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The Structure of Bis(diphenyldipyrazolylborato)nickel(II)

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The structure of bis(diphenyldipyrazolylborato)nickel(II), $[(C_6H_5)_2B(C_3H_3N_2)_2]_2Ni(II)$, has been determined by X-ray crystallography. The compound crystallizes in the monoclinic space group C2/m with unit cell dimensions $a = 18.225(5)$ Å, $b = 10.393(3)$ Å, $c = 8.851(2)$ Å, $\beta = 106.4(2)°$; with $V = 1608.0$ Å^3 and $Z = 2$, the calculated density is 1.357 gcm^{-3}. Using 817 reflections in the range $0° < 2\Theta < 47°$ (MoKα radiation) for which $I > 3\sigma(I)$, the structure refined to final values of discrepancy indices, defined in the usual way, of $R_1 = 0.041$ and $R_2 = 0.049$. The molecule has a crystallographically demanded inversion center at the nickel atom as well as a mirror plane. In contrast to the analogous compound in which the dipyrazolyl ligand is $(C_2H_5)_2B(pz)_2$ (pz = 1-pyrazolyl) where the dipyrazolylborate ligand interacts further with the nickel atom through one of the methylene C–H groups, there is no further interaction in this case. The ligand conformation is similar to that in the case of $[(C_6H_5)_2B(pz)_2](CO)_2$(2-methylallyl)Mo.

Introduction

In the past few years some X-ray determinations have been done on compounds containing molybdenum and dipyrazolylborate ligands of the type $(R_2B(pz)_2(CO)_2$(enyl)Mo.[1] They have shown that the dipyrazolylborate ligand interacts further with the molybdenum atom through one of the B–H groups or through a methylene C–H bond. Further studies on $(C_6H_5)_2B(pz)_2(CO)_2$(methylallyl)Mo[2] revealed no ortho C–H···Mo interaction. Recently, Echols and Dennis[3] studied the molecule, bis(diethyldipyrazolylborato) nickel(II) finding, as suggested by NMR studies,[4] that one of the methylene hydrogen atoms was interacting with the nickel atom at a distance of 2.46 Å. The same NMR studies done on $Ni[Bu_2B(pz)_2]_2$[4] (Bu = n-C_4H_9) also suggested an interaction of the nickel atom with one of the hydrogen atoms of the butyl group.

We decided to investigate the title compound using X-ray crystallography since NMR studies were not feasible on this compound because of its low solubility in suitable solvents and also because this structure should afford a test of our explanation of why there was no Mo···H interaction in $(C_6H_5)_2B(pz)_2(CO)_2$(methylallyl)Mo. We report here a structure analysis of $[(C_6H_5)_2B(pz)_2]_2Ni(II)$ that shows no interaction of the ortho C–H with the nickel atom.

Experimental

Bis[diphenylbis-(1-pyrazolyl)borato]nickel(II) was prepared according to the published[4] procedure. Suitable crystals for X-ray crystallography were grown after dissolving the title compound in hot *o*-dichlorobenzene and then letting the solution return to room temperature over a two day period.

Crystallographic Procedures

A clear orange crystal with dimensions 0.10 × 0.10 × 0.20 mm was mounted on a glass fiber with the longest dimension nearly parallel to the axis of the goniometer head, and examined on a Syntex P$\bar{1}$ four-circle automatic diffractometer.

Axial photographs as well as Θ–2Θ and ω scans of several intense reflections showed that the crystal was of good quality with satisfactory mosaicity. A peak width at half height of 0.2° was found. Cell constants and an orientation matrix for the monoclinic unit cell were determined from least-squares refinement of the setting angles of 15 computer-centered reflections. Some data points that were collected in order to find some reflections with higher 2Θ angle to recenter the crystal indicated that the cell was face-centered. Cell constants were then recalculated using least-squares refinement of the setting angles of 15 computer-centered reflections in the range $12° < 2\Theta < 24°$. The monoclinic parameters at 23 ± 1 °C are a = 18.225 (5) Å, b = 10.393(3) Å, c = 8.851(2) Å, β = 106.4(2)° and V = 1608.0(9) Å^3. With molecular weight 657.0 g mol^{-1}, the calculated density for Z = 2 is 1.357 gcm^{-3}. The pattern of systematic absences indicated that the possible space group could be C2/m, Cm or C2.

Data were collected at 23 ± 1 °C using graphite monochromatized MoKα radiation and Θ–2Θ scans varying from 2° to 24°/min depending on the intensity of the reflection. A total of 1319 independent reflections were collected in the range $0 < 2\Theta(\text{MoK}\alpha) < 47°$

with a scan range from 0.9° below the K_{α_1} peak to 0.9° above the K_{α_2} peak. From these reflections, 817 with $I>3\sigma(I)$ were retained as observed data. Three standard reflections measured at intervals of 100 scans were stable. The linear absorption coefficient of the compound is 6.46 cm^{-1} and no absorption correction was applied.

Solution and Refinement of the Structure[5]

The space group C2/m was chosen at the beginning of the analysis. Since there were two molecules in the unit cell, the Ni atom was restricted by symmetry to be located at the special position 2/m. A cycle of least-squares refinement with this atom located at the origin, in which only the scale factor was varied, resulted in agreement factors of $R_1 = \Sigma\|F_o|-|F_c\|/\Sigma|F_o| = 0.37$ and $R_2 = [\Sigma w(|F_o-F_c|^2/\Sigma wF_o^2)]^{1/2} = 0.42$. The error in an observation of unit weight was 9.1. Following this, a difference Fourier synthesis revealed 11 non-hydrogen atoms. Another cycle of least-squares refinement including these atoms followed by a difference electron density map gave the remaining non-hydrogen atoms. Several cycles of full matrix least-squares refinement with isotropic thermal parameters resulted in agreement factors $R_1 = 0.071$ and $R_2 = 0.084$.

After two more cycles of refinement using anisotropic thermal parameters, an analysis of $\Sigma w(|F_o|-|F_c|)^2$ as a function of $|F_o|$ showed that the original choice (0.05) for the p parameter used in the calculation of the standard deviation of the intensity (*cf.* the program DATARED[5]) was too small. The value 0.06 was indicated to be a more suitable choice and it was used in the final cycles of refinement. At this point the positions of the hydrogen atoms were calculated using a C–H distance of 0.95 Å and one more cycle of anisotropic refinement was carried out. The hydrogen atom positions were recalculated and two more final cycles of full matrix least-squares refinement carried out without varying the hydrogen atom positions. This gave final values of $R_1 = 0.041$ and $R_2 = 0.049$, with the error in an observation of unit weight of 1.02.

The successful refinement of the structure as well as the reasonable values of all bond lengths and angles

TABLE I. Positional and Temperature Parameters[a,b] for $Ni[(pz)_2BPh_2]_2$.

Atom	Wykoff Notation	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	a	0.0	0.0	0.0	18.0(5)	56(1)	91(2)	0	11.6(7)	0
N(1)	j	0.1447(2)	0.1187(3)	0.1395(4)	18(2)	68(4)	83(5)	0(1)	9(2)	–1(4)
N(2)	j	0.0674(2)	0.1277(3)	0.1129(4)	18(1)	68(5)	96(6)	6(2)	14(2)	–1(4)
C(11)	j	0.1767(2)	0.2211(5)	0.2255(5)	24(2)	79(6)	117(8)	–11(3)	13(3)	–14(5)
C(12)	j	0.1213(3)	0.2956(5)	0.2571(5)	34(2)	80(6)	139(8)	–9(3)	16(3)	–26(6)
C(13)	j	0.0538(2)	0.2342(5)	0.1850(5)	27(2)	75(6)	128(8)	10(3)	21(3)	–5(5)
B	i	0.1794(4)	0.0	0.0724(8)	19(2)	59(8)	87(11)	0	11(4)	0
C(1)	i	0.2714(3)	0.0	0.1407(7)	24(2)	70(7)	87(10)	0	17(4)	0
C(2)	i	0.3090(4)	0.0	0.3020(8)	25(2)	127(9)	97(11)	0	14(4)	0
C(3)	i	0.3875(4)	0.0	0.3580(8)	25(3)	141(10)	118(12)	0	–16(5)	0
C(4)	i	0.4318(4)	0.0	0.2559(9)	13(2)	124(9)	193(15)	0	3(5)	0
C(5)	i	0.3967(4)	0.0	0.0977(8)	20(2)	122(9)	139(13)	0	16(5)	0
C(6)	i	0.3174(3)	0.0	0.0428(7)	22(2)	90(8)	104(11)	0	15(4)	0
C(7)	i	0.1479(3)	0.0	–0.1175(7)	17(2)	77(8)	96(10)	0	13(4)	0
C(8)	j	0.1366(3)	0.1134(5)	–0.2045(5)	31(2)	76(6)	112(8)	–1(2)	16(3)	0(5)
C(9)	j	0.1159(3)	0.1148(5)	–0.3686(6)	45(2)	108(7)	112(9)	0(3)	11(4)	40(6)
C(10)	i	0.1058(5)	0.0	–0.4492(8)	52(4)	149(12)	82(12)	0	7(5)	0
H(11)	j	0.0046	0.2633	0.1866						
H(12)	j	0.1279	0.3734	0.3160						
H(13)	j	0.2300	0.2391	0.2596						
H(2)	i	0.2796	0.0	0.3751						
H(3)	i	0.4112	0.0	0.4683						
H(4)	i	0.4860	0.0	0.2947						
H(5)	i	0.4265	0.0	0.0254						
H(6)	i	0.2941	0.0	–0.0678						
H(8)	j	0.1433	0.1933	–0.1500						
H(9)	j	0.1088	0.1942	–0.4240						
H(10)	i	0.0918	0.0	–0.5612						

[a] All values for the temperature factors have been multiplied by 10^4. Temperature factors are in the form $\exp[-\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. [b] The isotropic temperature factor for all hydrogen atoms was fixed at 5.5 $Å^2$.

in the molecule shows that the space group C2/m is correct. Refinement was not attempted in the other possible space groups.

A final analysis of $\Sigma w(|F_o|-|F_c|)^2$ as a function of $|F_o|$ showed no unusual trends in $\Sigma w(|F_o|-|F_c|)^2$ as a function of reflection number, $\lambda^{-1}\sin\Theta$, or various classes of indices. A table of observed and calculated structure factor amplitudes is available from the Editor upon request.

Results

The positional and thermal parameters for the crystallographically independent atoms are listed in Table I. Ten of the non-hydrogen atoms are in special positions with the nickel atom located at an inversion center. The boron atom and all the atoms in one of the phenyl groups as well as two of the carbon atoms in the other phenyl ring lie on a mirror plane.

Figure 1 presents a stereoscopic view of the Ni $(pz_2BPh_2)_2$ molecule with hydrogen atoms omitted for clarity. Figure 2, showing only one half of the molecule, defines the numbering scheme. The interatomic distances are listed in Table II and bond angles are listed in Table III. Some important molecular planes are described in Table IV.

Discussion

The four nitrogen atoms from the pyrazolyl groups bonded to the nickel form a square complex. The six-membered ring formed by the nickel, four nitrogen and the boron atom has a boat configuration as seen in Figure 2. Since there is no significant attractive interaction between the nickel atom and either phenyl group, the observed buckling of the ring must be attributed to the various forces between nonbonded atoms. As a measure of the degree of buckling, which is sometimes useful when comparing such rings in different compounds, we have listed in Table II the Ni· · ·B distance, 3.149 Å.

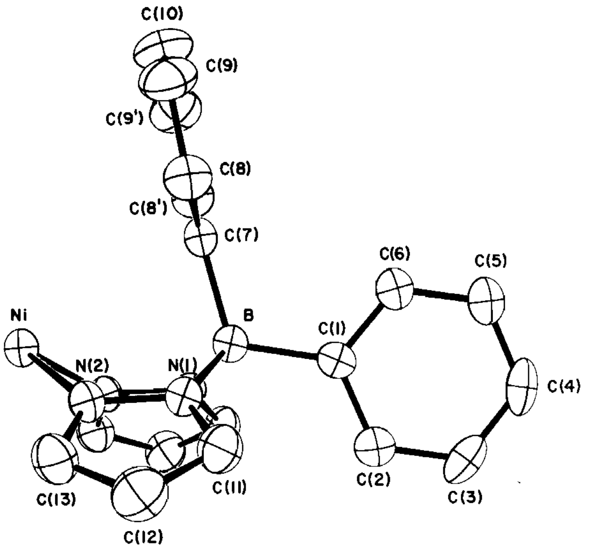

Figure 2. An ORTEP view of only one half of the molecule showing the boat conformation of the chelate ring. The atom numbering scheme used in all tables is defined. The atoms are represented by 50% probability thermal ellipsoids.

TABLE II. Interatomic Distances (Å)[a,b].

Atoms	Distance	Atoms	Distance
Ni–N(2)	1.891(3)	C(1)–C(2)	1.398(8)
N(2)–N(1)	1.364(4)	C(2)–C(3)	1.376(9)
N(1)–C(11)	1.343(5)	C(3)–C(4)	1.372(10)
C(11)–C(12)	1.363(6)	C(4)–C(5)	1.365(9)
C(12)–C(13)	1.372(6)	C(5)–C(6)	1.388(9)
C(13)–N(2)	1.335(5)	C(6)–C(1)	1.365(8)
B–N(1)	1.577(5)	C(7)–C(8)	1.391(5)
B–C(1)	1.613(9)	C(8)–C(9)	1.393(6)
B–C(7)	1.616(9)	C(9)–C(10)	1.375(6)
Ni–B	3.149(7)		

[a] Numbers in parentheses are the estimated standard deviations in the last significant digits. [b] Atoms are labeled as in Figure 2.

The most important result of this study is the observation that once again in a $(Bpz_2Ph_2)M$ complex there is no metal-hydrogen interaction even though such an interaction was quite pronounced[3] in a similar compound containing the ligand $Bpz_2Et_2^-$. In this case there is not even the slightest possibility that π electron density from one phenyl ring is partially

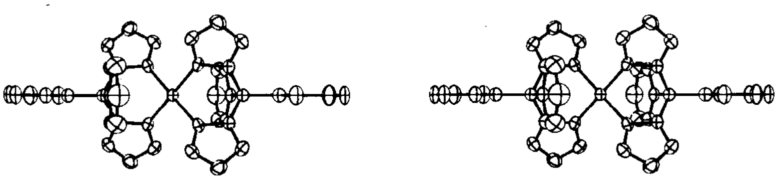

Figure 1. An ORTEP stereoscopic view of $Ni[(C_6H_5)_2B(pz)_2]_2$ clearly showing the mirror plane and inversion center on the molecule. The atoms are represented by 50% probability thermal ellipsoids.

TABLE III. Bond Angles (deg)[a].

Atoms	Angle	Atoms	Angle
N(2)–Ni–N(2′)	89.2(2)	B–C(1)–C(2)	122.6(6)
N(2)–Ni–N(2″)	90.8(2)	B–C(1)–C(6)	121.5(5)
Ni–N(2)–N(1)	121.8(3)	B–C(7)–C(8)	122.0(3)
Ni–N(2)–C(13)	130.9(3)	C(6)–C(1)–C(2)	115.9(6)
N(1)–N(2)–C(13)	107.2(3)	C(1)–C(2)–C(3)	121.8(6)
N(2)–C(13)–C(12)	110.2(4)	C(2)–C(3)–C(4)	120.6(6)
C(13)–C(12)–C(11)	105.0(4)	C(3)–C(4)–C(5)	118.9(6)
C(12)–C(11)–N(1)	109.8(4)	C(4)–C(5)–C(6)	119.9(6)
C(11)–N(1)–N(2)	107.8(3)	C(5)–C(6)–C(1)	122.9(6)
N(2)–N(1)–B	119.6(3)	C(8′)–C(7)–C(8)	115.9(5)
C(11)–N(1)–B	132.6(4)	C(7)–C(8)–C(9)	122.6(5)
N(1)–B–N(1′)	102.9(5)	C(8)–C(9)–C(10)	119.3(5)
N(1)–B–C(1)	110.1(3)	C(9)–C(10)–C(9′)	120.3(6)
N(1)–B–C(7)	109.2(3)		

[a] Primed atoms are symmetry-related to the corresponding unprimed atoms.

TABLE IV. Unweighted Least Squares Planes[a,b].

Plane I. Pyrazolyl Ring: $3.015x+5.272y-7.302z-0.048 = 0$

Deviations of Atoms from Plane

N(1)	N(2)	C(11)	C(12)	C(13)
0.005	–0.004	–0.004	0.001	0.002

Plane II. Phenyl Ring: $18.220x+0.0y-2.310z-2.964 = 0$

Deviations of Atoms from Plane

C(7)	C(8)	C(9)	C(10)	C(9′)	C(8′)
0.003	–0.001	–0.001	0.003	–0.001	–0.001

Plane III. BN_4Ni Chelate Ring: $2.907x+0.0y-8.438z+0.757 = 0$

Deviations of Atoms from Plane

B	N(1)	N(2)	N(1′)	N(2′)	Ni
–0.695	0.0	0.0	0.0	0.0	–0.788

[a] The equation of the plane has the form $Ax+By+Cz-D = 0$ where x, y, and z are the fractional coordinates. [b] The deviations of the atoms from the plane are given in Å.

donated to the metal atom since the distances from the nickel atom to the nearest phenyl carbon atoms, C(7) and C(8) are, respectively, 3.15 and 3.66 Å. Thus, the inability of $M(Bpz_2Ph_2)$ rings to allow M···H–C interactions seems to be general as would be expected on the basis of the steric factors discussed previously[2] in connection with the case of $(CH_2C(CH_3)CH_2)(CO)_2Mo(Bpz_2Ph_2)$.

Another interesting feature in the $(C_6H_5)_2B(pz)_2^-$ ligand is the appearance, once again, of large distortions of the angles within the phenyl rings, similar to those appearing in the $(C_6H_5)_4B^-$ species.[6]

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