

probe their kinetic behavior. For example, the formation of  $C_{70}^-$  can easily be monitored at 505 nm which is an isosbestic point for the absorption of ground and triplet excited states of  $C_{70}$ . In the absence of ZnO colloids, the formation of long-lived transients was negligibly small.

Further support for a ZnO-initiated reduction of carbon cluster was gathered by varying the concentration of the ZnO colloid. The long-lived transient absorbance ( $\Delta t = 125 \mu s$ ) at 420 ( $C_{60}^-$ ) and 400 ( $C_{70}^-$ ) nm was taken as a measure of the efficiency of charge transfer. The transient absorbance at these wavelengths increased sharply as the concentration of ZnO was varied (Figure 2). But at higher ZnO concentrations, it reached a saturation since the charge transfer at the ZnO surface was limited by the availability of carbon cluster. Steady-state photolysis of these carbon clusters in ZnO suspension also indicates changes in the absorption spectra of  $C_{60}$  and  $C_{70}$ . These spectral changes are different compared to the transient absorption spectra of  $C_{60}^-$  and  $C_{70}^-$  which were recorded immediately following the laser pulse excitation. This indicates the accumulation of fullerene-derived products during the steady-state photolysis. Further details of the charge transfer interaction between semiconductor and carbon clusters and the analysis of steady-state photolysis products are currently being studied.

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### Unidentate versus Bidentate Coordination of Nitrate Ligands: Relevance to Carbonic Anhydrase Activity

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Carbonic anhydrase is a zinc-containing enzyme whose essential function is to catalyze the reversible hydration of carbon dioxide to bicarbonate.<sup>1</sup> Structural studies on the enzyme have identified that the zinc center is coordinated to three histidine imidazole groups and a water molecule,  $[(\text{His})_3\text{Zn}-\text{OH}_2]^{2+}$  (His = histidine).<sup>2</sup> The catalytic mechanism of carbonic anhydrase activity has been the subject of both intense experimental<sup>1</sup> and theoretical investigations,<sup>3</sup> and these studies have led to the proposal that a zinc bicarbonate complex  $[(\text{His})_3\text{Zn}-\text{OCO}_2\text{H}]^+$  may be a key intermediate. However, structural details of the proposed bi-

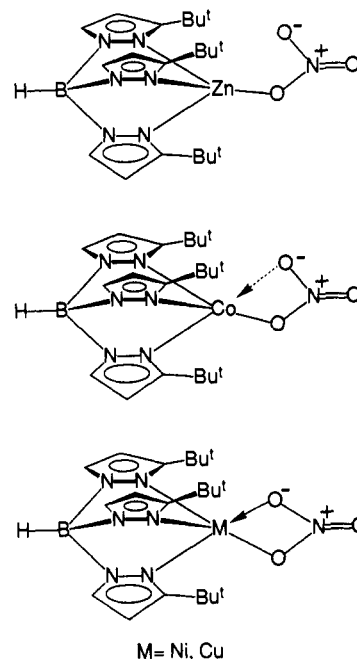


Figure 1. Molecular structures of  $\{\eta^3\text{-HB}(3\text{-Bu}^1\text{pz})_3\}\text{M}(\text{NO}_3)$  ( $\text{M} = \text{Zn}, \text{Co}, \text{Ni}, \text{Cu}$ ).

carbonate intermediate are not known, and theoretical treatments have explored the possibilities of both unidentate<sup>3</sup> and bidentate<sup>3d,e</sup> coordination modes. We are currently investigating model systems that are both *structural* and *chemical* mimics of the active site of carbonic anhydrase in order to provide support for the proposed mechanism of carbonic anhydrase activity, and have recently described the use of a tris(pyrazolyl)hydroborato ligand in the synthesis and structural characterization of the first monomeric 4-coordinate zinc hydroxide complex,  $\{\eta^3\text{-HB}(3\text{-Bu}^1\text{-5-Mepz})_3\}\text{-ZnOH}$  ( $3\text{-Bu}^1\text{-5-Mepz} = 3\text{-Bu}^1\text{-5-MeC}_3\text{N}_2\text{H}$ ).<sup>4</sup> Here we describe structural studies on a series of nitrate complexes  $\{\eta^3\text{-HB}(3\text{-Bu}^1\text{pz})_3\}\text{M}(\text{NO}_3)$  ( $\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ ;  $3\text{-Bu}^1\text{pz} = 3\text{-Bu}^1\text{C}_3\text{N}_2\text{H}_2$ )<sup>5</sup> which, in view of the isoelectronic relationship between bicarbonate and nitrate, are designed to provide insight as to the nature of the proposed bicarbonate intermediate of the carbonic anhydrase catalytic cycle.

Important information concerned with the structure and activity of carbonic anhydrase has been obtained by investigating metal-substituted enzymes<sup>1,6</sup> and also mutants.<sup>7</sup> Studies on metal-substituted enzymes have shown that cobalt(II) substitution reduces the activity to ca. 50% that of the zinc enzyme, whereas the corresponding Ni(II) and Cu(II) derivatives are effectively inactive.<sup>8</sup> The coordination mode of the bicarbonate ligand in the proposed intermediates  $[(\text{His})_3\text{M}(\text{OCO}_2\text{H})]^+$  ( $\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ ) may be expected to have a profound effect upon the activity of each derivative. In order to provide evidence for the coordination mode of the bicarbonate ligand in these intermediates, we have determined the X-ray structure of a series of nitrate complexes. Since the nitrate ligand is isoelectronic with bi-

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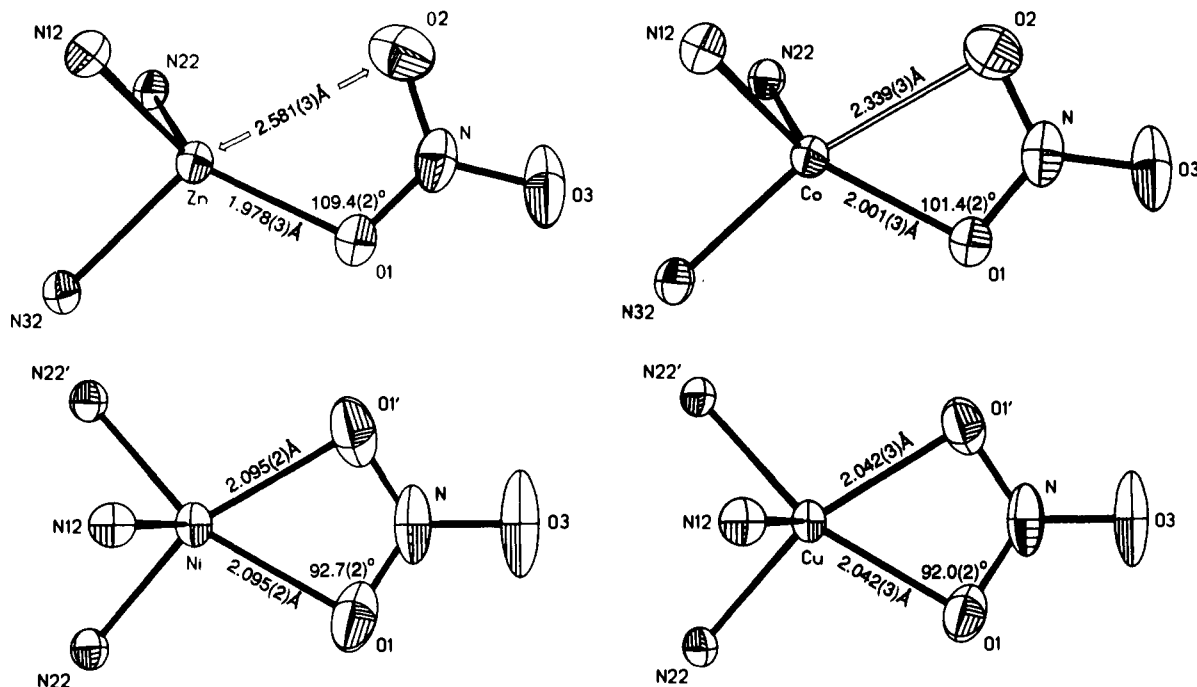


Figure 2. Coordination environment about the metal center in the plane of the nitrate ligand.

carbonate and may also exhibit both unidentate and bidentate coordination modes, observation of the structure of a metal–nitrate complex may provide a good indication as to the coordination mode of the corresponding bicarbonate derivative. The molecular structures of the cobalt, nickel, copper, and zinc complexes  $\{\eta^3\text{-HB}(3\text{-Bu}^i\text{pz})_3\text{M}(\text{NO}_3)\}$  ( $\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ ), shown in Figure 1, are observed to exhibit a variety of coordination modes of the nitrate ligand. Relevant bond lengths and angles for the complexes  $\{\eta^3\text{-HB}(3\text{-Bu}^i\text{pz})_3\text{M}(\text{NO}_3)\}$  are summarized in Figure 2. Significantly, whereas the nitrate ligand in  $\{\eta^3\text{-HB}(3\text{-Bu}^i\text{pz})_3\text{Zn}(\eta^1\text{-ONO}_2)\}$  is unidentate [ $\text{Zn}\cdots\text{O} = 1.978(3) \text{ \AA}$ ], with only a weak secondary interaction [ $\text{Zn}\cdots\text{O} = 2.581(3) \text{ \AA}$ ],<sup>9</sup> both the nickel and copper complexes exhibit perfectly symmetric bidentate coordination of the nitrate ligand with short M–O bond lengths [ $\text{Cu}\text{--}\text{O} = 2.042(3) \text{ \AA}$ ;  $\text{Ni}\text{--}\text{O} = 2.095(2) \text{ \AA}$ ]. In contrast, the cobalt derivative exhibits a noticeably asymmetric coordination mode [ $\text{Co}\text{--}\text{O} = 2.001(3)$  and  $2.339(3) \text{ \AA}$ ] which is intermediate between unidentate and symmetric bidentate. A simple indication of the increase in bidentate character of the nitrate ligand is provided by observing the decrease in the M–O(1)–N bond angle. Thus, the bond angle at oxygen decreases progressively from the tetrahedral value for Zn [ $109.4(2)^\circ$ ] with unidentate coordination to ca.  $92^\circ$  for Ni and Cu with symmetric bidentate coordination.

Although there are many factors, for example the  $\text{pK}_a$  of the coordinated water, that may be responsible for affecting the activity of metal-substituted carbonic anhydrases, the correlation between the order of activity ( $\text{Zn} > \text{Co} \gg \text{Ni}$  and  $\text{Cu}$ ) and the observed coordination mode of the nitrate ligands in the model complexes  $\{\eta^3\text{-HB}(3\text{-Bu}^i\text{pz})_3\text{M}(\text{NO}_3)\}$  ( $\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ ) is striking. One interpretation of these results, if they can be applied to the isoelectronic bicarbonate derivatives, is that a progressive ground-state stabilization of the bicarbonate ligand would be observed for the sequence  $\text{Zn} < \text{Co} < \text{Cu}$  and  $\text{Ni}$ . Stronger binding of the bicarbonate ligand across the series  $\text{Zn} < \text{Co} < \text{Cu}$  and  $\text{Ni}$  may result in slower displacement of the bicarbonate ligand by  $\text{H}_2\text{O}$  and thereby prevent a catalytic cycle operating for Cu and Ni derivatives. This suggestion supports the results of X-ray absorption studies on zinc- and cobalt-substituted carbonic anhydrase in the presence of bicarbonate<sup>11</sup> and also a recent theoretical analysis which indicates that 5-coordinate intermediates

are likely to behave as inhibitors for the carbonic anhydrase catalytic cycle.<sup>3b</sup>

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**Supplementary Material Available:** Tables of crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters and ORTEP drawings for all structures (33 pages); observed and calculated structure factors for all structures (57 pages). Ordering information is given on any current masthead page.

### Asymmetric Deprotonations: Enantioselective Syntheses of 2-Substituted (*tert*-Butoxycarbonyl)pyrrolidines

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The elaboration of secondary amines via dipole-stabilized carbanions has developed into a very useful synthetic method.<sup>1</sup> Syntheses of enantiomerically enriched benzylic 2-substituted secondary amines for derivatives which have a chiral activating group on nitrogen have been the most important asymmetric extensions of the methodology.<sup>2–4</sup> Analogous asymmetric sub-

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