Synthesis and Characterization of Enamine- and Schiff-Base Metal Complexes

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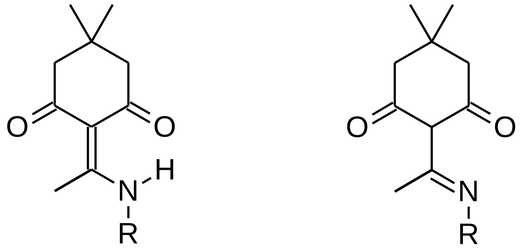
Abstract

Enamine- and Schiff-Base metal complexes have shown the potential to be catalysts in oxidation-reduction reactions. To model these potential catalytic abilities, acetylacetone and 2-acetyldimedone were used to prepare enamine- and Schiff-Base metal complexes. Preliminary characterization of the ligands and metal complexes was carried out using infrared spectroscopy and cyclic voltammetry. Cyclic voltammetry of [Mn(acacen)Cl] revealed an irreversible oxidation-reduction couple. The relative energies of the singlet, triplet, and quintet states of [Mn(acacen)Cl] and [Mn(dimedone-en)Cl] were calculated. Based on these calculations, the quintet spin states of both complexes have the lowest relative energies.

Future work will include further purification of the Mn(III) and Fe(III) complexes and the eventual testing of their catalytic capabilities.

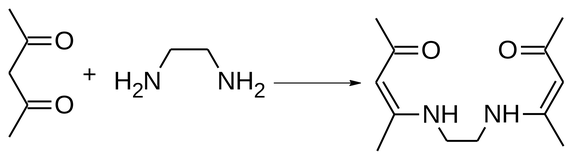
Enamine- vs. Schiff-Base



Enamine Schiff-Base

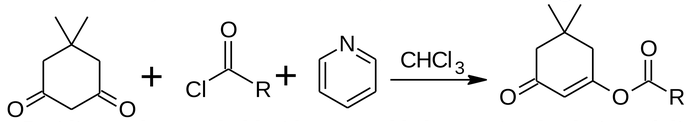
A structural comparison of the enamine form to the Schiff-Base form. Both the acacen and dde-en ligands favor the enamine tautomeric form.

Synthesis of Acacen Ligand



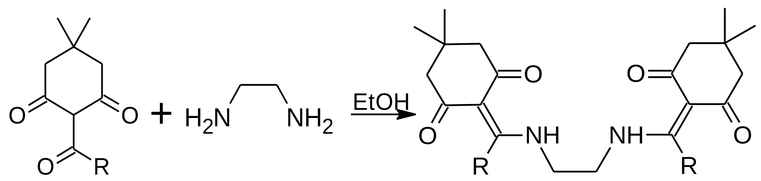
Ethylenediamine was slowly added to acetylacetone. The acacen ligand was purified by recrystallization from hot water.

Synthesis of 2-Acetyldimedone Ligand



Pyridine and an acyl chloride were added to a stirred solution of dimedone in chloroform to yield enol ester.

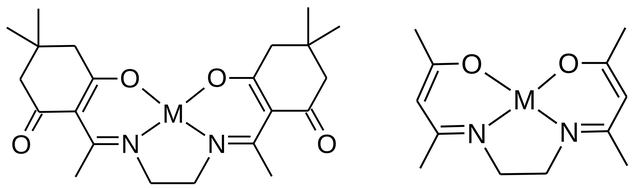
Enol ester was added to a stirred solution of aluminum chloride in 1,2-dichloroethane to yield 2-acetyldimedone.



2-acetyldimedone was dissolved in ethanol and ethylenediamine was added to yield the 2-acetyldimedoneethylenediamine (dde-en) product.

This project focused on R=methyl products but R=aryl compounds were also synthesized successfully.

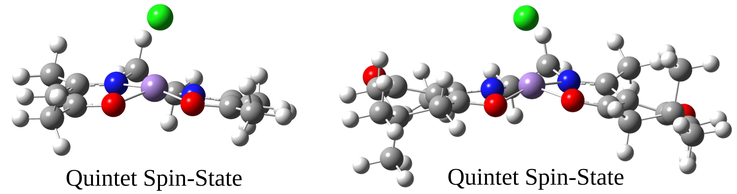
Synthesis of Metal Complexes



Ni(II) complexes can be synthesized from Ni(II) acetate. Fe(III) and Mn(III) complexes required the use of triethylamine as the base and the metal in the form of a chloride salt.

Computational Data

[Mn(acacen)Cl] [Mn(dde-en)Cl]



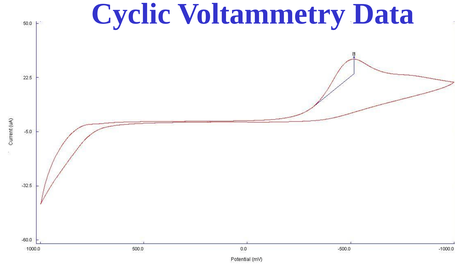
Quintet Spin-State E=0 Quintet Spin-State E=0

Triplet Spin-State E=+22.3 Triplet Spin-State E=+22.4

Singlet Spin-State E=+52.7 Singlet Spin-State E=+46.9

All energies are in kcal/mole and calculated by Density Functional Theory (DFT) at the B3LYP/ LanL2DZ/gas level.

Cyclic Voltammetry Data



The cyclic voltammogram of 1mM [Mn(acacen)Cl] in 0.1M NBu_4BF_4 DMF. Peak cathodic current shown at 7.4µA and peak cathodic potential at -520mV, giving an irreversible oxidation-reduction couple.