

University of Louisville
Department of Chemistry

Christine Burgan Research Seminar

When: January 19, 2022

Time: 2:30 p.m.

Location: CBL-16

Metal-ligand cooperativity for small molecule activation

Abstract:

Metal-ligand cooperativity is a promising alternative to using platinum-group metals for small molecule activation. In metal-ligand cooperativity, the ligand acts to confer nobility onto the transition metal lowering activation energies and improving activity.¹ Redox non-innocent ligands are one strategy of metal-ligand cooperativity and was studied using Ni(II) and Pd(II) complexes of diacetyl-2-(4-methylthiosemicarbazone)-3-(2-hydrazinopyridine); NiL¹, PdL¹. Both NiL¹ and PdL¹ were fully characterized as d⁸, square planar metal complexes. The non-aqueous p*K*_{a,MeCN} of NiL¹ and PdL¹ were determined spectrophotometrically to be 12.71 and 13.03, respectively.² Both complexes catalyze the hydrogen evolution reaction with a Faradaic efficiency of 90-95% and reach a max TOF with triethylammonium tetrafluoroborate of 6150 s⁻¹ and 8280 s⁻¹ for NiL¹ and PdL¹, respectively.

The Zn(II) complex, ZnL¹, is active for both the hydrogen evolution reaction and can capture CO₂ from dilute sources in methanol utilizing metal-ligand cooperativity.^{3,4} Zn(II) acts as a Lewis acid and utilizes the Bronsted-Lowrey basic non-coordinated hydrazino-nitrogen to concomitantly drive CO₂ capture from air. The CO₂ capture ability of the system was further investigated by changing the metal center and modification of the ligand and we found that CuL¹(MeOH), ZnL¹(MeOH), ZnL²(MeOH), ZnL³(MeOH), and ZnL⁴(MeOH) were active for CO₂ capture. The equilibrium constant for CO₂ capture increases from 88 ± 9 to 35,000 ± 200 moving across the series. Quantification of ligand basicity and metal ion Lewis acidity show that changes in CO₂ capture affinity are largely associated with ligand basicity upon substitution of Cu(II) with Zn(II), while variation of the thiosemicarbazone ligand enhances CO₂ affinity by tuning the metal ion Lewis acidity. Overall, the Zn(II) complexes effectively capture CO₂ from dilute sources with up to 90%, 86%, and 65% CO₂ capture efficiency from 400 ppm, 1000 ppm, and 2500 ppm CO₂ streams.

References:

1. 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.
2. Phipps, C. A.; Hofsommer, D. T.; Toda, M. J.; Nkurunziza, F.; Shah, B.; Spurgeon, J. M.; Kozlowski, P. M.; Buchanan, R. M.; Grapperhaus, C. A., Ligand-Centered Hydrogen Evolution with Ni(II) and Pd(II)DMTH. *Inorg. Chem.* **2022**, *61*, 9792-9800.
3. Cronin, S. P.; Mamun, A. A.; Toda, M. J.; Mashuta, M. S.; Losovyj, Y.; Kozlowski, P. M.; Buchanan, R. M.; Grapperhaus, C. A., Utilizing Charge Effects and Minimizing Intramolecular Proton Rearrangement to Improve the Overpotential of a Thiosemicarbazonato Zinc HER Catalyst. *Inorg. Chem.* **2019**, *58*, 12986-12997.
4. Cronin, S. P.; Strain, J. M.; Mashuta, M. S.; Spurgeon, J. M.; Buchanan, R. M.; Grapperhaus, C. A., Exploiting Metal–Ligand Cooperativity to Sequester, Activate, and Reduce Atmospheric Carbon Dioxide with a Neutral Zinc Complex. *Inorg. Chem.* **2020**, *59*, 4835-4841.