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Articles

Bis(pyrazolylethyl) Ether Ligation to Zinc and Cobalt: Meridional vs Facial Coordination and the Suitability of Such Ligands in Providing a NNO Donor Set for Modeling Bioinorganic Aspects of Zinc Chemistry

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The structures of bis(pyrazolylethyl) ether derivatives of zinc and cobalt, namely $[\eta^3\text{-O}(\mathrm{CH_2CH_2pz^{Pr^i_2}})_2]\mathrm{Zn(NO_3)_2}$ and $[\eta^3\text{-O}(\mathrm{CH_2CH_2pz^{Me_2}})_2]\mathrm{Co(NO_3)_2}$, have been determined with a view to addressing the applicability of such ligands in modeling bioinorganic aspects of zinc chemistry. Specific consideration is given to the possibility that bis(pyrazolylethyl) ether ligands may provide an NNO donor system which may model aspects of the binding of zinc to protein backbones in enzymes such as thermolysin. The structural studies demonstrate that the bis(pyrazolylethyl) ether ligands do indeed coordinate *via* each of their NNO functionalities but that the relationship to the enzyme is limited by the adoption of meridional rather than facial coordination geometries. $[\eta^3\text{-O}(\mathrm{CH_2CH_2pz^{Pr^i_2}})_2]\mathrm{Zn(NO_3)_2}$ is monoclinic, $P2_1/c$ (No. 14), with $a = 11.619(2)$ Å, $b = 14.380(3)$ Å, $c = 16.757(2)$ Å, $\beta = 90.44(2)°$, and $Z = 4$. $[\eta^3\text{-O}(\mathrm{CH_2CH_2pz^{Me_2}})_2]\mathrm{Co(NO_3)_2}$ is monoclinic, $C2/c$ (No. 15), with $a = 17.136(3)$ Å, $b = 10.505(2)$ Å, $c = 11.121(2)$ Å, $\beta = 104.62(3)°$, and $Z = 4$.

Introduction

The discovery of zinc in the active site of a variety of enzymes, such as carbonic anhydrase, carboxypeptidase, thermolysin, and alcohol dehydrogenase,[1] has stimulated much effort into the syntheses of simple model complexes that are designed to mimic the coordination environment of the active site. In particular, since the polypeptide backbone of zinc enzymes typically binds the metal *via* a combination of N, O, and S donors, a variety of ligands comprising $\mathrm{N}_x\mathrm{O}_y\mathrm{S}_z$ functionalities have been synthesized with a view to modeling such enzyme sites. For example, NNN donor ligands have been used to model the active site of carbonic anhydrase,[2−7] while NNO donor ligands have been studied in attempts to provide a model for the coordination environment of enzymes that also incorporate oxygen donors, *e.g.* carboxypeptidase and thermolysin.[8−14] In this paper, we discuss the suitability of bis(pyrazolylethyl) ether ligands in providing an NNO donor system that may model aspects of the binding of zinc to the protein backbone in enzymes such as thermolysin.[15−17]

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

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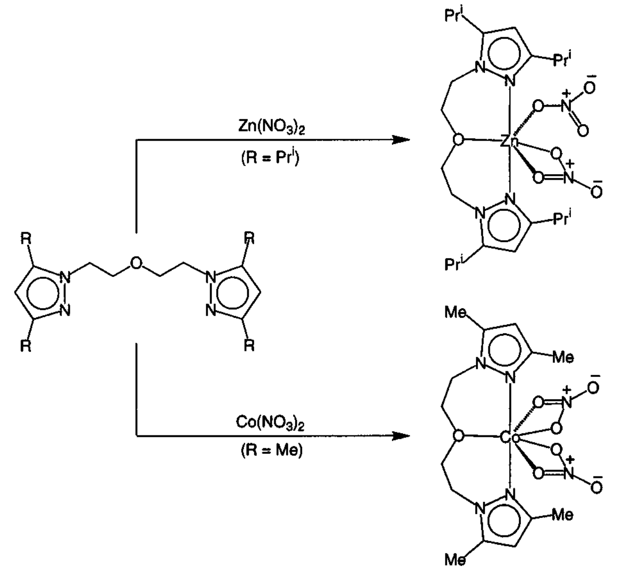
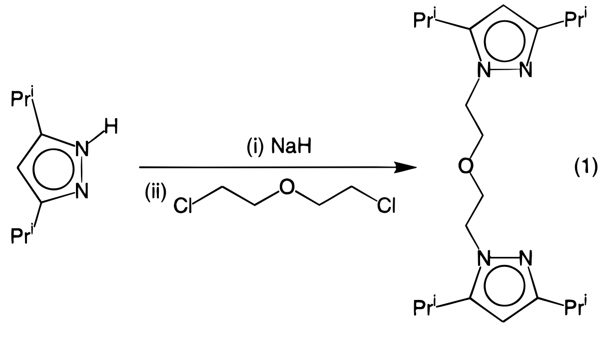
Scheme 1



Results and Discussion

(i) Meridional *vs* Facial Coordination of Bis(pyrazolylethyl) Ether Ligands. As an extension of our previous studies concerned with modeling the NNN donor environment of carbonic anhydrase,[3c] we are presently interested in evaluating ligands with related NNO functionalities as models for the active site of zinc enzymes such as thermolysin, an enzyme that hydrolyzes the amide bond of polypeptide substrates.[15,16] In particular, since the nitrogen donors in zinc enzymes are typically histidine residues, we are especially interested in NNO ligands that are derived from either imidazole or pyrazole functionalities. Our selection of bis(pyrazolylethyl) ether ligands for the present study is, in part, a consequence of the fact that related NNS and NNN donors are also known for this system[18] and that structural comparisons within the series should prove informative.

The bis[(3,5-diisopropylpyrazolyl)ethyl]ether ligand $O(CH_2CH_2pz^{Pr^i_2})_2$ is readily obtained by the reaction of $O(CH_2CH_2Cl)_2$ with 2 equiv of the sodium salt of 3,5-diisopropylpyrazole (eq 1), a procedure analogous to that described by Sorrell for the preparation of $O(CH_2CH_2pz^{Me_2})_2$.[18] The ability of $O(CH_2CH_2pz^{Pr^i_2})_2$ to act as a ligand for zinc is clearly indicated by the facile reaction with zinc nitrate to give $[\eta^3\text{-}O(CH_2CH_2pz^{Pr^i_2})_2]Zn(NO_3)_2$ (Scheme 1), which has been structurally characterized by X-ray diffraction (Figure 1). Since cobalt-substituted thermolysin is also an active enzyme (and, in fact, more active than the native enzyme by a factor of 2),[1a] we have also synthesized and structurally characterized the analogous cobalt complex $[\eta^3\text{-}O(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$ (Figure 2). Selected bond lengths and angles for $[\eta^3\text{-}O(CH_2CH_2pz^{Pr^i_2})_2]Zn(NO_3)_2$ and $[\eta^3\text{-}O(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$ are listed in Tables 1 and 2, respectively.



(1)

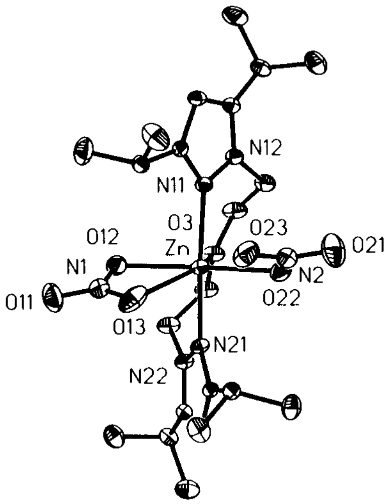


Figure 1. Molecular structure of $[\eta^3\text{-}O(CH_2CH_2pz^{Pr^i_2})_2]Zn(NO_3)_2$.

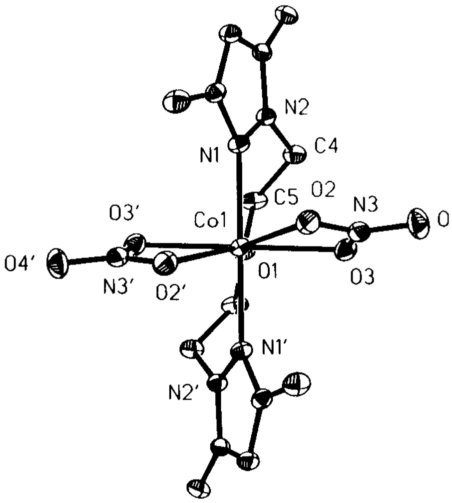


Figure 2. Molecular structure of $[\eta^3\text{-}O(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[\eta^3\text{-}O(CH_2CH_2pz^{Pr^i_2})_2]Zn(NO_3)_2$

Zn−O12	2.183(3)	Zn−O22	2.116(3)
Zn−O13	2.397(4)	Zn···O23	2.647(5)
Zn−N11	2.127(3)	Zn−N21	2.127(3)
Zn−O3	2.217(2)		
O12−Zn−O13	54.7(1)	O12−Zn−O22	174.7(1)
O13−Zn−O22	120.1(1)	O12−Zn−O3	91.0(1)
O13−Zn−O3	142.8(1)	O22−Zn−O3	94.2(1)
O12−Zn−N11	92.2(1)	O13−Zn−N11	108.0(1)
O22−Zn−N21	89.1(1)	O3−Zn−N11	84.9(1)
O22−Zn−N21	90.6(1)	O13−Zn−N21	81.0(1)
N11−Zn−N21	169.7(1)	O3−Zn−N21	84.8(1)
Zn−O13−N1	89.7(3)	Zn−O12−N1	99.7(3)
Zn−O23−N2	82.2(5)	Zn−O22−N2	106.1(3)

Of most interest to the present study are the coordination modes adopted by the bis(pyrazolylethyl) ether ligands in $[\eta^3\text{-}O(CH_2CH_2pz^{Pr^i_2})_2]Zn(NO_3)_2$ and $[\eta^3\text{-}O(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$. Specifically, since protein backbones typically bind zinc in a facial manner (*i.e.* the zinc has a *pseudo*tetrahedral

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[18] Sorrell has described the preparation of a series of bis[(3,5-dimethylpyrazolyl)ethyl] ether and sulfide, and bis[(3,5-dimethylpyrazolyl)ethyl]amine ligands, *i.e.* $O(CH_2CH_2pz^{Me_2})_2$, $S(CH_2CH_2pz^{Me_2})_2$, and $HN(CH_2CH_2pz^{Me_2})_2$. See: Sorrell, T. N.; Malachowski, M. R. *Inorg. Chem.* **1983**, *22*, 1883−1887.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[\eta^3\text{-O}(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$

Co1−O1	2.125(1)	Co1−O2	2.308(3)
Co1−O3	2.186(3)	Co1−N1	2.133(2)
O1−Co1−O2	141.3(1)	O1−Co1−O3	86.4(1)
O2−Co1−O3	56.8(1)	O1−Co1−N1	87.5(1)
O2−Co1−N1	82.5(1)	O3−Co1−N1	92.0(1)
O2−Co1−O2′	77.5(1)	Co1−O2−N3	90.9(2)
Co1−O3−N3	96.3(2)		

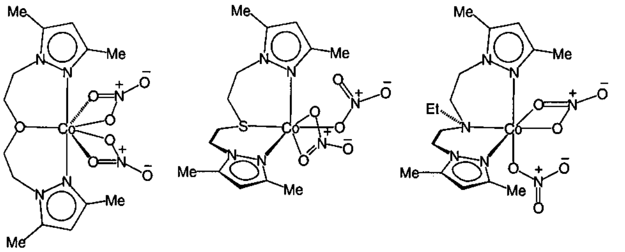

Figure 3. Meridional *vs* facial coordination modes in $[\eta^3\text{-X}(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$ derivatives (X = O, S, NEt).

coordination geometry), the bis(pyrazolylethyl) ether ligands are required to provide a coordination geometry with a facial array of NNO donors if they are to be useful in modeling the active site of zinc enzymes. However, examination of Figures 1 and 2 illustrates that such a coordination mode is not adopted by either of the zinc and cobalt complexes $[\eta^3\text{-O}(CH_2CH_2pz^{R_2})_2]M(NO_3)_2$. In preference, the bis(pyrazolylethyl) ether ligand adopts a "T-shaped" or meridional arrangement in which the nitrogen donors are *trans* to each other. Furthermore, the bis(pyrazolylethyl) ether ligand also exhibits a "T-shaped" coordination mode in the cadmium complex $[\eta^3\text{-O}(CH_2CH_2pz^{Me_2})_2]Cd(NO_3)_2$.[19] It is, therefore, apparent that the bis(pyrazolylethyl) ether ligand system is not particularly suitable with respect to modeling such bioinorganic aspects of zinc chemistry and that a greater degree of success would be achieved with ligands incapable of adopting such "T-shaped", meridional, geometries.

It is important to note that the adoption of a "T-shaped" coordination geometry by the bis(pyrazolylethyl) ether ligand system, $O(CH_2CH_2pz^{R_2})_2$, is in marked contrast to the geometries that are observed for the analogous NNS and NNN ligands, $S(CH_2CH_2pz^{Me_2})_2$ and $EtN(CH_2CH_2pz^{Me_2})_2$, in related complexes. Thus, the latter ligands adopt facial coordination modes in the cobalt nitrate derivatives $[\eta^3\text{-}fac\text{-S}(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$[20] and $[\eta^3\text{-}fac\text{-EtN}(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$,[21,22] as illustrated in Figure 3.[23] Interestingly, the variation in coordination mode of the $X(CH_2CH_2pz^{Me_2})_2$ ligands (X = O, S, NEt) is also accompanied by a change in nitrate coordination modes. Thus, whereas each of the nitrate ligands in $[\eta^3\text{-}mer\text{-O}(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$ are bidentate, $[\eta^3\text{-}fac\text{-S}(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$ and $[\eta^3\text{-}fac\text{-EtN}(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$ exhibit both unidentate and bidentate coordination modes (*vide infra*).

A further illustration of how the coordinating abilities of this class of NNX ligand system varies as a function of the bridging group is provided by the fact that the $PhN(CH_2pz^{Me_2})_2$ ligand adopts a facial coordination geometry in $[\eta^3\text{-PhN}(CH_2pz^{Me_2})_2]Co(NO_3)_2$: However, the Co-NPh interaction [2.401(5) Å] is significantly longer than the Co-pyrazolyl interactions [2.044 (5) and 2.051(5) Å].[24] A more extreme example of how reducing the size of the linker (*i.e.* CH_2 *vs* CH_2CH_2) influences the coordination geometry is illustrated by the observation that bis((5-methyl-4-imidazolyl)methyl) sulfide, $S(CH_2im^{Me})_2$, acts only as a bidentate ligand to zinc in the four-coordinate complex $[\eta^2\text{-S}(CH_2im^{Me})_2]Zn(NO_3)_2$, with the sulfur remaining uncoordinated.[25,26]

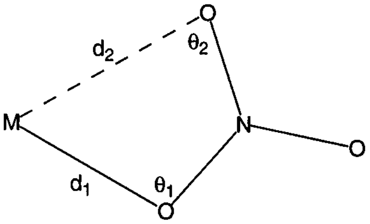

Figure 4. Criteria for assigning nitrate coordination modes.

Table 3. Criteria for Assigning Nitrate Coordination Modes (See Ref 27)

	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 4. Classification of Nitrate Coordination Modes for $[\eta^3\text{-O}(CH_2CH_2pz^{R_2})_2]M(NO_3)_2$

	$d_2 - d_1$ (Å)	$\theta_1 - \theta_2$ (deg)	classification
$[\eta^3\text{-O}(CH_2CH_2pz^{Pr^i_2})_2]Zn(NO_3)_2$	0.53	23.9	anisobidentate
	0.21	10.0	bidentate
$[\eta^3\text{-O}(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$	0.12	5.4	bidentate
	0.12	5.4	bidentate

(ii) Comparison of Nitrate Coordination Modes. Another feature of interest in comparison of the structures of $[\eta^3\text{-O}(CH_2CH_2pz^{Pr^i_2})_2]Zn(NO_3)_2$ and $[\eta^3\text{-O}(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$ is the difference in coordination modes adopted by the nitrate ligands. For reference, the nitrate ligand is known to bind to a single metal center by three different coordination modes, namely *(i)* bidentate, *(ii)* anisobidentate (or asymmetric bidentate), and *(iii)* unidentate,[27,28] which have been classified according to the geometrical criteria described in Figure 4 and Table 3.[27] On the basis of these criteria, the two nitrate ligands in $[\eta^3\text{-O}(CH_2CH_2pz^{Pr^i_2})_2]Zn(NO_3)_2$ are appropriately described as bidentate and anisobidentate (with the latter approaching that of a unidentate description), while both nitrate ligands of $[\eta^3\text{-O}(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$ exhibit bidentate coordination modes (Table 4).[29] For purposes of comparison, the nitrate

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(23) For a recent example of similar conformational changes in $HN(CH_2CH_2pz^{Me_2})_2$ and $PhCH_2N(CH_2CH_2pz^{Me_2})_2$ derivatives of Cu(II), see: Martens, C. F.; Schenning, A. P. H. J.; Feiters, M. C.; Berens, H. W.; van der Linden, J. G. M.; Admiraal, G.; Beurskens, P. T.; Kooijman, H.; Spek, A. L.; Nolte, R. J. M. *Inorg. Chem.* **1995**, *34*, 4735−4744.

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Table 5. Coordination Modes of Nitrate Ligands in Bis(nitrate) Complexes of Zn and Co(II)

compound[a]	*d*(M−O)/Å	$d_1 - d_2$/Å	classification[b]	ref
$[\eta^3\text{-}\mathit{mer}\text{-}(CH_2CH_2pz^{Pr^i_2})_2]Zn(NO_3)_2$	2.116(3), 2.647(5)	0.531	anisobidentate	this work
	2.183(3), 2.397(4)	0.214	bidentate	
$[\eta^3\text{-}P(C_5H_4N)_3]Zn(NO_3)_2$	2.085(4)		unidentate	*c*
	2.201(3), 2.269(4)	0.068	bidentate	
$[\eta^2\text{-}S(CH_2im^{Me})_2]Zn(NO_3)_2$	2.013(3)		unidentate	*d*
	2.031(3)		unidentate	
$(\eta^1\text{-}L_O)_2(H_2O)_2Zn(NO_3)_2$	2.123(2)		unidentate*	*e*
$(\eta^2\text{-}L_{O_2})_2Zn(NO_3)_2$	2.203(1)		unidentate*	*f*
$(\eta^3\text{-}L_{N_3})Zn(NO_3)_2$	2.179(6)		unidentate	*g*
	2.227(5), 2.253(5)	0.026	bidentate	
$(py)_3Zn(NO_3)_2$	2.232(13), 2.418(12)	0.186	bidentate*	*h*
$(py)_2Zn(NO_3)_2$	2.044(12)		unidentate	*i*
	2.047(13)		unidentate	
$(\eta^1\text{-}L_N)_2Zn(NO_3)_2$	1.970(3)		unidentate	*j*
	1.990(3)		unidentate	
$(\eta^1\text{-}L_N)_2Zn(NO_3)_2$	2.028(19)		unidentate	*k*
	2.268(32)		unidentate	
$(\eta^1\text{-}L_N)_2Zn(NO_3)_2$	2.03, 2.66	0.63	unidentate	*l*
	2.34, 2.35	0.01	bidentate	
$(\eta^1\text{-}L_O)_2Zn(NO_3)_2$	1.979(2)		unidentate	*n*
	2.037(2)		unidentate	
$[\eta^3\text{-}\mathit{mer}\text{-}O(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$	2.186(3), 2.308(3)	0.122	bidentate*	this work
$[\eta^3\text{-}\mathit{fac}\text{-}S(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$	2.062(3)		unidentate	*n*
	2.180(3), 2.249(3)	0.069	bidentate	
$[\eta^3\text{-}\mathit{fac}\text{-}EtN(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2$	2.060(8)		unidentate	*o*
	2.172(8), 2.216(8)	0.044	bidentate	
$[\eta^3\text{-}\mathit{mer}\text{-}PhN(CH_2pz^{Me_2})_2]Co(NO_3)_2$	2.045(5)		unidentate	*p*
	2.036(5), 2.470(5)	0.434	anisobidentate	
$[(\eta^4\text{-}12\text{-}crown\text{-}4)Co(NO_3)_2$	2.102(3)		unidentate	*q*
	2.202(4), 2.246(4)	0.044	bidentate	
$(\eta^1\text{-}L_O)_4Co(NO_3)_2$	2.107(3)		unidentate	*r*
	2.107(3)		unidentate	
$(\eta^1\text{-}L_O)_2(H_2O)_2Co(NO_3)_2$	2.121(2)		unidentate	*s*
$\mathit{trans}\text{-}(\eta^1\text{-}L_N)_4Co(NO_3)_2$	2.18(5)		unidentate*	*t*
$(\eta^1\text{-}L_N)_2(H_2O)_2Co(NO_3)_2$	2.140(1)		unidentate*	*u*
$(py)_3Co(NO_3)_2$	2.207(9), 2.311(9)	0.104	bidentate*	*v*
$[(Me_2N)_3PO]_3Co(NO_3)_2$	2.163(3), 2.198(3)	0.035	bidentate*	*w*
$(\eta^1\text{-}L_N)_2Co(NO_3)_2$	2.059(2), 2.277(2)	0.218	bidentate*	*x*
$(Me_3PO)_2Co(NO_3)_2$	2.14(2), 2.23(2)	0.09	bidentate	*y*
	2.15(2), 2.17(2)	0.02	bidentate	
$(Et_3PO)_2Co(NO_3)_2$	2.073(5), 2.295(6)	0.222	bidentate	*z*
	2.073(5), 2.295(6)	0.222	bidentate	
$(Ph_3PO)_2Co(NO_3)_2$	2.13(1), 2.17(1)	0.04	bidentate*	*aa*
$[\eta^1\text{-}(Me_2N)_2CS]_2Co(NO_3)_2$	2.036(3), 2.490(2)	0.454	anisobidentate	*ab*
	2.017(3), 2.377(3)	0.360	anisobidentate	

[a] The abbreviations $\eta^x\text{-}L_{E_x}$ (E = O, N) are intended to indicate the number and nature of the ligating atoms. See the appropriate literature reference for the complete ligand description. [b] Since the secondary M⋯O interactions were not listed for many of the complexes identified as unidentate, their assignment as such is based on descriptions provided in the literature reference. It must, therefore, be recognized that some of these interactions may possibly be better described an anisobidentate; an asterisk indicates that the two nitrate ligands are crystallographically identical. [c] Gregorzik, R.; Wirbser, J.; Vahrenkamp, H. *Chem. Ber.* **1992**, *125*, 1575−1581. [d] Gregorzik, R.; Vahrenkamp, H. *Chem. Ber.* **1994**, *127*, 1857−1863. [e] Sabirov, V. Kh.; Porai-Koshits, M. A.; Struchkov, Yu. T. *Koord. Khim.* **1993**, *19*, 81−85. [f] Nikolaev, V. P.; Khodashova, T. S.; Porai-Koshits, M. A.; Butman, L. A.; Tsintsadze, *Koord. Khim.* **1985**, *11*, 1386−1392. [g] Adam, K. R.; Dancey, K. P.; Harrison, B. A.; Leong, A. J.; Lindoy, L. F.; McPartlin, M.; Tasker, P. A. *J. Chem. Soc.*, *Chem. Commun.* **1983**, 1351−1353. Adam, K. R.; Dancey, K. P.; Leong, A. J.; Lindoy, L. F.; McCool, B. J.; McPartlin, M.; Tasker, P. A. *J. Am. Chem. Soc.* **1988**, *110*, 8471−8477. [h] Cameron, A. F.; Taylor, D. W.; Nuttall, R. H. *J. Chem. Soc.*, *Dalton Trans.* **1972**, 1603−1608. [i] Cameron, A. F.; Taylor, D. W.; Nuttall, R. H. *J. Chem. Soc. A* **1971**, 3402−3405. [j] Hergold-Brundic, A.; Kaitner, B.; Kamenar, B.; Leovac, V. M.; Iveges, Juranic, N. *Inorg. Chim. Acta* **1991**, *188*, 151−158. [k] Brassy, C.; Michaud, M.-C.; Delettré, J.; Mornon, J.-P. *Acta Crystallogr.* **1974**, *B30*, 2848−2852. [l] Laidoudi, A.; Kheddar, N.; Brianso, M.-C. *Acta Crystallogr.* **1978**, *B34*, 782−788. [m] Brown, C. J.; Lewis, J. F. P. *Acta Crystallogr.* **1984**, *C40*, 368−370. [n] Haanstra, W. G.; Driessen, W. L.; van Roon, M.; Stoffels, A. L. E.; Reedijk, J. *J. Chem. Soc.*, *Dalton Trans.* **1992**, 481−486. [o] Driessen, W. L.; de Graaff, R. A. G.; Parlevliet, P. J.; Reedijk, J.; de Vos, R. M. *Inorg. Chim. Acta* **1994**, *216*, 43−49. [p] Locher, K.; Blonk, H. L.; Driessen, W. L.; Reedijk, J. *Acta Crystallogr.* **1987**, *C43*, 651−653. [q] Holt, E. M.; Alcock, N. W.; Hendrixson, R. R.; Malpass, G. D., Jr.; Ghirardelli, R. G.; Palmer, R. A. *Acta Crystallogr.* **1981**, *B37*, 1080−1085. [r] Blake, A. J.; Gould, R. O.; Grant, C. M.; Milne, P. E. Y.; Winpenny, R. E. P. *Polyhedron* **1994**, *13*, 187−191. [s] Sabirov, V. Kh.; Porai-Koshits, M. A.; Struchkov, Yu. T. *Koord. Khim.* **1993**, *19*, 143−148. [t] Blaton, N. M.; Peeters, O. M.; De Ranter, C. J. *Acta Crystallogr.* **1978**, *B34*, 1854−1857. [u] Hänggi, G.; Schmalle, H.; Dubler, E. *Inorg. Chem.* **1993**, *32*, 6095−6101. [v] Cameron, A. F.; Taylor, D. W.; Nuttall, R. H. *J. Chem. Soc.*, *Dalton Trans.* **1972**, 1603−1608. [w] Michelet, A.; Viossat, B.; Khodadad, P.; Rodier, N. *Acta Crystallogr.* **1981**, *B37*, 678−680. [x] Plakatouras, J. C.; Perlepes, S. P.; Mentzafos, D.; Terzis, A.; Bakas, T.; Papaefthymiou. *Polyhedron* **1992**, *11*, 2657−2672. [y] Cotton, F. A.; Soderberg, R. H. *J. Am. Chem. Soc.* **1963**, *85*, 2402−2406. [z] Alnaji, O.; Dartiguenave, M.; Dartiguenave, Y.; Simard, M.; Beauchamp, A. L. *Inorg. Chim. Acta* **1991**, *187*, 31−38. [aa] Rodrigues, A. M. G. D.; Francisco, R. H. P.; Lechat, J. R. *Cryst. Struct. Commun.* **1982**, *11*, 847−852. [ab] Pignedoli, A.; Peyronel, G. *Acta Crystallogr.* **1978**, *B34*, 1477−1482.

coordination modes in other structurally characterized bis(nitrate) complexes of zinc and cobalt(II) are summarized in Table 5.[30]

Our previous studies on a series of tris(3-t-butylpyrazolyl)hydroborato $[Tp^{Bu^t}]M(NO_3)$ derivatives (M = Co, Ni, Cu, Zn) have demonstrated that for this system the preference for bidentate coordination increases across the series Zn < Co ≪ Cu and Ni.[31] Such an observation was of interest since these structural preferences were noted to correlate with the activity of metal-substituted carbonic anhydrases, suggesting that the coordination mode of the bicarbonate intermediates for the metal-substituted enzyme systems may also show such a trend. The increased preference for bidentate coordination of the nitrate ligand in $[\eta^3\text{-O}(\mathrm{CH_2CH_2pz^{Me_2}})_2]\mathrm{Co(NO_3)_2}$ *vs* $[\eta^3\text{-O}(\mathrm{CH_2CH_2pz^{Pr^i_2}})_2]\mathrm{Zn(NO_3)_2}$ is also in accord with our previous observations relating to the $[\mathrm{Tp^{Bu^t}}]\mathrm{M(NO_3)}$ system, and thereby supports the notion that the coordination mode of the bicarbonate ligand may be an important factor in influencing the activity of metal-substituted carbonic anhydrases. Moreover, the cadmium complex $[\eta^3\text{-O}(\mathrm{CH_2CH_2pz^{Me_2}})_2]\mathrm{Cd(NO_3)_2}$ has also been reported to exhibit bidentate coordination of both nitrate ligands,[32] in line with the observation that the activity of cadmium-substituted carbonic anhydrase is reduced substantially from that of the zinc enzyme at pH 7.[33,34]

Conclusions

In summary, the bis(pyrazolylethyl) ether ligands $\mathrm{O(CH_2CH_2pz^{R_2})_2}$ exhibit a "T-shaped" meridional coordination mode in the zinc and cobalt complexes $[\eta^3\text{-O}(\mathrm{CH_2CH_2pz^{Pr^i_2}})_2]\mathrm{Zn(NO_3)_2}$ and $[\eta^3\text{-O}(\mathrm{CH_2CH_2pz^{Me_2}})_2]\mathrm{Co(NO_3)_2}$. Such an observation is in marked contrast to the facial coordination geometries that have been reported for the related NNS and NNN ligands in $[\eta^3\text{-}fac\text{-S}(\mathrm{CH_2CH_2pz^{Me_2}})_2]\mathrm{Co(NO_3)_2}$ and $[\eta^3\text{-}fac\text{-EtN}(\mathrm{CH_2CH_2pz^{Me_2}})_2]\mathrm{Co(NO_3)_2}$. As such, it is evident that the bis(pyrazolylethyl) ether ligand is not particularly suitable with respect to modeling bioinorganic aspects of zinc chemistry. Finally, comparison of the structures of a pair of zinc and cobalt nitrate complexes supported by bis(pyrazolylethyl) ether ligation, $[\eta^3\text{-O}(\mathrm{CH_2CH_2pz^{Pr^i_2}})_2]\mathrm{Zn(NO_3)_2}$ and $[\eta^3\text{-O}(\mathrm{CH_2CH_2pz^{Me_2}})_2]\mathrm{Co(NO_3)_2}$, illustrates the greater preference for cobalt to adopt bidentate coordination of the nitrate ligand in this system.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques.[35] Solvents were purified and degassed by standard procedures. ^{1}H and ^{13}C NMR spectra (all *J* values in Hz) were measured on Varian VXR 200, 300, and 400 spectrometers. IR spectra were recorded as either thin-films or as KBr pellets on a Perkin-Elmer 1420 spectrophotometer and are reported in cm^{-1}. Elemental analyses were measured using a Perkin-Elmer 2400 CHN Elemental Analyzer. UV−visible spectra were recorded on a Perkin-Elmer Lambda 6 spectrophotometer. $\mathrm{O(CH_2CH_2pz^{Me_2})_2}$ was prepared as described in the literature.[18]

Synthesis of $\mathbf{O(CH_2CH_2pz^{Pr^i_2})_2}$. $\mathrm{O(CH_2CH_2pz^{Pr^i_2})_2}$ was prepared by a method analogous to that described for $\mathrm{O(CH_2CH_2pz^{Me_2})_2}$.[18] Diisopropylpyrazole[36] (12.0 g, 78.9 mmol) was added to a suspension of NaH (2.84 g, 118 mmol) in a mixture of DMF (150 mL) and THF (70 mL) and stirred at room temperature for 1 h. Bis(2-chloroethyl) ether (5.7 g, 39.9 mmol) in DMF (40 mL) was added slowly with stirring and then heated at 65 °C overnight. Water (10 mL) was added to destroy excess NaH (*Caution!*) and the solvent removed under reduced pressure. The crude product was extracted into $\mathrm{CH_2Cl_2}$ (400 mL), washed sequentially with 10% NaOH(aq) (2 × 100 mL) and water (1 × 100 mL), and dried over $\mathrm{MgSO_4}$. The solvent was removed under reduced pressure, giving $\mathrm{O(CH_2CH_2pz^iPr_2)_2}$ as a tan oil (10.0 g, 67%). IR data (cm^{-1}), neat on NaCl plates: 2963 (s), 2929 (s), 2870 (s), 1620 (w), 1543 (s), 1463 (s), 1382 (m), 1363 (m), 1290 (m), 1201 (w), 1180 (w), 1123 (s), 1062 (w), 998 (w), 786 (m). ^{1}H NMR ($\mathrm{CD_3CN}$): δ 1.17 [d, $J_{\mathrm{H-H}} = 6.8$, 2 CH(C*H*$_3$)$_2$], 2.82 [spt, $J_{\mathrm{H-H}} = 6.8$, C*H*(CH$_3$)$_2$], 2.93 [spt, $J_{\mathrm{H-H}} = 6.8$, C*H*(CH$_3$)$_2$], 3.67 [t, $J_{\mathrm{H-H}} = 5.6$, C*H*$_2$], 4.01 [t, $J_{\mathrm{H-H}} = 5.6$, C*H*$_2$], 5.84 [s, C*H*]. ^{13}C NMR ($\mathrm{CD_3CN}$): δ 23.3 [q, $J_{\mathrm{C-H}} = 126$, 2 CH(*C*H$_3$)$_2$], 25.8 [d, $J_{\mathrm{C-H}} = 127$, *C*H(CH$_3$)$_2$], 28.7 [d, $J_{\mathrm{C-H}} = 127$, *C*H(CH$_3$)$_2$], 49.0 [t, $J_{\mathrm{C-H}} = 138$, *C*H$_2$], 70.8 [t, $J_{\mathrm{C-H}} = 143$, *C*H$_2$], 98.7 [d, $J_{\mathrm{C-H}} = 171$, *C*H], 151.2 and 158.4 [s, *C*$_2$N$_2$CH].

Synthesis of $\mathbf{[\eta^3{-}O(CH_2CH_2pz^{Pr^i_2})_2]Zn(NO_3)_2}$. A mixture of $\mathrm{O(CH_2CH_2pz^{Pr^i_2})_2}$ (1.0 g, 2.67 mmol) and $\mathrm{Zn(NO_3)_2{\cdot}6H_2O}$ (0.78 g, 2.62 mmol) in acetonitrile (30 mL) was stirred at 60 °C for 1 h. The mixture was allowed to stand at room temperature overnight, after which the solvent was removed under reduced pressure. The product was washed with pentane and dried *in vacuo* to give $[\eta^3\text{-O}(\mathrm{CH_2CH_2pz^{Pr^i_2}})_2]\mathrm{Zn(NO_3)_2}$ as a white solid (1.4 g, 95%). Anal. Calcd for $[\eta^3\text{-O}(\mathrm{CH_2CH_2pz^{Pr^i_2}})_2]\mathrm{Zn(NO_3)_2}$: C, 46.9; H, 6.7; N, 14.9. Found: C, 46.5; H, 6.7; N, 14.1. IR data (cm^{-1}), KBr pellet: 2969 (s), 2935 (m), 2874 (m), 1548 (m), 1477 (s), 1408 (m), 1385 (m), 1365 (m), 1295 (s), 1222 (w), 1184 (w), 1157 (w), 1091 (m), 1021 (m), 920 (w), 813 (m), 728 (w), 692 (w), 642 (w), 556 (w). ^{1}H NMR ($\mathrm{CD_3CN}$): δ 1.16 [d, $J_{\mathrm{H-H}} = 6.7$, CH(C*H*$_3$)$_2$], 1.22 [d, $J_{\mathrm{H-H}} = 6.7$, CH(C*H*$_3$)$_2$], 2.99 [spt, $J_{\mathrm{H-H}} = 6.7$, C*H*(CH$_3$)$_2$], 3.15 [spt, $J_{\mathrm{H-H}} = 6.7$, C*H*(CH$_3$)$_2$], 4.01 [broad t, C*H*$_2$], 4.36 [broad t, C*H*$_2$], 6.20 [s, C*H*]. ^{13}C NMR ($\mathrm{CD_3CN}$): δ 22.6 [q, $J_{\mathrm{C-H}} = 127$, CH(*C*H$_3$)$_2$], 23.9, [q, $J_{\mathrm{C-H}} = 127$, CH(*C*H$_3$)$_2$], 26.1 [d, $J_{\mathrm{C-H}} = 130$, *C*H(CH$_3$)$_2$], 28.4 [d, $J_{\mathrm{C-H}} = 130$, *C*H(CH$_3$)$_2$], 47.7 [t, $J_{\mathrm{C-H}} = 141$, *C*H$_2$], 73.5 [t, $J_{\mathrm{C-H}} = 147$, *C*H$_2$], 100.3 [d, $J_{\mathrm{C-H}} = 176$, *C*H], 154.2 and 162.6 [s, *C*$_2$N$_2$CH].

Synthesis of $\mathbf{[\eta^3\text{-}O(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2}$. A mixture of $\mathrm{O(CH_2CH_2pz^{Me_2})_2}$ (1.0 g, 3.82 mmol) and $\mathrm{Co(NO_3)_2{\cdot}6H_2O}$ (1.1 g, 3.78 mmol) in methanol (50 mL) was stirred at 50 °C for 30 min. The mixture was allowed to stand at room temperature overnight, after which the solvent was removed under reduced pressure. The product was washed with pentane and benzene and dried *in vacuo* to give $[\eta^3\text{-O}(\mathrm{CH_2CH_2pz^{Me_2}})_2]\mathrm{Co(NO_3)_2}$ as a pink solid (1.5 g, 89%). Anal. Calcd for $[\eta^3\text{-O}(\mathrm{CH_2CH_2pz^{Me_2}})_2]\mathrm{Co(NO_3)_2{\cdot}0.5MeOH}$: C, 37.8; H, 5.2; N, 18.2. Found: C, 37.6; H, 4.8; N, 17.5. UV−vis: $\lambda = 535$ nm ($\epsilon \approx 40$ M^{-1} cm^{-1}). IR data (cm^{-1}), KBr pellet: 2968 (w), 2945 (w), 1554 (m), 1475 (s), 1433 (s), 1393 (s), 1356 (m), 1328 (s), 1311 (s), 1238 (m), 1155(w), 1134 (w), 1073 (m), 1037 (m), 997 (w), 912 (m), 813 (m), 794 (m), 744 (w), 627 (w), 520 (w).

X-ray Structure Determination of $\mathbf{[\eta^3\text{-}O(CH_2CH_2pz^{Pr^i_2})_2]Zn(NO_3)_2}$. Crystal data, data collection, and refinement parameters for $[\eta^3\text{-O}(\mathrm{CH_2CH_2pz^{Pr^i_2}})_2]\mathrm{Zn(NO_3)_2}$ are summarized in Table 6. A single crystal was mounted in a glass capillary and 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 Kα 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 using SHELXTL PC. Systematic absences were consistent uniquely with the space group $P2_1/c$ (No. 14). Hydrogens on carbon were included in calculated positions.

X-ray Structure Determination of $\mathbf{[\eta^3\text{-}O(CH_2CH_2pz^{Me_2})_2]Co(NO_3)_2}$. Crystal data, data collection, and refinement parameters for

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(30) Some zinc and cobalt nitrate complexes with more than two nitrate ligands, *e.g.* $[\mathrm{Zn(NO_3)_4}]^{2-}$, $[\mathrm{Co(NO_3)_4}]^{2-}$, and $[\mathrm{Co(NO_3)_3(NCMe)}]^{-}$ have also been structurally characterized. See: (a) Bellitto, C.; Gastaldi, L.; Tomlinson, A. A. G. *J. Chem. Soc., Dalton Trans.* **1976**, 989−992. (b) Bergman, J. G., Jr.; Cotton, F. A. *Inorg. Chem.* **1966**, *5*, 1208−1213. (c) Albright, J. O.; Clardy, J. C.; Verkade, J. G. *Inorg. Chem.* **1977**, *16*, 1575−1580.

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Table 6. Crystal and Intensity Collection Data for [η^3-O($CH_2CH_2pz^{Pr^i_2}$)$_2$]Zn(NO_3)$_2$ and [η^3-O($CH_2CH_2pz^{Me_2}$)$_2$]Co(NO_3)$_2$

	[η^3-O($CH_2CH_2pz^{Pr^i_2}$)$_2$]-Zn(NO_3)$_2$	[η^3-O($CH_2CH_2pz^{Me_2}$)$_2$]-Co(NO_3)$_2$
formula	$C_{22}H_{38}N_6O_7Zn$	$C_{14}H_{22}N_6O_7Co$
fw	564.0	445.3
lattice	monoclinic	monoclinic
cell consts		
a, Å	11.619(2)	17.136(3)
b, Å	14.380(3)	10.505(2)
c, Å	16.757(2)	11.121(2)
α, deg	90.0	90.0
β, deg	90.44(2)	104.62(3)
γ, deg	90.0	90.0
V, Å^3	2799(1)	1937(1)
Z	4	4
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
ρ(calcd), g cm^{-3}	1.34	1.53
μ(Mo, Kα), cm^{-1}	92.6	93.5
R^a	0.0366	0.0452
$R_w{}^a$	0.0466	0.0727

[a] $R = \sum|F_o - F_c|\}/\sum|F_o|$; $R_w = \sum w^{1/2}|F_o - F_c|/\sum w^{1/2}|F_o|$; $w = [\sigma^2(F) + gF^2]^{-1}$.

[η^3-O($CH_2CH_2pz^{Me_2}$)$_2$]Co(NO_3)$_2$ are summarized in Table 6. A single crystal was mounted in a glass capillary and 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 Kα X-radiation (λ = 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 using SHELXTL PC. Systematic absences were consistent with the space groups *C*2/*c* (No. 15) and *Cc* (No. 9), but the structure was successfully solved in the centrosymmetric alternative *C*2/*c*. Hydrogens on carbon were included in calculated positions.

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Supporting Information Available: Tables of crystal and intensity collection data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, and ORTEP drawings for [η^3-O($CH_2CH_2pz^{Pr^i_2}$)$_2$]Zn(NO_3)$_2$ and [η^3-O($CH_2CH_2pz^{Me_2}$)$_2$]Co(NO_3)$_2$ (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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