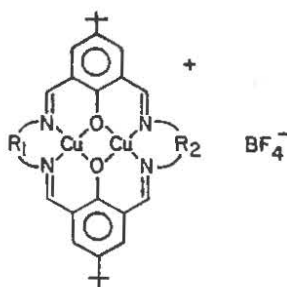


The properties of mixed-valence complexes have been of interest to experimental and theoretical researchers for a considerable period of time [1-4]. Recently, it has been pointed out that the need is still present to expand the theoretical models in order to more thoroughly understand the experimental results [5]. Another approach is the one employed here, where physical measurements are used to more thoroughly examine the properties of a particular class of mixed-valence complexes. This approach involves finding a particular class of mixed-valence complexes that have dynamical behavior on the timescale of a particular spectroscopic technique and then to introduce perturbations in the ligation of these complexes that will alter their observed dynamical behavior.

Slight perturbations have been imposed on the Robson macrocyclic ligand [6]. Gagné, *et al.* [7] have shown that the mixed-valence copper(II)-copper(I) complex of this ligand exhibits dynamical behavior on the epr timescale. This complex exhibited epr delocalized behavior at room temperature and localized behavior at 175 K. The complexes used in this work [8] are similar to that used in Gagné's, except that *t*-butyl groups have replaced the methyl groups para to the phenolic oxygen and the diimine linkages were altered throughout the series of complexes, shown below:



- I. $R_1=R_2$ =PROPYLENE
- II. $R_1=R_2$ =2,2'-DIMETHYLPROPYLENE
- III. $R_1=R_2$ =BUTYLENE
- IV. $R_1=R_2$ =2,2'-BIPHENYLENE
- V. R_1 =PROPYLENE; R_2 =2,2'-DIMETHYLPROPYLENE
- VI. R_1 =PROPYLENE; R_2 =2,2'-BIPHENYLENE
- VII. R_1 =PROPYLENE; R_2 =BUTYLENE
- VIII. $R_1=R_2$ =2-HYDROXYPROPYLENE
- IX. $R_1=R_2$ =1,3-CYCLOHEXYLENE
- X. R_1 =PROPYLENE; R_2 =1,8-NAPHTHALENE
- XI. R_1 =PROPYLENE; R_2 =2-HYDROXYPROPYLENE

The binuclear copper(II) complexes were prepared via metal template synthetic routes and mixed-valence complexes were obtained by reducing the binuclear copper(II) complexes with sodium dithionite.

Complexes I, II, III, IV and IX were prepared to impose steric constraints upon the ligation system, without altering the electronic interaction between the metal centers. A transition from epr delocalized to epr localized behavior occurs for complexes I, II and III in solution. The transition temperature, that is, where the change from delocalized to localized behavior occurs, varied for these three complexes in increasing order; I, II and III. Invoking a coalescence model provided electron transfer rates at room temperature for these mixed-valence complexes, which increased in the same order. Complexes IV and IX possessed localized epr spectra at all temperatures. Results obtained from electrochemical, epr and electronic absorption measurements indicated that the copper(II) centers in complexes I, II and IX have an approximately square planar geometry, while the copper(II) sites in complexes III and IV are distorted somewhat from this geometry. Since copper(II) ions prefer a planar geometry, it is thought that the possession of non-planar geometric sites in these two complexes indicates considerable steric inflexibility, which will lead to slower rates of electron transfer. Complexes II and IX have slower rates of electron transfer when compared to complex I, which is probably caused by the greater bulkiness found in the ligands of II and IX. Spectroscopic properties indicate approximately constant electronic coupling in this series of complexes. The theoretical analyses of the intravalence electron transfer bands for these complexes do not correlate well with the electron transfer rates obtained from the epr measurements.

Complexes V, VI, VII and X were synthesized to obtain asymmetric mixed-valence complexes, where electron transfer should be slower. Complexes VI, VII and X were totally localized in solution at all temperatures on the epr timescale. Complex V exhibited the dynamical behavior of complex II and this was not very surprising since its symmetric analogs, I and II, were very similar in their physical properties. Frozen solution epr studies on complexes VI and VII indicated that the unpaired electron in these complexes is localized on the propylene site. The location of the unpaired electron is yet to be determined for complex X.

Complexes VIII and XI and complex XII, the complex identical to complex III except that its imine groups are reduced to amine groups, were prepared in order to alter the electronic interactions present in these complexes. Complexes VIII and XI were generally very similar in their physical properties when compared to complex I. The reduced ligand complex XII exhibited large differences in its physical properties over those observed for complex III. This complex has very slow rates of electron transfer as indicated by its epr spectra and IT band.

The magnetic exchange interactions for the binuclear copper(II) complexes indicate that the electronic coupling is relatively constant in these complexes. Typically, values between -380 and -480 cm^{-1} were recorded for the magnetic exchange coupling term, J , for these

complexes. The large values indicate a strong magnetic exchange interaction and thus strong electronic coupling. Complexes III, X and XII has reduced magnetic exchange coupling terms, in that order, in comparison to the other complexes.

Finally, the best description for determining when the transition from delocalized to localized behavior occurs using epr spectroscopy has not been decided upon as yet. Therefore, the epr spectra and the transition phenomenon in general need to be analyzed further.

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