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Note

Synthesis and crystal structure of $[H_2B(3\text{-}Phpz)_2]_2Zn$

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Dedicated to Professor Sheldon Shore on the occasion of his 70th birthday.

Abstract

Our attempts to synthesize $[H_2B(3\text{-}Phpz)_2]Zn$(acetate) from $K[H_2B(3\text{-}Phpz)_2]$ and anhydrous zinc acetate has instead resulted in the formation of the 2:1 complex, $[H_2B(3\text{-}Phpz)_2]_2Zn$. This derivative was isolated and crystallized from THF at −10°C. Its structure has been defined as a distorted tetrahedron with an average Zn–N bond distance of 2.011(1) Å as revealed by X-ray crystallography. As anticipated, this complex is inactive at catalyzing the coupling of cyclohexene oxide and carbon dioxide.

Keywords: Zinc; Bis-(3-phenylpyrazolyl)dihydroborate; X-ray structure

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1. Introduction

The availability of poly(pyrazolyl)borates which span a broad range of steric and electronic properties has led to their utilization in diverse areas of chemistry [1]. For example, iridium and rhodium pyrazolylborates have been investigated for their role in C–H bond activation [2–5]. Not surprisingly, metal pyrazolylborates have been used as models in studies of certain biological processes such as enzyme assisted formation of oligonucleotides as well as the action of carbonic anhydrase [6–8]. Our laboratory has been interested in the chemistry of zinc, in particular as it pertains to the copolymerization of CO_2 and epoxides. Through these endeavors, we sought to explore the chemistry of trispyrazolylborate zinc systems [9,10]. However, the trispyrazolylborate ligand, along with the nucleophilic initiator group (e.g. a carboxylate ligand), rendered the zinc center to be coordinatively saturated and ineffective at binding the epoxide monomer. For example, η^3-HB(3-phenylpyrazolyl)$_3$Zn(carboxylate) derivatives, which typically contain unidentate or asymmetrically chelated carboxylate ligands, do not bind epoxides. Nevertheless, analogous trispyrazolylborate derivatives of cadmium have lead to many pertinent revelations about this process [11,12]. In an effort to optimize the catalytic activity of these systems we attempted the synthesis of dihydrobis(3-phenylpyrazolyl)borato zinc(II)acetate, where the congestion about the zinc center would be greatly reduced. Our efforts revealed the difficulty of avoiding the thermodynamic product $[H_2B(3\text{-phenylpyrazolyl})_2]_2$Zn(II), which is the dominant product, even when slow addition of the ligand to excess zinc acetate is employed. Herein we wish to report the synthesis and crystal structure of this latter zinc complex.

2. Experimental

Tetrahydrofuran was distilled over sodium under a dry nitrogen atmosphere prior to use. Anhydrous zinc acetate was purchased from Aldrich Chemical Co. and used as received. Potassium dihydrobis(3-phenyl-pyrazolyl)borate was prepared as described in the literature [13].

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2.1. Synthesis of [H_2B(3-phenylpyrazol)$_2$]$_2$Zn(II)

A THF solution of $KH_2B(3\text{-}Phpz)_2$ (2.71 g, 8.0 mmol) was prepared and added over a 5 h period to Zn(acetate)$_2$ (1.76 g, 8.0 mmol) in 20 ml of THF. The mixture was allowed to stir overnight at ambient temperature. The reaction solution was filtered to remove all zinc and potassium acetate, and the solvent was then removed by vacuum. 2.17 g of white powder (82% yield based on pyrazolylborate) was recovered. X-ray quality crystals were recrystallized from THF at −10°C.

2.2. X-ray crystallography

A Bausch and Lomb 10 × microscope was used to identify a suitable colorless crystal from a representative sample of crystals of the same habit. The crystal was coated in a cryogenic protectant, mineral oil, and was then fixed to a glass fiber which in turn was fashioned to a copper mounting pin. The mounted crystal was then placed in a cold nitrogen stream (Oxford) maintained at 110 K.

Crystal data and details of data collection for the complexes are provided in Table 1. The X-ray data were collected on a Bruker CCD diffractometer and covered more than a hemisphere of reciprocal space by a combination of three sets of exposures; each exposure set had a different φ angle for the crystal orientation and each exposure covered 0.3° in ω. The crystal-to-detector distance was 4.9 cm. Crystal decay was monitored by repeating the data collection for 50 initial frames at the end of the data set and analyzing the duplicate reflections; crystal decay was negligible. The space group was determined based on systematic absences and intensity statistics [14].

Table 1
Crystal data and structure refinement for [$H_2B(3\text{-}Phpz)_2$]$_2$Zn

Empirical formula	$C_{36}H_{32}B_2N_8Zn_1$
Formula weight	1359.37
Temperature (K)	110(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	
a (Å)	33.528(5)
b (Å)	10.9860(15)
c (Å)	17.387(3)
β (°)	92.081(3)
Volume (Å^3)	6400.0(15)
Z	8
D_{calc} (Mg m^{-3})	1.378
Absorption coefficient (mm^{-1})	2.842
F(000)	9856
θ Range for data collection (°)	1.95–28.28
Index ranges	$-44 \leq h \leq 36$, $-9 \leq k \leq 14$, $-23 \leq l \leq 22$
Reflections collected	15 807
Independent reflections	7111 [$R_{int} = 0.0175$]
Completeness to $\theta = 28.28°$	89.2%
Max. and min. transmission	0.0070 and 0.0069
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7111/0/440
Goodness-of-fit on F^2	1.054
Final $^a R$ indices [$I > 2\sigma(I)$]	$R_1 = 0.0275$, $wR_2 = 0.0695$
R indices (all data)	$R_1 = 0.0366$, $wR_2 = 0.0723$
Largest difference peak and hole (e Å^{-3})	0.303 and −0.325

[a] $R = \Sigma||F_o|-|F_c||/\Sigma F_o$, $wR = \{[\Sigma_w(F_o^2-F_c^2)^2]/[\Sigma_w(F_o^2)^2]\}^{1/2}$.

The structure was solved by direct methods. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded $R(F) = 0.0275$ and $wR(F^2) = 0.0695$ at convergence. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed 1.2 or 1.5 times the value of the attached atom. Neutral atom scattering factors and anomalous scattering factors were taken from the International Tables for X-ray Crystallography Vol. C.

For the title compound, data reduction: SAINTPLUS (Bruker [15]); program(s) used to solve the structure: SHELXS-86 (Sheldrick [16]); program(s) used to refine the structure: SHELXL-97 (Sheldrick [17]); program(s) used for molecular graphics: SHELXTL version 5.0 (Bruker [18]); software to prepare material for publication: SHELXTL version 5.0 (Bruker [18]).

3. Results and discussion

The symmetrical complex [$H_2B(3\text{-}Phpz)_2$]$_2$Zn was prepared from the reaction of one equivalent of the ligand salt and anhydrous zinc acetate in THF solution. Although the reaction was carried out under conditions where the concentration of K[$H_2B(3\text{-}Phpz)_2$] was kept less that the zinc acetate concentration, only the symmetrical product was isolated. Clearly, this 2:1 complex, which is the thermodynamically favored product, could be optimally prepared upon adding two equivalents of the ligand salt to zinc acetate.

Colorless crystals of [$H_2B(3\text{-}Phpz)_2$]$_2$Zn were obtained from a THF solution of the complex maintained at −10°C. A thermal ellipsoid drawing of the complex is depicted in Fig. 1, along with the atomic numbering scheme. Selected bond lengths and bond angles are listed in Table 2. The steric bulkiness of the phenyl substituents require these groups to arrange themselves in an interlocking fashion in order for the two poly(pyrazolyl)borate ligands to effectively bind to the zinc center. This situation is best visualized in the space-filling drawing shown in Fig. 2. Two of the Zn–N bond lengths in [$H_2B(3\text{-}Phpz)_2$]$_2$Zn are significantly shorter than the other two. That is, the Zn–N(2) and Zn–N(8) distances at 2.0065(13) and 2.0004(12) Å [average = 2.0035(13)], respectively, are shorter than the

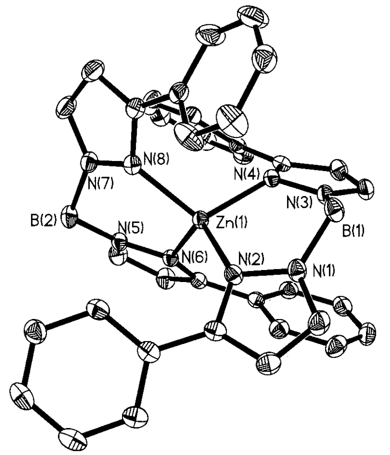


Fig. 1. Thermal ellipsoid representation of $[H_2B(3\text{-}Phpz)_2]_2Zn$.

Table 2
Selected bond lengths (Å) and angles (°) for $[H_2B(3\text{-}Phpz)_2]_2Zn$

Zn(1)–N(8)	2.0004(12)
Zn(1)–N(2)	2.0065(13)
Zn(1)–N(4)	2.0185(14)
Zn(1)–N(6)	2.0198(13)
B(1)–N(3)	1.552(2)
B(1)–N(1)	1.555(2)
B(2)–N(7)	1.554(2)
B(2)–N(5)	1.557(2)
N(1)–N(2)	1.3733(17)
N(5)–N(6)	1.3681(17)
N(7)–N(8)	1.3731(18)
N(8)–Zn(1)–N(2)	117.36(5)
N(8)–Zn(1)–N(4)	114.03(5)
N(2)–Zn(1)–N(4)	104.02(5)
N(8)–Zn(1)–N(6)	101.72(5)
N(2)–Zn(1)–N(6)	117.31(5)
N(4)–Zn(1)–N(6)	101.70(5)

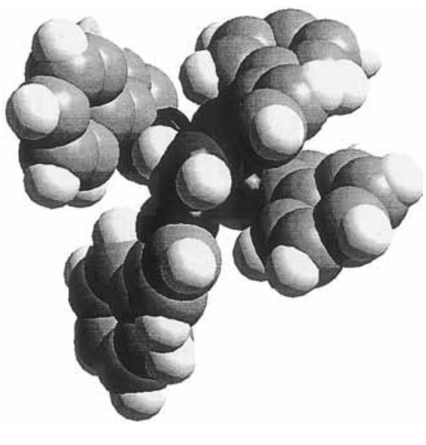
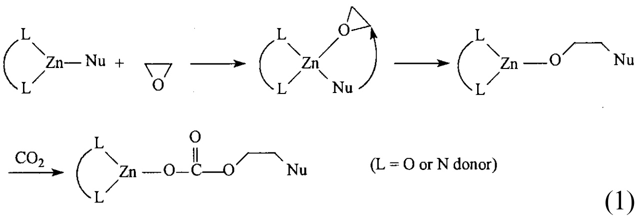


Fig. 2. Space-filling diagram of $[H_2B(3\text{-}Phpz)_2]_2Zn$, illustrating the *interlocking* arrangement of the phenyl substituents of the pyrazolylborate ligands.

Zn–N(4) and Zn–N(6) distances of 2.0185(14) and 2.0198(13) Å [average = 2.0192(14)]. This difference is a manifestation of the steric requirements associated with accommodating the two *bis*pyrazolylborate ligands about the zinc center. Nevertheless, the average Zn–N bond distances observed herein (2.0113 Å) is similar to those previously reported for trispyrazolylborate derivatives of zinc. For example, average Zn–N bond distances were determined as 2.051 Å in η^3–$HB(3\text{-}Phpz)_3Zn(O_2CCH_2CH_2CO_2C_2H_5)$, 2.036 Å in η^3–$HB(3\text{-}Phpz)_3Zn(O_2CCH_2CO_2H)$, and $HB(3\text{-}Phpz)_3Zn(O_2CCH_2CN)$ [10]. The N–Zn–N *intraligand* angles, i.e. N(2)–Zn–N(4) and N–(6)–Zn–N(8), average 102.9(1)°, whereas, the *interligand* angles average 112.6(1)°.

The 2:1 complex reported upon here exhibited no reactivity for the coupling of CO_2 and epoxides. This is not unanticipated since the reaction pathway for this process involves the availability of a binding site on the zinc center, along with the presence of a nucleophile to ring-open the activated (bound) epoxide monomer [19,20]. A skeletal representation of this process is depicted in Eq. (1) with a model catalyst based on our initial design.



(1)

4. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 148130 for the $[H_2B(3\text{-}Phpz)_2]_2Zn$ complex. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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