Chemical and Electrochemical Studies of Heterobimetallic Complexes and Catalysts

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Metals are involved in many aspects of contemporary energy production and utilization. Thus, an important area of current research in inorganic chemistry is focused on understanding and controlling the properties of metal-containing molecules and materials, so that their behavior can be harnessed for more efficient and effective reactivity. However, relatively few methods are available to quantitatively tune individual metal sites, leading to difficulties in rational design of technologies that deal with metals.

One project in the Blakemore Group is examining use of specialized molecules that can bind multiple metals. One metal center is typically a redox-active transition metal or f-element, which is targeted for tuning by incorporation into the specialized ligand. The second metal is chosen from among a set of commonly available, redox-inactive metal ions. Once prepared, studies of these so-called heterobimetallic compounds (compounds containing two different metals) are undertaken to reveal the properties of the assembly. Since there are a variety of redox-inactive metals available for study, incorporation of targeted choice metals gives a tunable site. Of specific interest is the correlation between the Lewis acidity of the redox-inactive metal and the reduction potential of the redox-active metal. Through such studies, free energy relationships and changes in structure and reactivity can be understood as a function of the quantified Lewis acidity of the redox-inactive ion.

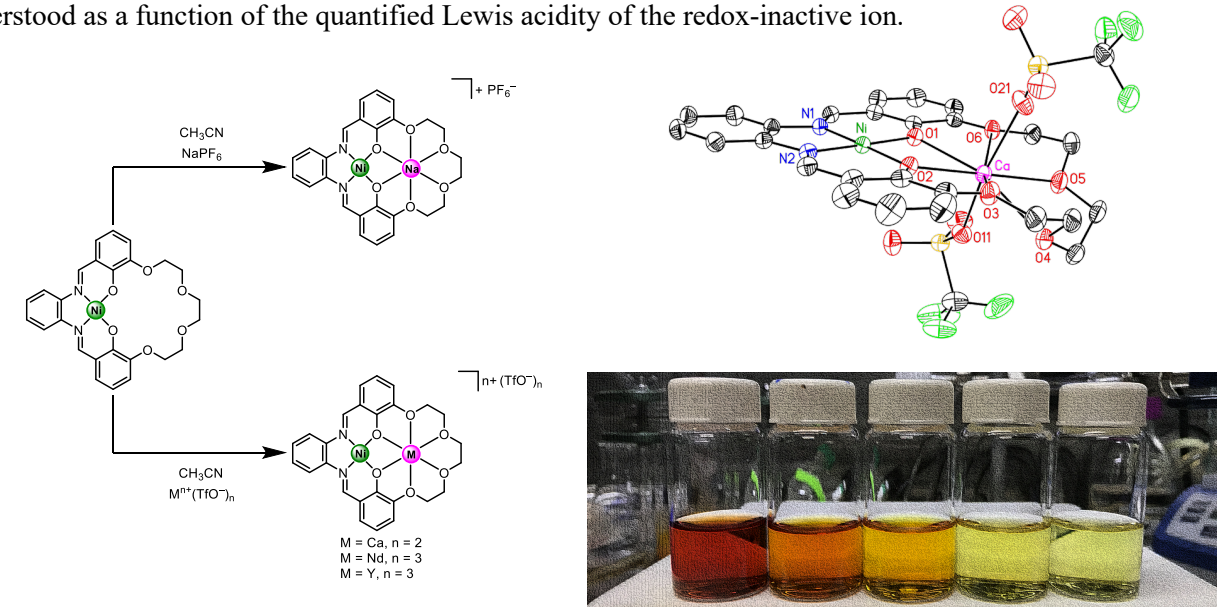

Figure shows the synthetic route for preparation of new nickel compounds, a sample structure from X-ray crystallographic studies, and a photo showing color change as a function of Lewis acidity.

In order to carry out these experiments, REU students working in the Blakemore Lab are mentored in the needed experimental techniques. These include handling of air- and moisture-sensitive reagents, enabled by use of Schlenk lines, inert-atmosphere gloveboxes, and custom-made glassware. Students are also trained in hands-on use of more advanced equipment available at KU, including EPR spectroscopy, electrochemistry, and photochemical apparatus, in order to study the reactivity of the new compounds prepared by the students.

Lead references to recently published articles:

1. Kumar, Blakemore,* *et al.*, *Chem. Eur. J.,* **2018**, *24*, 141-149, doi: 10.1002/chem.201704006
2. Moore, Blakemore,* *et al.*, *Molecules*, **2018**, *23*, 2857; doi: 10.3390/molecules23112857