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C_3-Symmetric Chiral Amidate Complexes: Effects of Ligand Binding on Cavity Structure

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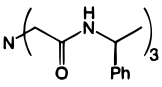
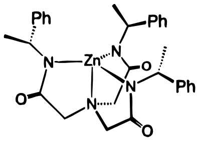
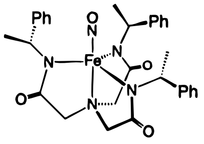
Polydentate ligands that form cavity motifs around a metal ion(s) are known to influence the structural and functional properties of metal complexes.[1] For example, complexes containing chiral C_3-symmetric ligands show promising enantioselectivity when used in transition metal catalyzed reactions.[2] Yet, to date, only a limited number of chiral C_3-symmetric ligands have been reported.[3] We have described recently the synthesis of metal complexes containing tripodal ligands derived from tris(*N*-alkylcarbamoylmethyl)amine: these ligands, when coordinated to a metal ion, create cavities about the vacant coordinate site in trigonal monopyramidal (TMP) complexes.[4] This class of C_3-symmetric ligands can be readily modified with optically active groups attached to the amidate nitrogens, affecting the formation of chiral cavities upon metal ion binding. We report herein the structural properties for the Zn(II) and Fe−NO complexes of a new homochiral tripodal ligand, tris(*N*-(*S*)-(−)-(α)-methylbenzylcarbamoylmethyl)amine ($\mathrm{H_3}\mathbf{1}^{S-\mathrm{mbz}}$).[5] Our results demonstrate that the chiral cavities formed with $\mathrm{H_3}\mathbf{1}^{S-\mathrm{mbz}}$ are flexible, leading to cavities whose structures are altered by additional ligands binding to the metal ion.



$\mathrm{H_3}\mathbf{1}^{S\text{-mbz}}$



$[\mathrm{Zn}\mathbf{1}^{S\text{-mbz}}]^-$



$[\mathrm{Fe}\mathbf{1}^{S\text{-mbz}}(\mathrm{NO})]^-$

We are interested in the interdependence between cavity structure and the coordination chemistry of a metal ion within that cavity. The chemistry of these types of metal complexes often follows from the orientation or position of external ligands within the cavity. Structural changes associated with external ligand binding within a chiral cavity can be examined with complexes of $\mathrm{H_3}\mathbf{1}^{S-\mathrm{mbz}}$ because its properties allow for the isolation of coordinately unsaturated TMP complexes. In particular, changes in cavity structure in the presence and absence of external ligands can be studied; this type of analysis is often difficult because complexes with C_3-symmetric ligands usually require additional ligands bonded to the metal ion for isolation.[1,3] $[\mathrm{Zn}\mathbf{1}^{S-\mathrm{mbz}}]^-$ was thus synthesized to investigate the structure of a chiral cavity in the absence of additional ligands.[5]

Results from NMR studies on $[\mathrm{Zn}\mathbf{1}^{S-\mathrm{mbz}}]^-$ support the presence of a symmetric chiral cavity for this complex in solution. The ^{1}H NMR spectrum of the diamagnetic $[\mathrm{Zn}\mathbf{1}^{S-\mathrm{mbz}}]^-$ contains diastereotopic methylene protons (from the tripodal arms) and a single set of resonances for the chiral methyl/benzyl moieties, consistent with the complex having 3-fold rotational symmetry. The solid-state structure of $\mathrm{K}[\mathrm{Zn}\mathbf{1}^{S-\mathrm{mbz}}]$ agrees qualitatively with this picture. The complex crystallized with two crystallographically independent, but virtually identical, anions ($[\mathrm{Zn}\mathbf{1}^{S-\mathrm{mbz}}]^-$ and $\{[\mathrm{Zn}\mathbf{1}^{S-\mathrm{mbz}}]^-\}'$).[6] Both complexes have trigonal monopyramidal coordination geometry about the zinc(II) ion. In $[\mathrm{Zn}\mathbf{1}^{S-\mathrm{mbz}}]^-$ (Figure 1), the three amidate nitrogens bind in the trigonal plane with an average $\mathrm{Zn{-}N_{amide}}$ distance of 1.980(5) Å and $\mathrm{N_{amide}{-}Zn{-}N_{amide}}$ angle of 119.2(2)°. The apical nitrogen N(4) is positioned nearly perpendicular to the trigonal plane (the average $\mathrm{N_{amide}{-}Zn{-}N(4)} = 84.9(2)°$) with a Zn−N(4) distance of 2.097(7) Å. The zinc ion lies 0.18 Å out of the trigonal plane toward the vacant axial coordination site. This site is encompassed by the appended chiral groups that orient to form a cavity walled by alternating methyl and phenyl groups. The structure of $[\mathrm{Zn}\mathbf{1}^{S-\mathrm{mbz}}]^-$ also reveals intramolecular $\mathrm{CH_3}\cdots\mathrm{Ph}$ interactions between adjacent chiral groups, with an average methyl carbon to phenyl ring centroid distance of 4.424 Å. However, the chiral substituents are not arranged symmetrically, illustrating the flexible nature of the cavity architecture. The lack of 3-fold symmetry in $[\mathrm{Zn}\mathbf{1}^{S-\mathrm{mbz}}]^-$ undoubtedly is caused by the crystal lattice,[7] where intermolecular aryl−methylene interactions are present and hinder a symmetrical arrangement of chiral groups within the complex.

The flexibility of the chiral cavity in $[\mathrm{Zn}\mathbf{1}^{S-\mathrm{mbz}}]^-$ suggests that the orientation of an external ligand upon binding to the metal ion should influence the structure of the chiral cavity. To probe this effect, $[\mathrm{Fe}\mathbf{1}^{S-\mathrm{mbz}}(\mathrm{NO})]^-$ was synthesized.[5,8] Iron nitrosyl complexes containing a $\{\mathrm{FeNO}\}^7$ moiety, such as in $[\mathrm{Fe}\mathbf{1}^{S-\mathrm{mbz}}(\mathrm{NO})]^-$,[9] are known to have variable Fe−N−O angles

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(1) Recent review: Kitajima, N.; Tolman, W. B. In *Progress in Inorganic Chemistry*; Karlin, K. D.; Ed.; Wiley: New York, 1995; p 419 and references therein.

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(4) (a) Ray, M.; Yap, G. P. A.; Rheingold, A., Borovik, A. S. *J. Chem. Soc., Chem. Commun.* **1995**, 1777. (b) Ray, M.; Golombek, A. P.; Hendrich, M. P.; Young, V. G., Jr.; Borovik, A. S. *J. Am. Chem. Soc.* **1996**, *118*, 6084.

(5) Synthesis details and characterization data for all new compounds are given in Supporting Information.

(6) $\mathrm{K}[\mathrm{Zn}\mathbf{1}^{S-\mathrm{mbz}}]$ crystallized with two crystallographically independent anions and $^1/_2$ of an $\mathrm{H_2O}$ solvate in the asymmetric unit in the monoclinic space group *C*2 with the following cell constants: $a = 28.931(6)$ Å, $b = 12.722(5)$ Å, and $c = 17.742(3)$ Å; $\beta = 101.39(2)°$; $V = 6402(3)$ Å^3, $Z = 4$. Of 7838 reflections collected ($2.02 \leq \theta \leq 21.01°$; 247(2) K), 6708 were unique data ($R_{int} = 0.0500$); R1 = 0.0596 and wR2 = 0.1537 with a GOF (F^2) = 1.0047.

(7) Both $[\mathrm{Zn}\mathbf{1}^{S-\mathrm{mbz}}]^-$ and $\{[\mathrm{Zn}\mathbf{1}^{S-\mathrm{mbz}}]^-\}'$ have three intermolecular $\mathrm{CH_2}\cdots$Ph interactions per molecule in the crystal lattice.

(8) Treating $[\mathrm{Zn}\mathbf{1}^{S-\mathrm{mbz}}]^-$ with additional ligands yields a mixture of products that could not be readily separated.

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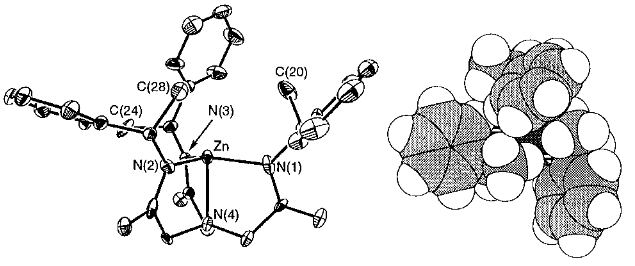

Figure 1. Thermal ellipsoid diagram of $[\mathrm{Zn}\mathbf{1}^{S\text{−mbz}}]^-$ and a space-filling representation of the complex. The ellipsoids are drawn at the 40% probability level, and hydrogens are removed for clarity. Selected bond distances (Å): Zn−N(1) = 1.973(9), Zn−N(2) = 1.987(9), Zn−N(3) = 1.981(6), Zn−N(4) = 2.097(7), C(20)···$\mathrm{Ph}_{\mathrm{N(3)}}$ = 3.533, C(24)···$\mathrm{Ph}_{\mathrm{N(2)}}$ = 5.292, C(28)···$\mathrm{Ph}_{\mathrm{N(1)}}$ = 4.446.

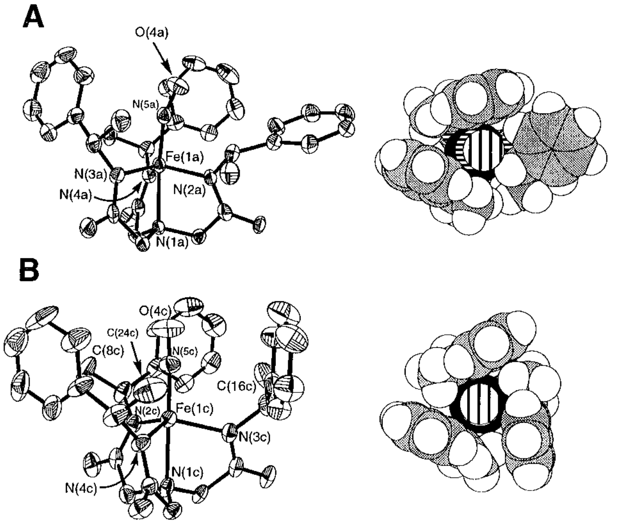

Figure 2. Thermal ellipsoid diagrams of $[\mathrm{Fe}^{(\mathbf{a})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$ (A, left) and $[\mathrm{Fe}^{(\mathbf{c})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$ (B, left) and space-filling representations of each complex. The ellipsoids are drawn at the 50% probability level, and hydrogens are removed for clarity. Selected bond distances (Å) and angles (deg): $[\mathrm{Fe}^{(\mathbf{a})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$, Fe(1a)−N(5a) = 1.745(5), Fe(1a)−N(5a)−O(1a) = 157.0(5); $[\mathrm{Fe}^{(\mathbf{c})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$, Fe(1c)−N(5c) = 1.737(5), Fe(1c)−N(5c)−O(1c) = 175.6(5), C(8c)···$\mathrm{Ph}_{\mathrm{N(4c)}}$ = 3.614, C(16c)···$\mathrm{Ph}_{\mathrm{N(2c)}}$ = 3.580, C(24c)···$\mathrm{Ph}_{\mathrm{N(3c)}}$ = 4.060.

that are responsive to the environment in which the iron nitrosyl resides.[10] We reasoned that conformational isomers may be isolated,[11] containing different Fe−N−O angles, and thus allow the examination of how cavity architecture is related to ligand orientation. Evidence for more than one mononitrosyl iron species is provided by the solid-state IR spectra of a crystalline sample of $\mathrm{K}[\mathrm{Fe}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]$, which shows three distinct NO features at 1760, 1748, and 1731 cm^{-1}.

A single-crystal X-ray diffraction study on $\mathrm{K}[\mathrm{Fe}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]$ corroborates the formation of multiple Fe−NO species. $\mathrm{K}[\mathrm{Fe}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]$ crystallized with *four* crystallographically independent complexes in the asymmetric unit.[12,13] The molecular structures for two of these complexes, $[\mathrm{Fe}^{(\mathbf{a})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$ and $[\mathrm{Fe}^{(\mathbf{c})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$ are presented in Figure 2. All the complexes have trigonal bipyramidal coordination geometry about the iron where the amidate nitrogens are arranged in the trigonal plane, and the amine nitrogens and NO moieties occupy the axial positions. Three of these complexes, $[\mathrm{Fe}^{(\mathbf{b})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$, $[\mathrm{Fe}^{(\mathbf{c})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$, and $[\mathrm{Fe}^{(\mathbf{d})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$ are structurally similar, having $\mathrm{Fe{-}N_{amide}}$ and $\mathrm{Fe{-}N_{apical}}$ distances and $\mathrm{N_{amide}{-}Fe{-}N_{amide}}$ and $\mathrm{N_{amide}{-}Fe{-}N_{apical}}$ angles that are not significantly different.[14] A major structural difference between these three complexes is in their Fe−N−O angle: $[\mathrm{Fe}^{(\mathbf{b})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$ and $[\mathrm{Fe}^{(\mathbf{d})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$ have Fe−N−O angles of 165.7(5) and 165.2(5)° whereas this angle in $[\mathrm{Fe}^{(\mathbf{c})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$ is 175.6(5)°. Each of these complexes has a nearly 3-fold symmetric chiral cavity around the nitrosyl, formed by alternating methyl and phenyl moieties of the optically active benzyl groups (the benzylic hydrogens are disposed outside the cavity toward the carbonyl groups of the tripodal amides). In addition, the intramolecular $\mathrm{CH_3}$···Ph distances in these iron nitrosyl complexes are significantly shorter than those observed in $[\mathrm{Zn}\mathbf{1}^{S\text{−mbz}}]^-$: In $[\mathrm{Fe}^{(\mathbf{c})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$, for example, the average methyl carbon to phenyl ring centroid distance is 3.751 Å (Figure 2b).[15]

The above results demonstrate that symmetric chiral cavities are formed with nearly linear Fe−NO motifs. Structurally distinct cavities are however observed when a more “bent” Fe−NO unit (smaller Fe−NO angle) is contained within the cavity. This effect is illustrated by the molecular structure of $[\mathrm{Fe}^{(\mathbf{a})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$, which has an Fe−N−O angle of 157.0(5)° and a cavity that no longer has 3-fold rotational symmetry (Figure 2b). This decrease in symmetry results from one of the appended benzyl methyl groups orienting such that the benzylic hydrogen is positioned toward the Fe−NO moiety with the phenyl-methyl groups positioned over the amidate carbonyl. Note also that the Fe−NO moiety is positioned in the direction of the benzylic hydrogen suggesting that this orientation of a chiral appended group, which leads to an enlarged cavity, is required to accommodate a nonlinear metal−ligand motif.[16]

In summary, the structural studies on $[\mathrm{Zn}\mathbf{1}^{S\text{−mbz}}]^-$ and $[\mathrm{Fe}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$ indicate that the electron-rich tripodal amidate ligand $[\mathbf{1}^{S\text{−mbz}}]^{3-}$ produces chiral cavities when coordinated to transition metal ions. The varied cavity structures exhibited by $[\mathrm{Zn}\mathbf{1}^{S\text{−mbz}}]^-$ and $[\mathrm{Fe}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$ illustrate the importance of the structural relationship between metal−ligand motifs and the architecture of chiral cavities. Utilization of these chiral systems in stereoselective processes are in progress.

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Supporting Information Available: Tables of structure determination summaries and X-ray structural data for $\mathrm{K}[\mathrm{Zn}\mathbf{1}^{S\text{−mbz}}]$ and $\mathrm{K}[\mathrm{Fe}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]$, structural diagrams of the complexes $[\mathrm{Zn}\mathbf{1}^{S\text{−mbz}}]^-$ and $[\mathrm{Fe}^{(\mathbf{b})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$, ^{1}H NMR spectra of $\mathrm{K}[\mathrm{Zn}\mathbf{1}^{S\text{−mbz}}]$, and FTIR spectra of $[\mathrm{Fe}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$ (Figures S1−S6), and synthetic details of all compounds (36 pages). Ordering information is given on any current masthead page.

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(9) Magnetic moment and EPR data are consistent with the complex having a $S = {}^3/_2$ ground state.

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(11) Modeling studies (CPK and CAChe) indicated that only mononitrosyl iron complexes can be formed with $[\mathbf{1}^{S\text{−mbz}}]^{3-}$.

(12) $\mathrm{K}[\mathrm{Fe}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]$ crystallized with four crystallographically independent anions with one DMF and diethyl ether solvate in the asymmetric unit in monoclinic space group $P2_1$ with the following cell constants: a = 11.4342(6) Å, b = 35.790(2) Å and c = 16.7595(9) Å; β = 101.39(2)°; V = 6494.7(6) Å^3, Z = 2. Of 34 504 reflections collected ($1.14 \leq \theta \leq 25.06°$; 173(2) K) 19662 were unique data (R_{int} = 0.0589); R1 = 0.0556 and wR2 = 0.1082 with a GOF (F^2) = 1.109.

(13) The four independent Fe−NO complexes in the crystal structure of $\mathrm{K}[\mathrm{Fe}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]$ are denoted $[\mathrm{Fe}^{(\mathbf{a-d})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$.

(14) Average $\mathrm{Fe{-}N_{amide}}$ (Å), average $\mathrm{N_{amide}\text{-}Fe{-}N_{amide}}$ (deg), and average $\mathrm{N_{amide}{-}Fe{-}N_{apical}}$ (deg): $[\mathrm{Fe}(\mathbf{a})\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$, 2.020(3), 116.3(1), 79.5(1); $[\mathrm{Fe}^{(\mathbf{b})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$, 2.039(3), 115.7(1), 77.8(1); $[\mathrm{Fe}^{(\mathbf{c})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$, 2.040(3), 115.3(1), 77.3(1); $[\mathrm{Fe}^{(\mathbf{d})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$, 2.048(3), 115.6(1), 77.8(1). Not significant at $P < 0.05$ using an analysis of variance test.

(15) The average methyl carbon to phenyl ring centroid distances in $[\mathrm{Fe}^{(\mathbf{b})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$ and $[\mathrm{Fe}^{(\mathbf{d})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$ are 3.938 and 4.348 Å.

(16) Solution FTIR spectra of $[\mathrm{Fe}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$ (THF, dichloroethane, $\mathrm{CH_3CN}$) show two Fe−NO bands at ca. 1710 and 1735 cm^{-1} suggesting that the bent Fe−NO motif observed in $[\mathrm{Fe}^{(\mathbf{d})}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]^-$ is present in solution. A similar two-band spectrum was observed for a powder sample of $\mathrm{K}[\mathrm{Fe}\mathbf{1}^{S\text{−mbz}}(\mathrm{NO})]$.