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Dissertation Defense

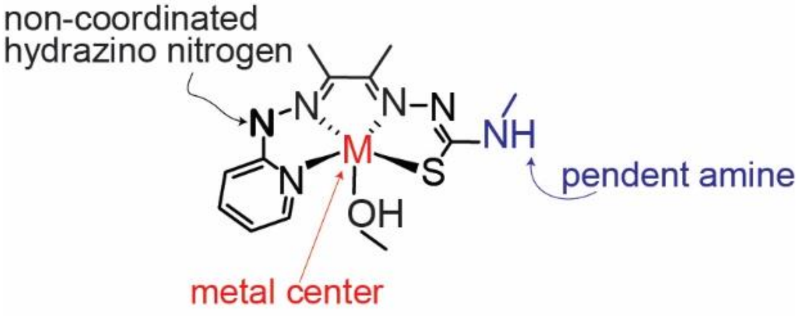
When: March 28, 2024
Time: 9:30 AM
Location: SRB, Room 139

Utilizing Metal Ligand Cooperativity to Activate Small Molecules

ABSTRACT:

The excessive use of fossil fuels since the Industrial Revolution has led to the buildup of carbon dioxide (CO_2) in the atmosphere and current alternatives to fossil fuel are too expensive for large scale use.[1] This problem can be approached from two directions: capture the CO_2 from the atmosphere or develop alternative energy sources. The current industrial standards for these are environmental and/or health hazards and utilize precious metals, respectively. Metal ligand cooperativity (MLC) has emerged as a promising alternative to using precious metals to activate small molecules.[2] In MLC, the ligand acts to confer nobility onto the transition metal (usually first row) which lowers the activation energy making small molecule activation thermodynamically feasible.[3]

In this talk, we focus on a series of metal complexes based on the ligand diacetyl-2-(4-methyl-thiosemicarbazone)-3-(2-hydrazinopyridine) (H_2L^1) for CO_2 capture.[4] The structure of the ligand is an important part of the talk. The non-coordinated hydrazinato nitrogen acts as a BrØnsted base, which is quantified for all complexes in this talk in methanol. The metal center acts as a Lewis acid and together the metal and ligand are analogous to a frustrated Lewis pair (FLP). The Co(III), Ni(II), Pd(II), Cu(II), and Zn(II) complexes of H_2L^1 were studied for CO_2 capture and only the Cu(II) and Zn(II) complexes showed CO_2 chemistry by UV-Visible spectroscopy and ^{1}H NMR. Interestingly, the Zn(II) complexes capture dilute CO_2 from the atmosphere and the pendent amine was systematically changed to understand how the pendent amine influences CO_2 chemistry. The CO_2 equilibrium constant is quantified and used to extrapolate the metal Lewis acidity.



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2. Elsby, M. R.; Baker, R. T., Strategies and mechanisms of metal–ligand cooperativity in first-row transition metal complex catalysts. *Chem. Soc. Rev.* **2020,** *49*, 8933-8987.
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4. Phipps, C. A.; Hofsommer, D. T.; Zirilli, C. D.; Duff, B. G.; Mashuta, M. S.; Buchanan, R. M.; Grapperhaus, C. A., Metal–Ligand Cooperativity Promotes Reversible Capture of Dilute CO2 as a Zn(II)-Methylcarbonate. *Inorg. Chem.* **2023,** *62*, 2751-2759.