

Mössbauer and Structural Studies:  
Characterization of Mixed-Valence Biferrocenes and Iron-Semiquinone Complexes

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Mixed-valence and spin-coupled systems owe their seeming ubiquity in biological reaction centers and molecular metals (both conducting and magnetic) to their ability to undergo electron transfer and magnetic exchange processes, respectively. In order to understand the fundamental nature of these processes and ultimately, to design molecules which utilize these processes in attaining desired properties, the determination of the electronic structure of these systems and related inorganic and organometallic compounds has been of continuing interest [1-3].

Mössbauer spectroscopy both with and without an applied magnetic field was found to be useful in characterizing the electronic ground state for a number of mixed-valence biferrocene-type compounds and iron complexes with *o*-quinone derived ligands. Possible pathways for electron transfer and magnetic exchange interactions were indicated by determining the amount of unpaired spin actually at the iron sites in these compounds.

The magnetic hyperfine properties of four spin-coupled *o*-semiquinone ( $S=1/2$ ) complexes were studied with high magnetic field Mössbauer spectroscopy and compared to a closely related high-spin ferric ( $S=5/2$ ) complex. The number of unpaired electrons found from magnetic susceptibility studies correlates linearly with the hyperfine interaction, while the magnitude and sign indicates a primarily Fermi-contact interaction. By using a vector coupling approach to find the hyperfine interaction at the component high-spin ferric ion of each exchange coupled unit, good agreement was found between these values and that of the related high spin ferric complex in this study and others in similar environments. These compounds appear to be best formulated as having high-spin ferric ions strongly coupled with semiquinone ligands and having little or no covalency.

The small internal field found at the iron(III) ion in the mixed-valence biferrocenium cation was found to be a result of spin-relaxation effects rather than the "unpaired electron resides in an orbital of predominantly ligand character" as previously suggested [4]. The effective magnetic field at a number of ferrocenium salts (which relaxed at rates either slow, intermediate, or fast with respect to the Larmor precession frequency) and at several other biferrocenium cations (both localized and delocalized with respect to the zero-field Mössbauer timescale) was measured as a function of temperature and applied magnetic field. Two biferrocenium salts apparently unaffected by relaxation were simulated with an  $S=1/2$  spin Hamiltonian. In all cases the unpaired electron appeared to reside in a highly anisotropic orbital characteristic of a low-spin ferric ion [5].

The intramolecular electron transfer characteristics of biferrocenium triiodide were studied by variable-temperature Mössbauer spectroscopy. A sample history dependence of the electron transfer properties was found indicating intermolecular control of this intramolecular process [6]. A determination of the factors involved was attempted by a comparison of the single-crystal X-ray diffraction study [7] with powder X-ray diffraction measurements, and also by

obtaining differential scanning calorimetry measurements on the phase transition seen for this compound. Single crystal conductivity measurements gave low conductivity values and a linear  $\log(\sigma)$  vs  $1/T$  plot, indicating that intermolecular electron transfer processes were at most minimally involved.

#### References

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