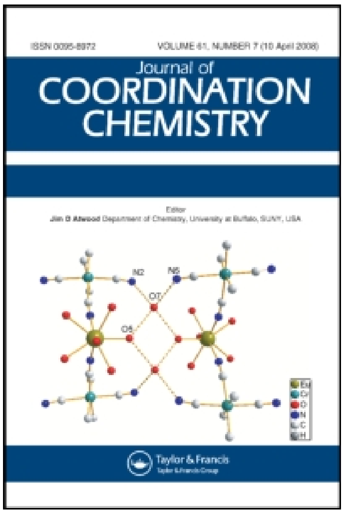

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Syntheses, solid-state structures and thermal analyses of M(Bp)$_2$ (M=Cu, Ni) (Bp=H$_2$B(pyrazolyl)$_2$)

Yong Heng Xing[a]; Hou Qun Yuan[a]; Bao Li Zhang[a]; Yuan Hong Zhang[a]; Shu Yun Niu[a]; Feng Ying Bai[a]
[a] College of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, China

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Syntheses, solid-state structures and thermal analyses of $M(Bp)_2$ ($M = Cu$, Ni) ($Bp = H_2B(pyrazolyl)_2$)

YONG HENG XING*, HOU QUN YUAN, BAO LI ZHANG,
YUAN HONG ZHANG, SHU YUN NIU and FENG YING BAI

College of Chemistry and Chemical Engineering, Liaoning Normal University,
Huanghe Road 850#, Dalian, China, 116029

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Reaction of a mixture of $CuCl_2$, $Ni(CH_3COO)_2$ and $NaH_2B(pz)_2$ in methanol solution, resulted in the dihydrobis(pyrazolyl)borate complexes $Cu(H_2B(pz)_2)_2$ and $Ni(H_2B(pz)_2)_2$, respectively. Complexes **1** and **2** were characterized by IR, elemental analyses, thermal analyses and X-ray diffraction. The two complexes both crystallize in the space group *Pbca*, with crystal parameters for complex **1** $a = 14.443(3)$ Å, $b = 6.2162(12)$ Å, $c = 17.865(4)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 1604.0(5)$ Å^3, $Z = 4$; for complex **2** $a = 14.5264(4)$ Å, $b = 6.3235(2)$ Å, $c = 17.4720(4)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 1604.94(8)$ Å^3, $Z = 4$, respectively. X-ray structure analysis has shown that complexes **1** and **2** are both monomeric neutral complexes, and possess similar coordination modes around the metal centers.

Keywords: Dihydrobis(pyrazolyl)borate; Copper and nickel complexes; Crystal structure; Thermal analyses

1. Introduction

Since their introduction by Trofimenko [1–4], coordination chemistry of poly(pyrazolyl)borate ligands $[H_xB(pz)_{4-x}]$, which are anionic nitrogen-donor ligands, has been extensively developed with particular interest arising from the ability of this class of ligands to modify or control the electronic and steric environment about the metal center by changing the number and nature of the substituents on the pyrazolyl moieties [5–8]. They also play a potential role in multimetal-centered catalysis in both biological and industrial reactions [9].

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*Corresponding author. Email: yhxing2000@yahoo.com

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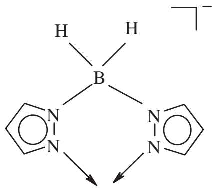
The parent compounds of poly(pyrazolyl)borate ligands are dihydrobis(pyrazolyl)-borate (Bp, **1**) and hydrotris(pyrazolyl)borate (Tp, **2**). Recently, many modified poly(pyrazolyl)borate ligands have been synthesized, such as bis- and tris(1,2,4-triazolyl)borate (**3** and **4**), bis(tetrazolyl)borate (**5**), bis- and tris(imidazolyl)borate (**6**) or bis- and tris(indazolyl)borate (**7** and **8**) and their derivatives [10].



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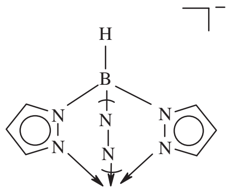

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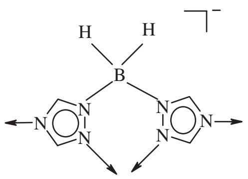

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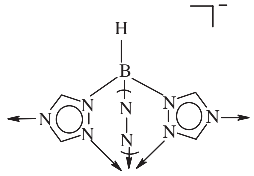

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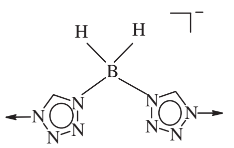

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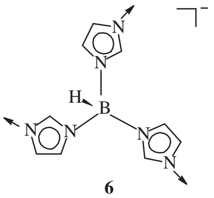

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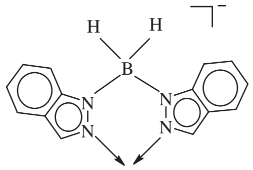

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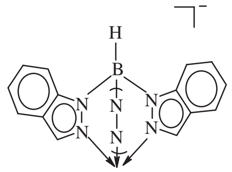
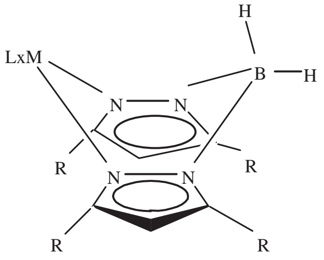
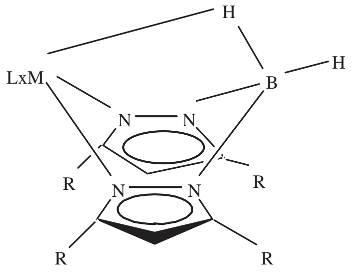


8

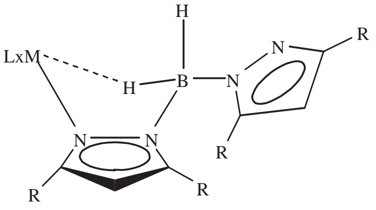
Because of the close similarity between the imidazole moiety of the amino acid histidine and pyrazole, the poly(pyrazolyl)borate complexes can be considered as model complexes of metalloenzymes, such as carbonic anhydrase (CA), nitrite reductases (NiR), hemocyanin (Hc) and blue copper proteins [11]. With this bioinorganic interest, our group has been interested in the investigation of complexes with tris(pyrazolyl) borate ligands [12–15]. Our strategy is to implement polypyrazolylborate or modified poly(pyrazolyl)borate ligands as supporting ligands and to change the remaining ligands of the metal center to control the structure and physical and chemical character of the complexes. To date, numerous syntheses and properties of complexes with tris(pyrazolyl)borate ligands have been reported, but considerably fewer with bis(pyrazolyl)borate are known. As a part of a continuing effort to synthesize model complexes of metalloenzymes, we extend our studies into the development of bis(pyrazolyl)borate ligands. Generally, the four modes of coordination for a bis(pyrazolyl)borate are as follows [16]:



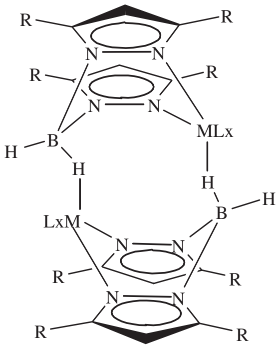
A



B



C



D

Type **A** is the most common bonding mode, and type **B**, **C** and **D** is considered to be unusual for a bis(pyrazolyl)borate coordinating a metal through only one nitrogen atom. In the present artilce, we report two new bis(pyrazolyl)borate complexes, $Cu(H_2B(pz)_2)_2$ and $Ni(H_2B(pz)_2)_2$. Relevant examples of such complexes derived from the ubiquitous Bp ligand are the complexes $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]CuL$ ($L = PPh_3, N{\equiv}CCH_3$, $HC{\equiv}CPh, H_2C{=}CHPh$), $\{[H_2B(3,5\text{-}(CF_3)_2pz)_2]Cu\}_2(1,5\text{-}COD)$ (1,5-COD = 1,5-cyclooctadiene) [17], $(NEt_4)_2[WS_4(CuBp)_4]$ [18], $[H_2B(3,5\text{-}(CF_3)_2pz)_2]_2Cu$ [19], $\{[H_2B(3,5\text{-}(CF_3)_2pz)_2]CuCNBu^t\}_2$ [20], $[H_2B(3,5\text{-}(CF_3)_2pz)_2]Cu(PPh_3)_2$, $[H_2B(3,5\text{-}(CF_3)_2pz)_2]Cu(2,4,6\text{-collidine})$ [21] etc. Although Trofimenko has investigated the magnetic properties and spectra of $Cu(H_2B(pz)_2)_2$ and $Ni(H_2B(pz)_2)_2$, and the crystal structure of $Ni(H_2B(pz)_2)_2$ has been reported [22,23], comparison of synthesis, IR spectra, structures and properties of $M(Bp)_2$ (M = Cu, Ni) ($Bp = H_2B(pyrazolyl)_2$) has not been reported in detail.

2. Experimental

2.1. *Materials*

All reactions were carried out at room temperature. Solvents were dried with molecular sieves (4 Å). All reactants were used as purchased. The infrared spectra were recorded on a FT/IR-480 PLUS Fourier Transform spectrometer with pressed KBr pellets at 4000–220 cm^{-1}. The thermal curves were recorded on a Perkin-Elmer Diamond TG/DTA. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer 240C automatic analyzer. The precursor $NaH_2B(pz)_2$ was prepared according to literature methods [4].

2.2. *Syntheses of the title complexes*

2.2.1. Synthesis of $Cu(H_2B(pz)_2)_2$ (1). To a solution of $CuCl_2$ (0.20 g, 1 mmol) in 15 mL of dry MeOH was added $NaH_2B(pz)_2$ (0.35 g, 2 mmol). The green solution changed to dark blue gradually. The mixture was stirred for 2 h to form a little bit of violet–red precipitates. The precipitates were isolated from the solution by filtration, washed with MeOH extensively, and dried in air. Violet–red crystals were obtained from the filtration after 2 days. Elemental Anal. Calcd for $C_{12}H_{16}N_8B_2Cu$ (%) (FW 357.49): C, 40.28; H, 4.48; N, 31.33. Found: C, 40.35; H, 4.50; N, 31.11. IR (KBr, ν cm^{-1}): 3136, 3127, 2924, 2607, 2439, 2394, 2345, 2297, 2280, 2238, 1739, 1626, 1502, 1436, 1405, 1306, 1210, 1186, 1164, 1154, 1097, 1063, 988, 900, 886, 862, 776, 761, 721, 661, 634, 620, 376, 323, 295, 277.

2.2.2. Synthesis of $Ni(H_2B(pz)_2)_2$ (2). To a solution of $Ni(CH_3COO)_2$ (0.25 g, 1 mmol) in 15 mL of dry MeOH was added $NaH_2B(pz)_2$ (0.35 g, 2 mmol). The green solution gradually turned darker. The mixture was stirred for 2 h to form a little bit of orange red precipitate. The precipitate was isolated from the solution by filtration, washed with MeOH extensively, and dried in air. The orange–red crystals were obtained from filtration after 2 days. Elemental Anal. Calcd for $C_{12}H_{16}N_8B_2Ni$ (%) (FW 352.66): C, 40.83; H, 4.54; N, 31.76. Found: C, 40.75; H, 4.33; N, 31.81. IR (KBr, ν cm^{-1}): 3139, 3129, 2925, 2437, 2399, 2346, 2283, 1727, 1617, 1499, 1408, 1311, 1213, 1199, 1182, 1166, 1154, 1101, 1067, 997, 902, 888, 856, 769, 756, 721, 634, 620, 431, 402, 356, 325, 226.

2.3. *X-ray crystallography determination*

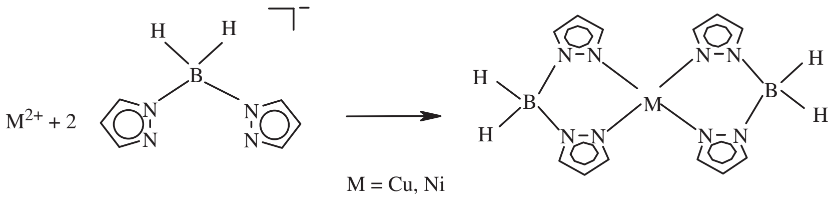
Suitable single crystals of both complexes were mounted on glass fibers for X-ray measurement. All diffraction data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) and ω–2θ scan mode. Data were corrected for Lorentz and polarization effects. Crystal structures were solved by Direct Methods, and the remaining atoms were located from difference Fourier syntheses. All programs used were part of SHELX-97. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed at calculated positions and forced to ride on the attached carbon and boron atoms. Atomic scattering factors and anomalous dispersion terms were taken form SHELX-97. Crystal data and details of the data collection and the structure refinement are given in table 1.

Table 1. Crystal data and structure refinement for complexes **1** and **2**.

Complexes	**1**	**2**
Formula	$C_{12}H_{16}N_8B_2Cu$	$C_{12}H_{16}N_8B_2Ni$
M ($g\,mol^{-1}$)	357.49	352.66
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*
a (Å)	14.443(3)	14.5264(4)
b (Å)	6.2162(12)	6.3235(2)
c (Å)	17.865(4)	17.4720(4)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å^3)	1604.0(5)	1604.94(8)
Z	4	4
D_{Calcd}	1.48	1.460
Crystal size (mm^3)	$0.15 \times 0.05 \times 0.20$	$0.17 \times 0.04 \times 0.25$
$F(000)$	7320	7280
μ(Mo-Kα) (cm^{-1})	1.371	1.218
2θ (°)	5.36–57.92	4.66–66.84
Reflections collected	9516	8413
Independent reflections ($I > 2\sigma(I)$)	2017	2589
Parameters	106	106
$\Delta(\rho)$ (e Å^{-3})	0.265 and −0.539	0.275 and −0.474
Goodness-of-fit	1.072	1.013
R^{a}	0.0271 (0.0346)^{b}	0.0374 (0.0722)^{b}
$wR_2{}^{a}$	0.0834 (0.0886)^{b}	0.0894 (0.1038)^{b}

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(|F_o|^2 - |F_c|^2)^2/[\Sigma(w(|F_o|^2)^2]^{1/2}$; $[|F_o| > 4\alpha(|F_o|)]$.

[b] Based on all data.



Scheme 1. Capital: The reaction process of complexes **1** and **2**.

3. Results and discussion

3.1. *Synthesis and spectroscopic characterization*

The complexes **1** and **2** were obtained by reaction of $CuCl_2$ and $Ni(CH_3COO)_2$ with $NaH_2B(pz)_2$ in MeOH (see scheme 1 below), respectively. Crystals of complex **1** are violet–red and those of **2** are orange red. The IR spectra of the precipitates of the two complexes were identical to those of their single crystals, showing that the precipitates were the final products too. In addition, using $Cu(CH_3COO)_2$ or $Cu(NO_3)_2$ as a starting material in the reaction with $NaH_2B(pz)_2$, resulted in complex **1** (by IR testing).

To study the influence of the molar ratio of the starting materials on the composition of the final products, a systematic study was carried out. It was found that complexes **1** and **2** were obtained whether the molar ratio of Cu(Ni): ligand was 1 : 1 or 1 : 2.

Complexes **1** and **2** are stable in air at room temperature, and soluble in $CHCl_3$, CH_2Cl_2, CH_3CN, THF, and CH_3COCH_3, slightly soluble in MeOH and EtOH and insoluble in water, diethyl ether and hexane.

The IR spectrum of complex **1** showed weak bands at 3136 and 3127 cm^{-1}, assigned to stretching vibrations of C–H. There are multiple peaks in the range of 3000–2000 cm^{-1}, 2439, 2394, 2345 and 2280 cm^{-1}, which are assigned to the B–H and B–H $\cdots$ Cu stretching vibrations. These bands resemble the B–H stretching frequencies of $\{[H_2B(3,5\text{-}(CF_3)_2Pz)_2]CuCNBu^t\}_2$, 2568 cm^{-1}, 2303 and 2344 cm^{-1} [20], $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PPh_3)_2$, 2505 and 2215 cm^{-1} [21]. The peaks of complex **2** in the same range are 2437, 2399, 2346, 2283 cm^{-1}. In the range 2000–1000 cm^{-1}, the bands are complicated. The characteristic bands of **1** are: 1502, 1405, 1306, 1210, 1154, 1063 cm^{-1}; the characteristic bands of **2** are 1499, 1408, 1311, 1213, 1154, 1067 cm^{-1}. These bands are associated with the characteristic absorptions of the pyrazole ring of the coordinated dihydrobis(pyrazolyl)borate. These are similar to those of free dihydrobis(pyrazolyl)borate, and include characteristic absorptions of $\nu_{C=N}$, $\nu_{C=C}$, $\nu_{N–N}$, $\nu_{B–H}$, $\nu_{C–H}$, but it was hard to identify the bands due to the peaks overlapping. In the range of 1000–220 cm^{-1}, the characteristic bands of complex **1** were 886, 761, 721, 634, 376 cm^{-1}, and those of complex **2** were at 888, 756, 721, 620, 356 cm^{-1}, respectively. The first three bands may be assigned to the absorption of $\nu_{C–H}$, $\nu_{B–N}$ and $\nu_{N–B–N}$, the last may be related to $\nu_{M–N}$ (M = Cu, Ni) [24].

3.2. *The crystal structures of* $Cu(H_2B(pz)_2)_2$ *(1) and* $Ni(H_2B(pz)_2)_2$ *(2)*

The structure and atomic labeling scheme for complex **1** is presented in figure 1. A selection of interatomic distances and bond angles relevant to the coordination spheres of the copper and nickel for the title complexes are listed in table 2.

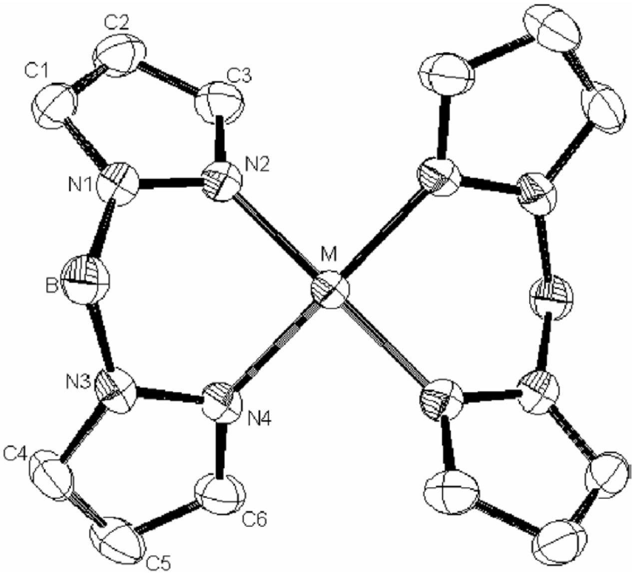


Figure 1. Molecular structure of the complex **1** and **2** (M = Cu, Ni).

Table 2. Selected bond lengths (Å) and angles (°) for the complexes **1** and **2**.

Bonds/angles	Complex **1**	Complex **2**	Bonds/angles	Complex **1**	Complex **2**
M–N(2)#1	1.9901(13)	1.8919(14)	M–N(2)	1.9902(13)	1.8919(14)
M–N(4)#1	1.9837(12)	1.8966(15)	M–N(4)	1.9837(12)	1.8965(15)
N(1)–C(1)	1.3335(19)	1.335(2)	N(1)–N(2)	1.3583(17)	1.360(2)
N(1)–B	1.543(2)	1.555(3)	N(2)–C(3)	1.337(2)	1.337(2)
N(3)–C(4)	1.3335(19)	1.338(2)	N(3)–N(4)	1.3590(16)	1.359(2)
N(3)–B	1.553(2)	1.544(2)	N(4)–C(6)	1.336(2)	1.337(2)
N(4)#1–M–N(4)	180.00(5)	180.0	N(4)#1–M–N(2)#1	90.98(5)	90.91(6)
N(4)–M–N(2)#1	89.02(5)	89.09(6)	N(4)#1–M–N(2)	89.02(5)	89.09(6)
N(4)–M–N(2)	90.98(5)	90.91(6)	N(2)#1–M–N(2)	180.00(7)	180.0
C(1)–N(1)–B	131.70(14)	131.38(17)	N(2)–N(1)–B	119.51(12)	119.51(15)
N(1)–N(2)–M	121.21(10)	121.68(11)	C(4)–N(3)–B	130.98(13)	132.04(17)
N(4)–N(3)–B	119.85(11)	119.17(15)	C(6)–N(4)–M	131.05(11)	130.09(14)
N(3)–N(4)–M	121.39(9)	121.90(11)	N(1)–B–N(3)	105.50(12)	104.14(16)

#1: symmetry operation for complex **1**: $-x+1$, $-y$, $-z+1$; for complex **2**: $-x$, $-y$, $-z$.

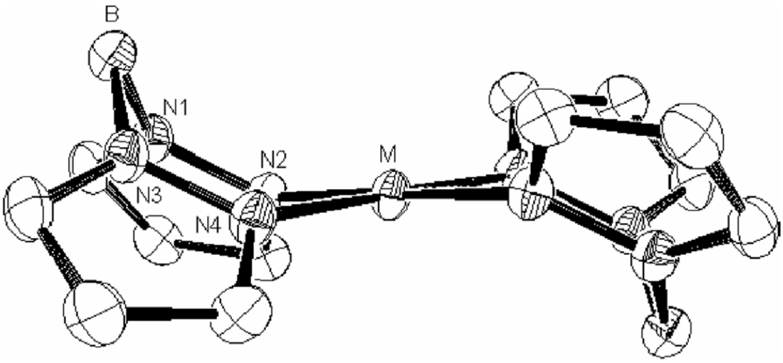


Figure 2. Molecular structure of the title complex **1** and **2** (M = Cu, Ni).

The structure of complex **1** consists of one Cu atom, two bidentate coordinated dihydrobis(pyrazolyl)borate ligands crystallizing in the orthorhombic space group *Pbca*, in which the Cu atom has a slightly distorted square environment.

As shown in figure 1, the copper atom is in a square-planar geometry (the N–Cu–N angles are 89.02(5)° and 90.98(5)°) with four nitrogen atoms coordinated from two dihydrobis(pyrazolyl)borate ligands. The copper resides on an inversion center. The Cu(N–N)$_2$B unit in complex **1** adopts the characteristic boat conformation. As a result, the endo hydrogens of each BH$_2$ moiety shield the copper center from above and below the CuN$_4$ plane as shown in figure 2. The Cu–N distances of **1** (1.9837(12) Å, 1.9902(13) Å) are somewhat similar to other copper poly(pyrazolyl)borates. For example, the Cu–N distances of (NEt$_4$)$_2$[WS$_4$(CuBp)$_4$] [18] are 2.021(3) Å and 2.093(3) Å. These distances can also be compared to the Cu–N distances involving the fluorinated bis(pyrazolyl)borates, [H$_2$B(3,5-(CF$_3$)$_2$pz)$_2$]$_2$Cu [19] (1.997(5) Å, 2.004(6) Å), {[H$_2$B(3,5-(CF$_3$)$_2$pz)$_2$]CuCNBu^t}$_2$ [20] (2.018(3) Å, 2.014(3) Å), [H$_2$B(3,5-(CF$_3$)$_2$pz)$_2$]Cu(PPh$_3$)$_2$ [21] (2.057(2) Å), [H$_2$B(3,5-(CF$_3$)$_2$pz)$_2$]Cu(2,4,6-collidine) [21]

(1.9734(16) Å, 2.0830(15) Å), [$H_2B(3,5\text{-}(CF_3)_2pz)_2$]Cu(PhC≡CH) [17] (1.989(3) Å, 1.991(3) Å) and {[$H_2B(3,5\text{-}(CF_3)_2pz)_2$]Cu}$_2$(1,5-COD) (1,5-COD = 1,5-cyclooctadiene) [17] (1.989(3) Å, 1.994(3) Å). The nonbonding Cu···H–B distance in complex **1** is 3.121 Å, which is close to that of Ni···H–B (3.131 Å), much longer than the typical Cu–H bond distances (average 1.87 Å) observed in copper borohydride complexes [19], showing that the interaction between Cu and H is very weak. The B–N distances are unequal, the distance B–N_1 (1.543(2) Å) is slightly shorter than that of B–N_3 (1.553(2) Å), and the N_1–B–N_3 angle is 105.50(12)°, implying that the boron atom is tetrahedral. The torsion angle of $C_5C_6N_4Cu$ is $-169.3°$, but the torsion angle of $C_2C_3N_2Cu$ is 163.5°, showing that the distortion of the two pyrazole moieties is different.

Complex **2** is isomorphous and isostructural with the copper complex and crystallizes in the orthorhombic crystal system with the same space group of *Pbca*. The average Ni–N distance (1.8942(15) Å) is obviously shorter than Cu–N (1.9870(13) Å). The N_1–B–N_3 angle is 104.14°, which is slightly smaller than in complex **1**. The torsion angle of $C_5C_6N_4Ni$ is $-168.6°$, but the torsion angle of $C_2C_3N_2Ni$ is 172.1°, showing that distortion of the two pyrazole units in **2** is obviously larger than in **1**.

3.3. *Thermal properties*

Complexes **1** and **2** are very stable in air at ambient temperature. Thermal gravimetric analyses (TGA) were carried out to examine the thermal stability of **1** and **2**. The samples were heated in N_2 at 1 atm with a heating rate of 10°C min^{-1}. The TGA curves show that the decomposition of complexes **1** and **2** were complicated. **1** is stable up to 145°C. A total weight loss of 43.68% occurred in the temperature range 145–270°C, presumably due to the removal of 2.3 pyrazole fractions of the dihydrobis(pyrazolyl)borate ligands per formula unit (Calcd 43.79%). A weight loss of 24.08% occurred in the temperature range 310–455°C, corresponding to the removal of 1.3 pyrazole fractions (Calcd 24.76%). The TGA curve shows that **2** is stable up to 150°C. A total weight loss of 13.00% occurred in the temperature range 150–200°C, mainly corresponding to removal of the about 0.7 pyrazole fractions of the dihydrobis(pyrazolyl)borate ligands per formula unit (Calcd 13.52%). An apparent weight loss of 66% occurred in the temperature range 240–300°C, consistent with the removal of about 3.3 pyrazole fractions (Calcd 64.41%). The results indicate that although the molecular structures of the two complexes are similar, their thermal decomposition courses are different.

Supplementary material

Tables of atomic coordinates, isotropic thermal parameters, and complete bond distances and angles have been deposited with the Cambridge Crystallographic Data Center. Copies of this information may be obtained free of charge, by quoting the publication citation and deposition numbers CCDC: 290749 and 290750, from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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