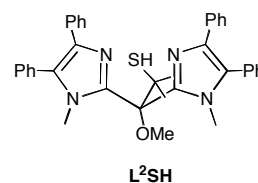
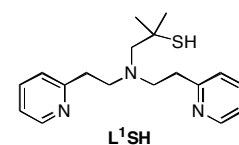


# Synthesis of N<sub>x</sub>S Ligands and their M(II) complexes Nuclearity Control, Incorporation of Bridging Hydroxide Ligands and Magnetic Behavior.

Divya Krishnamurthy<sup>1</sup>, Vivek Karambelkar<sup>1</sup>, Federico Totti<sup>2</sup>, Andrea Caneschi<sup>2</sup>, and David P. Goldberg<sup>1</sup>

<sup>1</sup>Department of Chemistry, Johns Hopkins University, <sup>2</sup>Dipartimento di Chimica e UdR INSTM di Firenze.

Mixed nitrogen/thiolate donor sets are common to the active sites of the mononuclear iron enzymes peptide deformylase, superoxide reductase, and nitrile hydratase. In order to synthesize structural and functional model complexes of these systems, polydentate N<sub>x</sub>S<sub>y</sub>(thiolate) ligands need to be developed. A number of new iron(II) and zinc(II) complexes have been prepared using tetradentate N<sub>3</sub>S(thiolate) (L<sup>1</sup>SH) and tridentate N<sub>2</sub>S(thiolate) (L<sup>2</sup>SH) ligands, and their structural and spectroscopic properties will be described. In particular, synthetic efforts have been directed toward preparing metal-hydroxide species with the goal of preparing models of peptide deformylase (PDF). PDF likely employs an Fe(II)-OH unit as the active nucleophile in the hydrolysis of formylated substrates. We have used the ligand L<sup>1</sup>SH to synthesize four iron(II) complexes: (L<sup>1</sup>S)FeCl (**1**), (L<sup>1</sup>S)FeBr (**2**), [(L<sup>1</sup>S)<sub>4</sub>Fe<sup>II</sup><sub>5</sub>(μ-OH)<sub>2</sub>](BF<sub>4</sub>)<sub>4</sub> (**3**), and [(L<sup>1</sup>S)<sub>2</sub>Fe<sup>II</sup><sub>2</sub>(μ-OH)](BF<sub>4</sub>) (**4**).<sup>[1]</sup> Control over the production of **3** or **4**, and hence over the nuclearity of these complexes, was accomplished by changing the ligand-to-metal stoichiometry. The magnetic properties of these complexes will be presented. In addition, the new sterically encumbered imidazole-based ligand L<sup>2</sup>SH<sup>[2],[3]</sup> was synthesized and employed in the synthesis of the zinc complexes (L<sup>2</sup>S)ZnMe (**5**) and [(L<sup>2</sup>S)<sub>2</sub>Zn<sub>2</sub>(μ-OH)]X, where X = BF<sub>4</sub>, triflate, (**6**). Reaction of (L<sup>2</sup>S)ZnMe with strong acid in acetonitrile gives the μ-hydroxide complex [(Im<sub>2</sub>S)<sub>2</sub>Zn<sub>2</sub>(μ-OH)]X. Together these results reveal new synthetic methods for incorporating hydroxide ligands into the coordination sphere of zinc(II) and iron(II).



- [1] Divya Krishnamurthy, Amy Sarjeant, David P. Goldberg, Andrea Caneschi, Federico Totti, Lev N. Zakharov, and Arnold L. Rheingold *Chem-A Eur. J.* submitted
- [2] Karambelkar, V. V.; Krishnamurthy, D.; Stern, C. L.; Zakharov, L. N.; Rheingold, A. L.; Goldberg, D. P. *Chem. Commun.* **2002**, 2772-2773.
- [3] Karambelkar, V. V.; diTargiani, R. C.; Incarvito, C. D.; Zakharov, L. N.; Rheingold, A. L.; Stern, C. L.; Goldberg, D. P. *Polyhedron* **2004**, 23, 471-480.