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# Molecular Structure of $\{\eta^3\text{-HB(pz)}_3\}\text{ZnNO}_3$: Comparison between Theory and Experiment in a Model Carbonic Anhydrase System

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## Introduction

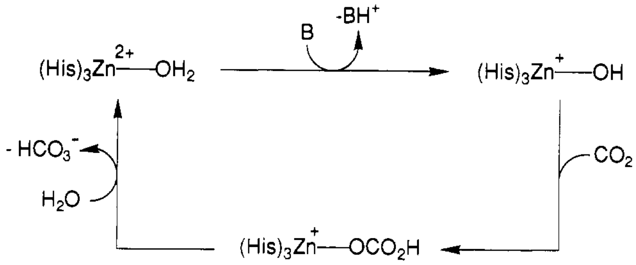
Carbonic anhydrase is a zinc enzyme with the essential role of catalyzing the reversible hydration of carbon dioxide (eq 1).[1,2]

$$CO_2 + H_2O \rightleftarrows HCO_3^- + H^+ \qquad (1)$$

The enzyme has been the subject of numerous experimental and theoretical studies designed to address both the composition of the active site and the mechanism of the catalytic cycle. The active site of the enzyme is a pseudotetrahedral zinc center coordinated to three histidine (His) imidazole groups and a water molecule $[(\text{His})_3\text{Zn–OH}_2]^{2+}$ (or a hydroxide anion, depending upon pH),[3,4] and the catalytic cycle has been proposed to involve a sequence that is summarized in Scheme 1.[1,2,5]

Studies on metal-substituted carbonic anhydrases have revealed that the order of activity decreases across the series Zn > Co ≫ Ni, Cu.[1,6,7] We recently proposed that, among other factors (*e.g.* the p$K_a$ of the coordinated water), the coordination mode exhibited in the bicarbonate intermediate (*i.e.* unidentate *versus* bidentate) for each of the metal-substituted enzyme systems may be an important factor in influencing enzyme activity, since the catalytic cycle requires rapid displacement of the bicarbonate ligand by water.[8–11] However, since bicarbonate complexes are not common and a series of $L_n\text{M(OCO}_2\text{H)}$ (M = Co, Ni, Cu, Zn) complexes has not been structurally characterized, our recent investigations centered on the series of nitrate derivatives $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{M(NO}_3)$ (M = Co, Ni, Cu, Zn), on the basis that structural changes across this series would provide an indication of the changes that may be expected for the corresponding bicarbonate complexes.[8–10] It is, however, important to emphasize that this argument is not intended to imply a direct correlation between the coordination mode of a nitrate ligand and that of a bicarbonate ligand to a given metal center.[12] Rather, the studies on the complexes $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{M(NO}_3)$ (M = Co, Ni, Cu, Zn) are specifically intended to indicate the relative tendencies of different metal centers to support unidentate *versus* bidentate coordination for a particular ligand.

**Scheme 1.** Proposed Catalytic Cycle for Carbonic Anhydrase (His = Histidine Imidazole Groups; B = Buffer)



The structural variations that are observed for the series of nitrate complexes $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{M(NO}_3)$ (M = Co, Ni, Cu, Zn) reveal that the preference for bidentate coordination increases across the series Zn < Co ≪ Cu, Ni.[13] The coordination modes of the nitrate ligands in the complexes $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{M(NO}_3)$ (M = Co, Ni, Cu, Zn) vary from unidentate for Zn to symmetric bidentate for Ni and Cu, with the cobalt derivative exhibiting an anisobidentate (also known as asymmetric bidentate) coordination mode, which is intermediate between the two extremes (Figure 1).[14] Significantly, these structural preferences of the nitrate ligand correlate with the activity of the metal-substituted enzymes: zinc, the metal with the greatest tendency to exhibit unidentate coordination of the nitrate ligand, is the most active, while nickel and copper, the metals with the greatest tendency to exhibit bidentate coordination of the nitrate ligand, are effectively inactive.

In this paper we report the structure of a related zinc nitrate derivative $\{\eta^3\text{-HB(pz)}_3\}\text{Zn(NO}_3)$ in order to demonstrate the importance of steric effects in determining unidentate *versus* bidentate coordination. Furthermore, this study allows a comparison to be made between the coordination mode of the nitrate ligand in $\{\eta^3\text{-HB(pz)}_3\}\text{Zn(NO}_3)$ as determined experimentally with that predicted by a recent theoretical calculation.[15]

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(12) Indeed, nitrate and bicarbonate do not bind in an identical fashion to the zinc center of carbonic anhydrase. Thus, the bicarbonate ligand is coordinated to the zinc center of a *mutant* of carbonic anhydrase (Thr-200 → His human CA II) with Zn–O bond lengths of 2.2 and 2.5 Å,[12a] whereas the nitrate ligand is coordinated to the zinc center of human carbonic anhydrase II *via* only one oxygen atom with a Zn–O distance of 2.8 Å (a water molecule also remains coordinated to zinc in this derivative).[12b] However, it must be recognized that two different forms of carbonic anhydrase are being compared in the above examples and that no electron density corresponding to a bicarbonate ligand was detected upon crystallizing native human carbonic anhydrase II in the presence of bicarbonate.[12c] (a) Xue, Y.; Vidgren, J.; Svensson, L. A.; Liljas, A.; Jonsson, B.-H.; Lindskog, S. *Proteins* **1993**, *15*, 80–87. (b) Mangani, S.; Håkansson, K. *Eur. J. Biochem.* **1992**, *210*, 867–871. (c) Håkansson, K.; Wehnert, A. *J. Mol. Biol.* **1992**, *228*, 1212–1218.

(13) Furthermore, structural studies on a series of dinuclear carbonate complexes $[\{\eta^3\text{-HB(3,5-Pr}^i{}_2\text{pz)}_3\}\text{M}]_2(\mu\text{-CO}_3)$ (M = Fe, Co, Ni, Cu, Zn) indicate that zinc exhibits a lesser tendency to adopt bidentate coordination than do the other metals. See ref 17 and: Kitajima, N.; Fujisawa, K.; Koda, T.; Hikichi, S.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 1357–1358.

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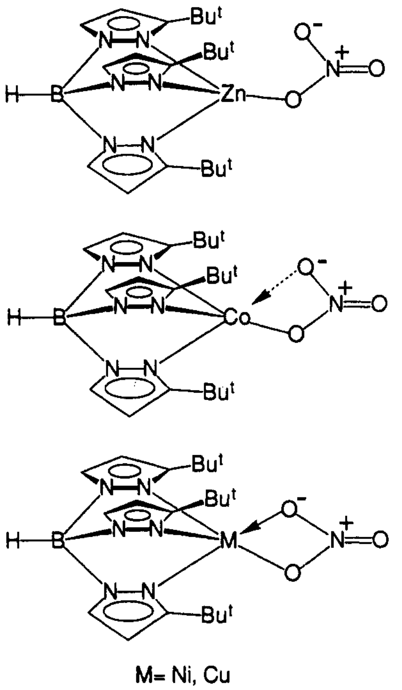


**Figure 1.** Unidentate *versus* bidentate coordination of the nitrate ligands in the complexes $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}M(NO_3)$ (M = Co, Ni, Cu, Zn).

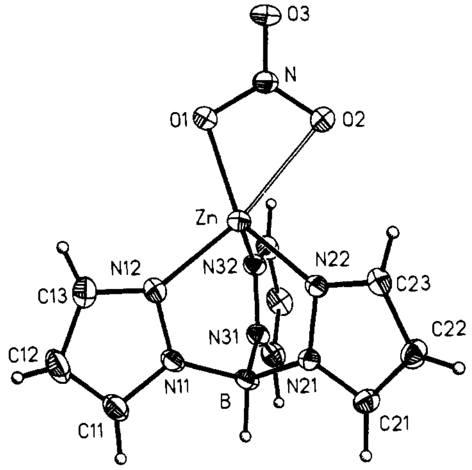
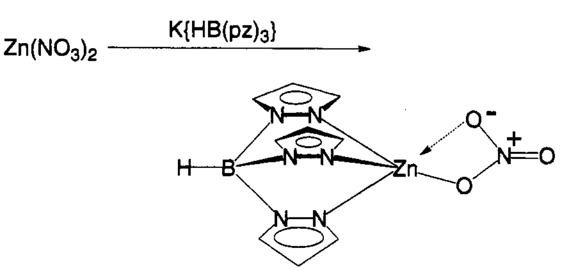


**Figure 2.** Molecular structure of $\{\eta^3\text{-HBpz}_3\}Zn(NO_3)$.

## Results

The zinc nitrate complex $\{\eta^3\text{-HB(pz)}_3\}Zn(NO_3)$ is prepared by the reaction of $Zn(NO_3)_2$ with $K\{HB(pz)_3\}$ (eq 2). The molecular structure of $\{\eta^3\text{-HB(pz)}_3\}Zn(NO_3)$ was determined by single-crystal X-ray diffraction, as shown in Figure 2. Selected bond lengths and angles are presented in Tables 1 and 2 with atomic coordinates in Table 3. Further details of the structure are described in the Discussion.



(2)

**Table 1.** Selected Bond Lengths (Å)

| | | | |
|---|---|---|---|
| Zn–O(1) | 1.981(2) | Zn–O(2) | 2.399(3) |
| Zn–N(12) | 2.038(3) | Zn–N(22) | 2.026(2) |
| Zn–N(32) | 2.010(3) | N–O(2) | 1.239(4) |
| N–O(1) | 1.275(4) | N–O(3) | 1.209(4) |

**Table 2.** Selected Bond Angles (deg)

| | | | |
|---|---|---|---|
| O(1)–Zn–O(2) | 57.6(1) | O(2)–Zn–N(12) | 156.6(1) |
| O(1)–Zn–N(12) | 109.8(1) | O(2)–Zn–N(22) | 88.1(1) |
| O(1)–Zn–N(22) | 137.3(1) | N(12)–Zn–N(22) | 91.8(1) |
| O(2)–Zn–N(32) | 108.9(1) | O(1)–Zn–N(32) | 119.2(1) |
| N(12)–Zn–N(32) | 94.4(1) | N(22)–Zn–N(32) | 94.2(1) |
| O(1)–N–O(2) | 116.8(3) | O(2)–N–O(3) | 122.6(3) |
| O(1)–N–O(3) | 120.6(3) | Zn–O(2)–N | 83.5(2) |
| Zn–O(1)–N | 102.2(2) | N(12)–N(11)–C(11) | 108.8(3) |

**Table 3.** Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$)

| atom | *x* | *y* | *z* | $U^a$ |
|---|---|---|---|---|
| Zn | 1380(1) | 6234(1) | 6913(1) | 44(1) |
| N | 715(2) | 7772(2) | 5917(2) | 49(1) |
| O(1) | 561(2) | 7497(2) | 6688(2) | 52(1) |
| O(2) | 1277(2) | 7219(2) | 5562(2) | 71(1) |
| O(3) | 331(2) | 8543(2) | 5563(2) | 88(1) |
| N(11) | 2069(2) | 5038(2) | 8402(2) | 47(1) |
| N(12) | 1649(2) | 6005(2) | 8224(2) | 50(1) |
| N(21) | 2958(2) | 4883(2) | 7109(2) | 40(1) |
| N(22) | 2669(2) | 5822(2) | 6695(2) | 41(1) |
| N(31) | 1438(2) | 3949(2) | 7088(2) | 45(1) |
| N(32) | 884(2) | 4730(2) | 6686(2) | 44(1) |
| C(11) | 2293(3) | 4963(4) | 9278(2) | 62(1) |
| C(12) | 2001(3) | 5878(4) | 9659(3) | 74(2) |
| C(13) | 1607(3) | 6514(3) | 8994(3) | 59(1) |
| C(21) | 3792(2) | 4640(3) | 6891(2) | 49(1) |
| C(22) | 4053(2) | 5428(3) | 6334(2) | 55(1) |
| C(23) | 3341(2) | 6143(3) | 6238(2) | 47(1) |
| C(31) | 1108(2) | 2973(3) | 6844(2) | 55(1) |
| C(32) | 345(3) | 3111(3) | 6288(3) | 63(1) |
| C(33) | 223(2) | 4212(3) | 6214(2) | 53(1) |
| B | 2312(2) | 4266(3) | 7677(2) | 44(1) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

## Discussion

In order to provide well-defined precedents for the steps summarized in Scheme 1, our recent studies focused on systems that are designed to be both structural and functional models for carbonic anhydrase. For this purpose, we and others have utilized the sterically demanding tris(pyrazolyl)hydroborato ligand system, $[HB(3,5\text{-RR}'pz)_3]^-$ (RR′pz = substituted pyrazole), in which the three nitrogen atom donors of the tris(pyrazolyl)hydroborato ligand bind to the zinc center in $\{\eta^3\text{-HB(3,5-RR}'\text{pz)}_3\}ZnOH$ by a manner analogous to those of the histidine imidazole groups in carbonic anhydrase.[9,16–18] In particular, the complex $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}ZnOH$ reacts reversibly with $CO_2$ to give the bicarbonate derivative $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}Zn(OCO_2H)$. Spectroscopic evidence suggests that the bicarbonate ligand in $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}Zn(OCO_2H)$ is unidentate, a result that is supported by structural studies on the related derivatives $[\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}Zn]_2(\mu\text{-}\eta^1,\eta^1\text{-}CO_3)$,[10] $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}Zn(OCO_2Me)$,[18] and $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}Zn(NO_3)$.[8,10]

The unidentate coordination mode of the bicarbonate ligand in $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}Zn(OCO_2H)$ may be a consequence of the steric demands of the bulky $[HB(3\text{-Bu}^t\text{-5-Mepz)}_3]^-$ ligand. Hence, a less sterically-demanding ligand would be expected to favor more bidentate coordination of bicarbonate. For example, the carbonate ligand in $[\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}Zn]_2(\mu\text{-}\eta^1,\eta^1\text{-}CO_3)$ bridges in a symmetric unidentate fashion, whereas in the less sterically-demanding derivative $[\{\eta^3\text{-HB(3,5-Pr}^i{}_2\text{pz)}_3\}Zn]_2(\mu\text{-}\eta^1,\eta^2\text{-}CO_3)$ the carbonate ligand is coordinated in an asym-

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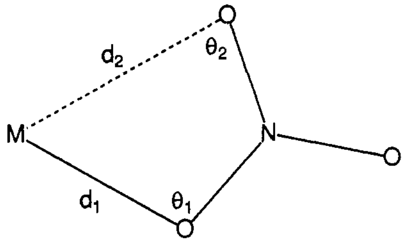

**Figure 3.** Criteria for distinguishing nitrate coordination modes.

**Table 4.** Criteria for Distinguishing Nitrate Coordination Modes

| | unidentate | anisobidentate | bidentate |
|---|---|---|---|
| $d_2 - d_1$, Å | >0.6 | 0.3–0.6 | <0.3 |
| $\theta_1 - \theta_2$, deg | >28 | 14–28 | <14 |

**Table 5.** Comparison of Nitrate Coordination Modes As Determined by X-ray Diffraction and Theoretical Calculation

| | $d_2 - d_1$, Å | $\theta_1 - \theta_2$, deg | coordn mode |
|---|---|---|---|
| | Experimental | | |
| $\{\eta^3$-HB(3-Bu$^t$pz)$_3\}$Zn(NO$_3$) | 0.60 | 29.6 | unidentate |
| $\{\eta^3$-HB(pz)$_3\}$Zn(NO$_3$) | 0.42 | 18.7 | anisobidentate |
| | Theoretical[a] | | |
| $\{\eta^3$-HB(3-Bu$^t$pz)$_3\}$Zn(NO$_3$) | 1.49 | 72 | unidentate |
| $\{\eta^3$-HB(pz)$_3\}$Zn(NO$_3$) | 1.25 | 58 | unidentate |

[a] Taken or calculated from data provided in ref 15.

metric manner, with unidentate coordination to one zinc center and bidentate to the other.[9,10]

In order to address the importance of steric effects in influencing unidentate *versus* bidentate coordination to a zinc center, we have determined the X-ray structure of the unsubstituted tris(pyrazolyl)hydroborato derivative $\{\eta^3$-HB(pz)$_3\}$Zn(NO$_3$), which allows for comparison with that of the more sterically-encumbered $\{\eta^3$-HB(3-Bu$^t$pz)$_3\}$Zn(NO$_3$) derivative. The molecular structure of $\{\eta^3$-HB(pz)$_3\}$Zn(NO$_3$) is illustrated in Figure 2. As far as the tris(pyrazolyl)hydroborato ligands are concerned, both complexes $\{\eta^3$-HB(pz)$_3\}$Zn(NO$_3$) and $\{\eta^3$-HB(3-Bu$^t$pz)$_3\}$Zn(NO$_3$) exhibit analogous coordination geometries, as illustrated by the similar average Zn–N bond lengths and N–Zn–N bond angles: $\{\eta^3$-HB(pz)$_3\}$Zn(NO$_3$), 2.03 Å, 94°; $\{\eta^3$-HB(3-Bu$^t$pz)$_3\}$Zn(NO$_3$), 2.05 Å, 96°. However, as described below, the nitrate ligands in the two complexes are not bound by the same coordination mode.

In principle, the nitrate ligand may bind to a single metal center by three different coordination modes, namely (i) symmetric bidentate, (ii) anisobidentate, and (iii) unidentate.[19,20] In order to provide a consistent classification of nitrate coordination modes in different compounds, some simple geometrical criteria have been proposed to distinguish between the different coordination modes, as shown in Figure 3 and Table 4.[19] Thus, complexes in which (i) the difference in M–O bond lengths ($d_2 - d_1$) is greater than 0.6 Å and (ii) the difference in bond angles at oxygen ($\theta_1 - \theta_2$) is greater than 28° are classified as unidentate. Correspondingly, complexes with (i) $d_2 - d_1$ in the range 0.3–0.6 Å and (ii) $\theta_1 - \theta_2$ in the range 14–28° are classified as anisobidentate.

The results of the application of these criteria to the nitrate derivatives $\{\eta^3$-HB(3-Bu$^t$pz)$_3\}$Zn(NO$_3$) and $\{\eta^3$-HB(pz)$_3\}$Zn(NO$_3$) are summarized in Table 5. It is evident from these data that, whereas the nitrate ligand in $\{\eta^3$-HB(3-Bu$^t$pz)$_3\}$M(NO$_3$) may be described as unidentate, the nitrate ligand in $\{\eta^3$-HB(pz)$_3\}$Zn(NO$_3$) is best described as anisobidentate. For example, although the shorter Zn–O interactions are similar in both molecules [$\{\eta^3$-HB(3-Bu$^t$pz)$_3\}$Zn(NO$_3$), 1.978(3) Å; $\{\eta^3$-HB(pz)$_3\}$Zn(NO$_3$), 1.981(2) Å], the secondary Zn···O interaction in $\{\eta^3$-HB(pz)$_3\}$Zn(NO$_3$) [2.399(3) Å] is much shorter than that in the more sterically-demanding derivative $\{\eta^3$-HB(3-Bu$^t$pz)$_3\}$Zn(NO$_3$) [2.581(3) Å]. Correspondingly, the bond angle at oxygen is also reduced from the tetrahedral value in $\{\eta^3$-HB(3-Bu$^t$pz)$_3\}$Zn(NO$_3$) [109.4(2)°] to 102.2(2)° in $\{\eta^3$-HB(pz)$_3\}$Zn(NO$_3$). Furthermore, the related nitrate derivative $\{\eta^3$-HB(3,5-Ph$_2$pz)$_3\}$Zn(NO$_3$),[21] with Zn–O interactions of 1.947(3) and 2.475(3) Å (*i.e.* $d_2 - d_1 = 0.53$ Å), can be seen to possess a nitrate coordination mode that is intermediate between those in $\{\eta^3$-HB(3-Bu$^t$pz)$_3\}$Zn(NO$_3$) and $\{\eta^3$-HB(pz)$_3\}$Zn(NO$_3$). Thus, the degree of interaction of the nitrate ligand with the zinc center in these complexes clearly correlates with the steric demands of the substituent (H < Ph < Bu$^t$) at the 3-position of the tris(pyrazolyl)hydroborato ligand.

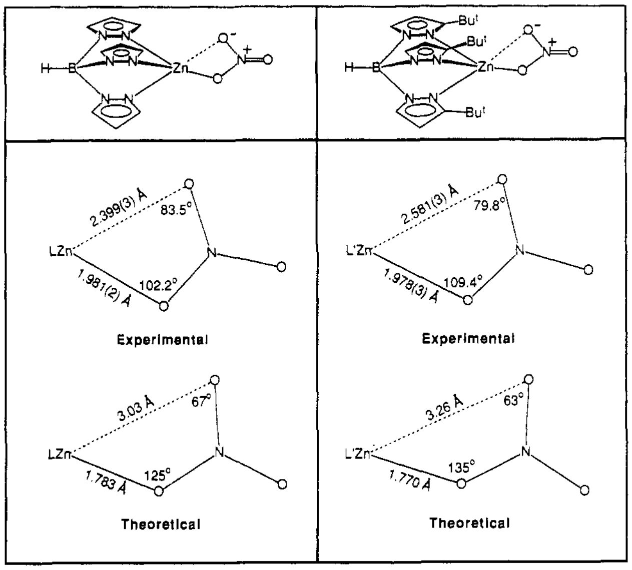

**Figure 4.** Comparison of nitrate coordination modes as determined by X-ray diffraction and theoretical calculation [L = $\eta^3$-HB(pz)$_3$; L' = $\eta^3$-HB(3-Bu$^t$pz)$_3$].

Recent theoretical calculations designed specifically to compare the ligating abilities of nitrate and bicarbonate have been carried out on $\{\eta^3$-HB(3,5-RR'pz)$_3\}$Zn(NO$_3$) and $\{\eta^3$-HB(3,5-RR'pz)$_3\}$Zn(OCO$_2$H) derivatives.[15] At the time that these calculations were carried out, only the structure of $\{\eta^3$-HB(3-Bu$^t$pz)$_3\}$Zn(NO$_3$) had been determined experimentally. With the structure of $\{\eta^3$-HB(pz)$_3\}$Zn(NO$_3$) now available, it is of some interest to compare in detail the experimentally determined structures of $\{\eta^3$-HB(3-Bu$^t$pz)$_3\}$Zn(NO$_3$) and $\{\eta^3$-HB(pz)$_3\}$Zn(NO$_3$) with those predicted for the ground state by the aforementioned theoretical calculations.[15]

The results of the experimental and theoretical studies are summarized in Figure 4, from which it is evident that there is a degree of discrepancy. For example, with regard to $\{\eta^3$-HB(pz)$_3\}$Zn(NO$_3$), (i) the 102.2(2)° bond angle for Zn–O–N in the experimentally determined structure is substantially less than the value of 125° obtained by theoretical calculations and (ii) the Zn–O bond length of 1.981(2) Å in the experimentally determined structure is substantially longer than the value of 1.783 Å obtained by theoretical calculations, whereas the secondary Zn···O interaction of 2.399(3) Å is substantially shorter than that obtained by theoretical calculations (*ca.* 3.03 Å).[22] In essence, the structure obtained by theoretical calculations differs from the experimentally determined structure by its inability to reflect the fact that the coordination mode is not unidentate. Thus, the theoretical values of (i) $d_2 - d_1 = 1.25$ Å and (ii) $\theta_1 - \theta_2 = 58°$ very strongly indicate a unidentate coordination mode, whereas the true

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(22) Since the Zn···O distance was not provided in ref 15, we have estimated the value of 3.03 Å on the basis that the O–N–O bond angle is 120° and that the atoms of the ZnNO$_3$ group are coplanar.

coordination mode is anisobidentate according to the criteria described above. Similarly, for the more highly substituted derivative {$\eta^3$-HB(3-Bu$^t$pz)$_3$}Zn(NO$_3$), there is also a discrepancy between the experimentally determined structure and that predicted by theoretical calculations, which were described as being in "qualitative agreement with experiment, although the experimental structure exhibits a somewhat smaller value of $\theta$ ($\sim$110°)". However, the calculated value of $\theta$ is in fact 135°, a difference of 25°. Moreover, the difference in Zn–O bond lengths is 1.49 Å, compared to only 0.60 Å for the experimental structure. It has been suggested that the inadequacy of the theoretical calculations to model accurately the experimental structure is a consequence of the calculations being performed on isolated molecules in the gas phase.[23]

The catalytic mechanism of carbonic anhydrase has been the subject of numerous theoretical studies.[24] In addition to determining the energies of species on the catalytic energy surface, the ability to predict accurately the structures of proposed intermediates is also of central importance. Since different theoretical studies may differ in their reliability, especially when different methods are used, it is of importance to perform further calculations of the structures of both enzyme and model complexes, whose structures may be determined experimentally, in order to provide a test for the accuracy of such predictions. Such a combination of theoretical and experimental studies would be fruitful in providing an understanding of the catalytic cycle of carbonic anhydrase and other metalloenzymes.

## Experimental Section

**General Considerations.** All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques.[25] Solvents were purified and degassed by standard procedures. $^1$H and $^{13}$C NMR spectra were recorded on Varian VXR 200, 300, and 400 spectrometers. IR spectra were recorded as Nujol mulls between KBr disks on a Perkin-Elmer 1420 spectrophotometer and are reported in cm$^{-1}$. Mass spectra were obtained on a Nermag R10–10 mass spectrometer using chemical ionization (NH$_3$ or CH$_4$) techniques. Elemental analyses were obtained using a Perkin-Elmer 2400 CHN elemental analyzer. K{HB(pz)$_3$} was prepared by the literature method.[26]

**Synthesis of {$\eta^3$-HB(pz)$_3$}Zn(NO$_3$).** A fine suspension of Zn(NO$_3$)$_2$·6H$_2$O (1.4 g, 4.7 mmol) in THF (25 mL) was added dropwise to a fine suspension of K{HB(pz)$_3$} (1.0 g, 3.9 mmol) in THF (15 mL), resulting in the immediate formation of a white precipitate. The mixture was stirred overnight at room temperature and filtered. The solvent was removed from the filtrate under reduced pressure, and the residue obtained was washed with pentane. The residue was crystallized from a mixture of THF and pentane at 0 °C, giving colorless crystals of {$\eta^3$-HB(pz)$_3$}Zn(NO$_3$), which were isolated by filtration, washed with pentane, and dried *in vacuo* (0.6 g, 45%). Anal. Calcd for {$\eta^3$-HB(pz)$_3$}Zn(NO$_3$): C, 31.8; H, 3.0; N, 28.8. Found: C, 32.1; H, 3.0; N, 27.5. MS: $m/z$ 340 (M$^+$ + 1). IR data: 2490 cm$^{-1}$ ($\nu_{B-H}$). $^1$H NMR (CDCl$_3$): $\delta$ 6.25 [3H, t, $^3J_{H-H}$ = 2, 3H of $\eta^3$-HB(C$_3$N$_2$$H_3$)$_3$], 7.69 [3H, d, $^3J_{H-H}$ = 2, 3H of $\eta^3$-HB(C$_3$N$_2$$H_3$)$_3$], 7.72 [3H, d, $^3J_{H-H}$ = 2, 3H of $\eta^3$-HB(C$_3$N$_2$$H_3$)$_3$]. $^{13}$C NMR (CDCl$_3$): $\delta$ 105.3 [d, $^1J_{C-H}$ = 179, 3C of $\eta^3$-HB($C_3$N$_2$H$_3$)$_3$], 136.1 [d, $^1J_{C-H}$ = 187, 3C of $\eta^3$-HB($C_3$N$_2$H$_3$)$_3$], 140 [d, $^1J_{C-H}$ = 187, 3C of $\eta^3$-HB($C_3$N$_2$H$_3$)$_3$].

**Table 6.** Crystal and Intensity Collection Data

| | |
|---|---|
| formula | C$_9$H$_{10}$N$_7$BO$_3$Zn |
| fw | 340.4 |
| lattice | monoclinic |
| cell constants | |
| $a$, Å | 14.746(4) |
| $b$, Å | 12.319(2) |
| $c$, Å | 15.387(3) |
| $\alpha$, deg | 90.0 |
| $\beta$, deg | 95.47(2) |
| $\gamma$, deg | 90.0 |
| $V$, Å$^3$ | 2782(1) |
| $Z$ | 8 |
| radiation ($\lambda$, Å) | Mo K$\alpha$ (0.710 73) |
| space group | C2/$c$ (No. 15) |
| $\rho$(calcd), g cm$^{-3}$ | 1.63 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 18.4 |
| goodness of fit | 1.066 |
| $R$ | 0.0293 |
| $R_w$[a] | 0.0399 |

[a] Weighting scheme: w = [$\sigma^2(F)$ + 0.0008$F^2$]$^{-1}$.

**X-ray Structure Determination of {$\eta^3$-HB(pz)$_3$}Zn(NO$_3$).** Crystal data and data collection and refinement parameters for {$\eta^3$-HB(pz)$_3$}Zn(NO$_3$) are summarized in Table 6. A single crystal of {$\eta^3$-HB(pz)$_3$}Zn(NO$_3$) grown from THF was mounted in a glass capillary that was then placed on a Nicolet R3m diffractometer. The unit cell was determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Intensity data were collected using graphite-monochromated Mo K$\alpha$ X-radiation ($\lambda$ = 0.710 73 Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects. The structure was solved using direct methods and standard difference map techniques on a Data General NOVA 4 computer using SHELXTL.[27] Systematic absences were consistent with the space groups $C2/c$ (No. 15) and $Cc$ (No. 9), but the structure was successfully solved with the space group $C2/c$ (No. 15). All of the hydrogen atoms were located and were refined isotropically. Block-diagonal least-squares refinement converged to $R$ = 0.0293 ($R_w$ = 0.0399). Atomic coordinates and thermal parameters for non-hydrogen atoms are listed in Table 3, and selected bond distances and angles are listed in Tables 1 and 2.

## Conclusion

In summary, the nitrate ligand in {$\eta^3$-HB(pz)$_3$}Zn(NO$_3$) is coordinated to the zinc center in an anisobidentate fashion, with Zn–O bond lengths of 1.981(2) and 2.399(3) Å. In contrast, the complex {$\eta^3$-HB(3-Bu$^t$pz)$_3$}Zn(NO$_3$) exhibits a unidentate coordination mode, thereby demonstrating the role that steric effects may play in influencing the coordination mode of a nitrate ligand in a mononuclear system. Furthermore, the experimental observation of an anisobidentate coordination mode in {$\eta^3$-HB(pz)$_3$}Zn(NO$_3$) is contrary to a recent theoretical calculation which predicts a unidentate coordination mode for this complex.

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**Supplementary Material Available:** Tables of crystal and intensity collection data, hydrogen atom coordinates, bond distances and angles, and anisotropic displacement parameters for {$\eta^3$-HB(pz)$_3$}Zn(NO$_3$) (5 pages). Ordering information is given on any current masthead page.

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(23) It has also been proposed that the discrepancy between the theoretical and experimental results may be due to a different local symmetry ($C_s$) being imposed on the nitrate ligand for the purpose of the calculations, although this was not described in ref 15. Marynick, D. S. Personal communication.

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