

STEREODYNAMIC COORDINATION COMPLEXES

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We have shown that certain metal ion complexes of tripodal ligands exhibiting conformational enantiomerism can be biased to adopt single enantiomer, propeller-like structures when a chiral center is incorporated into the ligand scaffold.¹ Since the ligand conformation is fluxional and dependent upon metal ion coordination, circular dichroism spectra of the ligand are highly dependent upon the identity and oxidation state of the metal ion, as well as on the coordination of counter ions of varied size and shape. Several coordination complexes have been prepared and studied in order to prototype novel strategies for the development of metal ion sensors² and redox-switched chiroptical materials.³⁻⁵

Alkylation of amino acids with bromomethylquinoline followed by addition of copper salts results in complexes whose circular dichroism spectra can be used to assign the absolute configuration of the starting amino acid (Figure 1). Recently, the methodology was extended to be applicable to nearly any primary amine.⁶

These studies subsequently led to the observation of redox-induced inversion of helicity in Cu(I) and Cu(II) complexes of derivatives of amino acids and amino alcohols with two N-atom appended chromophores. Upon one-electron oxidation/reduction, the complexes display mirror image circular dichroism spectra. The unique chiroptical properties arise from an inversion of the orientation of the appended chromophores. The change in oxidation state induces an intramolecular ligand exchange event that, in turn, inverts the propeller-like orientation of the three coordinated ligand arms through a gearing mechanism (Figure 2). Thus, an electrochemical event induces an inversion of a element of helical chirality in the molecule.³

Incorporation of chromophores that absorb at longer wavelength would increase the potential utility of this unique chemistry and would facilitate some of the physical characterization studies. This presentation will describe preliminary results from studies of complexes similar to those shown in Figures 1 and 2 that include porphyrins as chromophores.

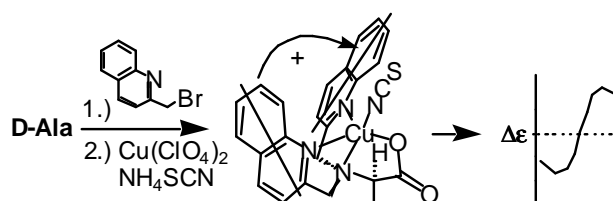


Figure 1. Derivatization of D-alanine followed by addition of a copper salt gives a complex whose absolute configuration can be assigned by analysis of its circular dichroism spectrum.

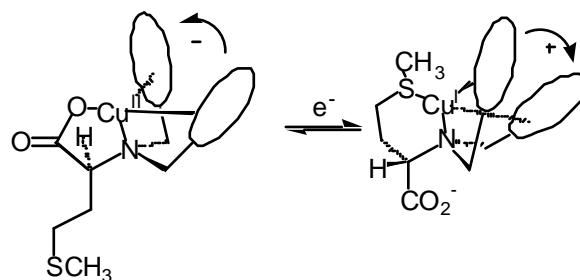


Figure 2. Derivatives of methionine form carboxylate-coordinated complexes with Cu(II), but sulfide-coordinated complexes with Cu(I). Certain chromophores result in characteristic changes in the circular dichroism spectra of these complexes.

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