B$_2$Br$_3$N$_{12}$Ni, $M_r = 931\cdot88$, orthorhombic, *Pbca*, $a = 20\cdot65$ (1), $b = 29\cdot158$ (3), $c = 13\cdot306$ (2) Å, $V = 8012$ (4) Å^3, $Z = 8$, $D_x = 1\cdot545$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 34\cdot9$ cm^{-1}, $F(000) = 3776$, $T = 294$ K, $R = 0\cdot054$ for 1976 reflections. The molecule has octahedral coordination geometry with the Ni—N distances involving the sterically more demanding ^{i}Pr/Br ligand [2·13–2·16 (1) Å] longer than those involving the Me$_2$ ligand [2·05–2·08 (1) Å].

Experimental. Crystal dimensions $0\cdot25 \times 0\cdot30 \times 0\cdot45$ mm. Rigaku AFC6 diffractometer, monochromatized Mo $K\alpha$ radiation, lattice parameters from 25 reflections with $\theta = 10$–17°. Intensities for θ

* Tris[4-bromo-3-(2-methylethyl)pyrazolyl]hydroboratotris(3,5-dimethylpyrazolyl)hydroboratonickel.