Influence of substitution on the pyridine ring within NNN-type pincer molecules

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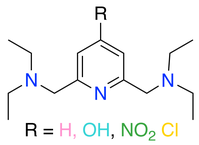
Abstract

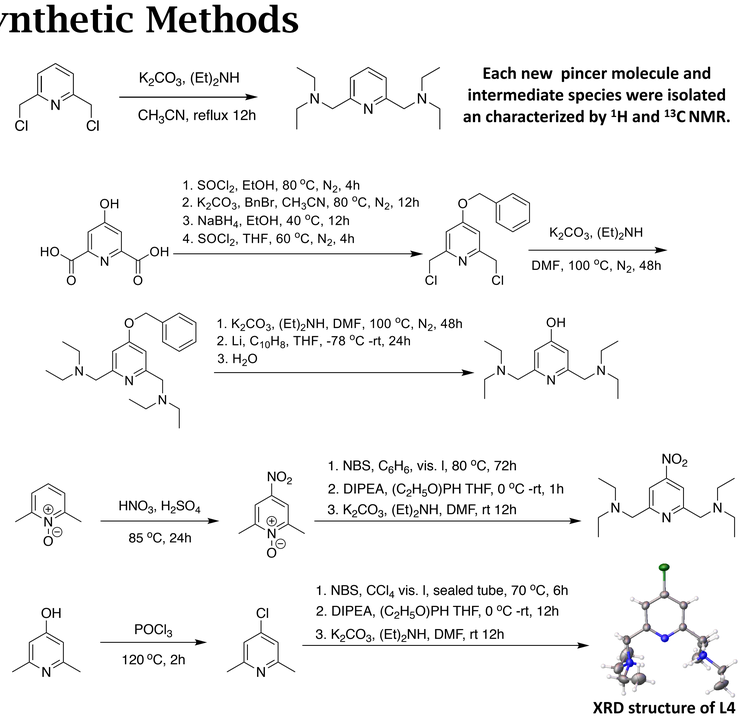
Pincer type ligands are of increasing interest due to the planarity and open coordination sites available when bound to a metal-ion. A range of pincer type molecules are known, including those with a X-N-X arrangement, where X=P, N, C, or other donor atoms. Often times the central N-atom in this arrangement is derived from a pyridine ring. Many studies have been conducted regarding the electronic nature of the two appendage arms (X), but little has been explored with electronic modifications of the central pyridine moiety. In order to fully understand the implications of such modifications and potential applications of these molecules, functional groups with different electronic properties were attached to 4-position of the aromatic ring of a N-N-N type pincer. Synthesis and characterization of these new ligands and the corresponding copper complexes is well underway. Synthetic methods, DFT, and representative examples of characterization are presented here.

Goals

1. Synthesize pincers and metalate with copper(II) salts
2. Determine connectivity with XRD
3. Examine redox behavior with DFT analysis



Synthetic Methods



Each new pincer molecule and intermediate species were isolated an characterized by ^{1}H and ^{13}C NMR.

XRD structure of L4

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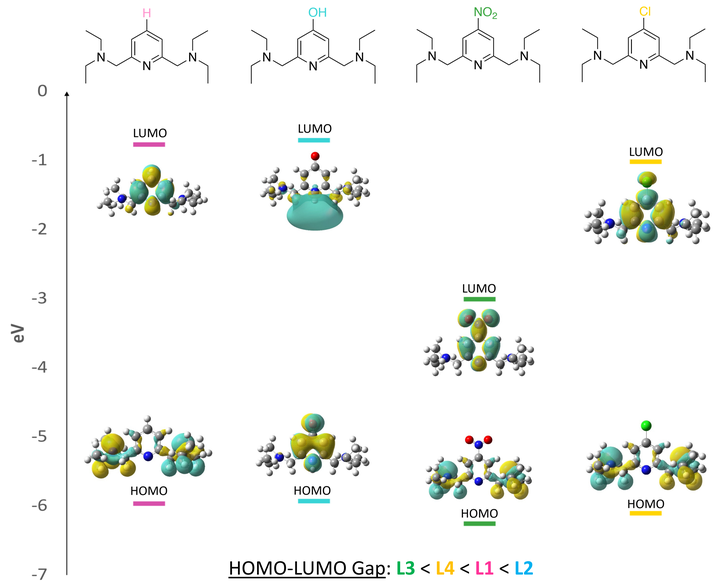
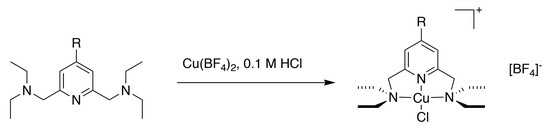
Pincer Frontier Molecular Orbitals



HOMO-LUMO Gap: L3 < L4 < L1 < L2

DFT Method: B3LYP 6-31 ++ g(d,p)

Synthesis of Cu(II) complexes



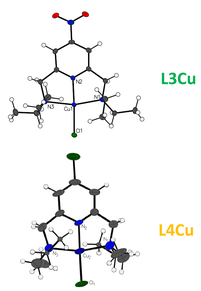
L1Cu, (H); L2Cu, (OH); L3Cu, (NO_2); L4Cu, (Cl)

XRD Structures

X-ray quality crystals were prepared using vapor diffusion methods, in order to examine connectivity.

Selected bond lengths (Å)	L3Cu	L4Cu
N1-Cu	2.128	2.083
N2-Cu	1.945	1.903
N3-Cu	2.125	2.079

Selected bond angles (°)	L3Cu	L4Cu
N1-Cu-N3	157.4	164.0
N2-Cu-Cl	175.0	178.5



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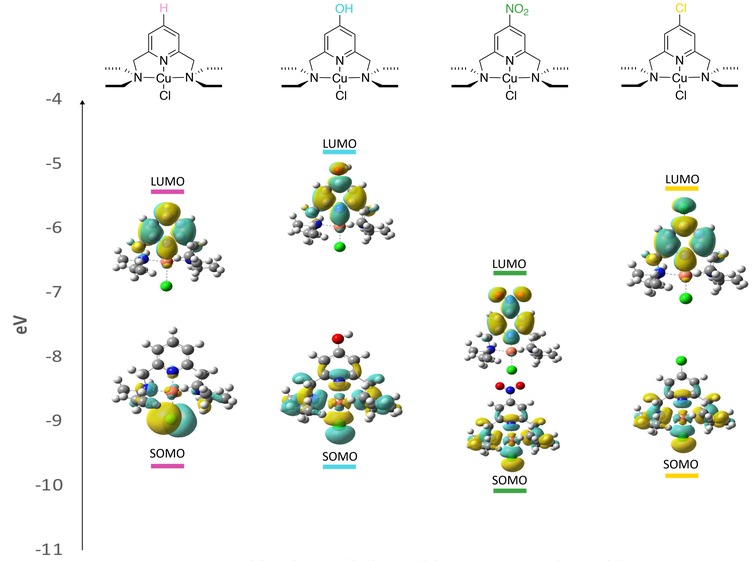
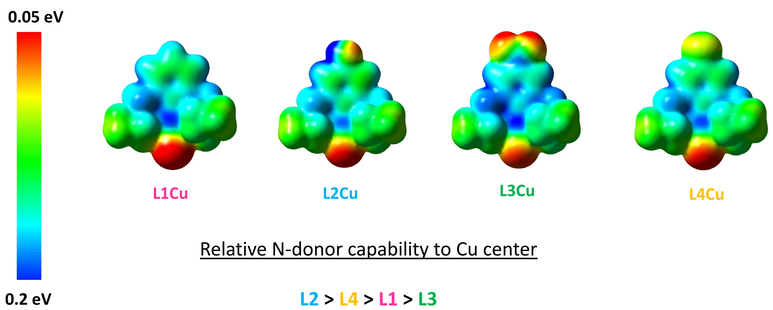
Cu-complex Frontier Molecular Orbitals



SOMO-LUMO Gap: L3Cu < L4Cu < L1Cu < L2Cu

DFT Method: B3LYP 6-31 ++ g(d,p)

Electrostatic Potential Maps



Relative N-donor capability to Cu center

L2 > L4 > L1 > L3

DFT Method: B3LYP 6-31 ++ g(d,p)

Conclusions

1. Measurable differences are observed between ligands with electron withdrawing and donating groups.
2. NO_2 substitution (**L3**) results in a smaller HOMO-LUMO gap, suggesting non-innocent redox ligand behavior, confirmed through through previously conducted electrochemistry experiments.
3. Stronger Cu-N bonds are observed with pyridine substitution via electron donating moieties.

Future Work

1. Study redox behavior through electrochemistry experiments.
2. Characterize pincer library with other metal centers.
3. Make changes to the pincer arms while preserving modification to the pyridine ring.