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Photochemical Activation and Reactivity
of Polynuclear Transition Metal Complex Molecules

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Abstract

During this contract year several new ligands and binuclear metal complexes have been prepared including many that can be expected to exhibit long-lived excited states. The metal ions represented are Cu(II), Ni(II), Co(II), Mn(II), Cr(III), Ti(IV), V(IV), U(VI), and Pd(II). In addition, many mononuclear complexes that are precursors in the formation of heterobinuclear complexes were prepared. These include complexes of Cu(II), Ni(II), Pd(II) and Ru(II). Many of these compounds will be used in photochemical and electron transfer studies.

Polarographic, cyclic voltammetric and coulometric studies have been carried out on a number of binuclear Cu(II) triketonates and their Schiff-base derivatives. Most of these compounds undergo reversible or quasi-reversible two electron transfer reactions which makes them potentially useful electron transfer reagents. Much of the electrochemical data can be rationalized by the formation of dimers which are new electroactive species. The importance of such species in multi-electron transfer processes is being investigated.

Work on this project to date has proceeded along two paths. The first path involves the synthesis of new polynucleating ligands and polynuclear transition metal complexes with special attention to complexes that (1) exhibit multi-electron transfer reactions, (2) can be expected to have long-lived excited states, and/or (3) are capable of efficiently absorbing light in the visible region. The second path is the electrochemical investigation of multi-electron transfer reactions of polynuclear transition metal complexes.

I. SYNTHESIS

Several new polynucleating ligands have been prepared and from them new metal complexes with potentially interesting redox and photochemical properties. The metal ions represented in this group of new complexes are Cu(II), Ni(II), Co(II), Mn(II), Cr(III), Ti(IV), VO^{2+} , UO_2^{2+} , Pd(II), and Ru(II). Some specific examples including mononuclear complexes that are useful precursors to binuclear complexes are discussed below.

a. Binuclear Triketonates.

In these cases, with the exception of Cr(III), each metal ion can be expected to undergo an oxidation state change of two upon oxidation or reduction. Therefore, the binuclear molecule may well be reducible or oxidizable by

four electrons, giving rise to interesting electron transfer possibilities and reactive species. In addition, some of these complexes may be expected to have long-lived excited states by analogy to mononuclear compounds.

b. Heterobinuclear Complexes and Their Mononuclear Precursors.

We continue to be very interested in the properties of heterobinuclear complexes of the type shown above. In this regard, preparation and characterization of the mononuclear precursors is an important first step. These mononuclear complexes will be used as ligands and a second metal ion will be added.

c. Schiff-base and Macrocyclic Complexes.

These ligands and others like them (containing different amines and diamines) furnish an unusual environment for the metal centers which will influence their excited state properties and reactivity. The mononuclear macrocyclics will be used to add a second metal ion (either the same metal or different) yielding binuclear macrocyclics.

d. Binuclear Complexes with Fused Ring Ligands

These complexes are extremely intensely colored. The anthraquinone derivatives all have absorptions in the 500-600 nm region with extinction coefficients of more than $10^4 \text{ (M}^{-1} \text{ cm}^{-1})$. When solubility problems are solved these compounds are excellent candidates for photo-initiated electron transfer reagents.

The synthetic procedures developed for the ligands and complexes allow us to prepare a large variety of binuclear complexes. These techniques should furnish us with the compounds necessary to proceed to the next stages of the project.

II. Multi-electron Transfer in Binuclear Complexes.

A number of binuclear Cu(II) have been electrochemically investigated since our original observation that they are capable of a reversible, sequential two electron transfer at a single potential.^{1,2} In addition, a study of the temperature dependence of the electron transfer process has begun. The initial result shows that throughout the temperature range -30 to 80°C the nature of the sequential transfer of two electrons does not change. The only change in the cyclic voltammogram is a linear shift of $E_{1/2}$ with temperature. Thus, in the sequential transfer

the two steps do not appear to be separated by any significant entropy differences.

Several binuclear complexes, many of which are Schiff-base derivatives of the triketonates, have been electrochemically investigated.³ Most of these compounds are well behaved showing a high degree of reversibility. However, often the information about the number of electrons transferred from polarography and coulometry is not consistent. In addition, the cyclic voltammograms of freshly prepared solutions of several compounds contain two waves, the more negative of which decreases with time while the more positive wave grows. The former completely disappears in time. Thus, the two electroactive species are in equilibrium. Associated with the final, stable species is a CV wave characteristic of a two-electron transfer. These results can be explained if the electroactive species is actually a dimer of binuclear molecules. The formation of dimers would explain the equilibrium in the CV. They would give polarographic

diffusion constants consistent with two-electron transfer which is observed in the controlled potential electrolysis experiment. The possibility that such phenomena are important in multi-electron transfer at a single potential has ramifications for the design of reagents useful in multi-electron transfer reactions.

Another aspect of the electron transfer study is to determine the effect of the ligands on the reduction potentials. Understanding the ligand's role will allow one to design compounds with redox potentials in useful regions of the potential range. This will ultimately be important in excited state reactivity and in ground state electron transfer reactions. Our initial discussion of this topic has recently been published (preprint attached).

Bibliographic References

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III. Statement of Activity

During the summer of 1979, Professors Endicott and Lintvedt each spent one man month on the project. Dr. Peter Roder completed one year on the project, October 1, 1978 - September 30, 1979. During this time he was concerned mainly with synthetic problems. James Wishart, an undergraduate, spent three months during the summer of 1979 on this project doing synthesis and electrochemistry. Dr. L. Ramakrishnan joined the group as a post-doctoral fellow on Dec. 1, 1979. Dr. Nasir Ahmed on leave from the University of Islamabad, Pakistan began

working on the project Jan. 15, 1980. Offers were made to both of these people earlier in the contract year, but for personal and professional reasons they were unable to begin work until the dates indicated. For the remainder of the contract year, both will continue to spend 100% of their time on the project. A technician has worked part time on the project.

Professors Endicott and Lintvedt will continue to allot 12.5% of their efforts to this work which is a contribution supported by the University.