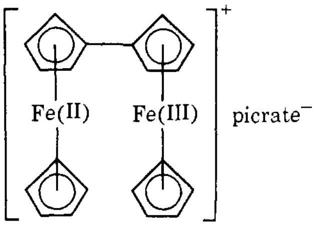
The Organic Solid State. Electron Transfer in a Mixed Valence Salt of Biferrocene

Sir:

Mixed valence inorganic compounds have been shown to have a number of unique physical and chemical properties.[1] These properties range from color, magnetism, and solid state conductivity to chemical reactivity.

By combining the synthetic possibilities inherent in organometallic chemistry with the concepts developed in mixed valence inorganic chemistry, it may be possible to obtain mixed valence organometallic compounds with a wide variety of electrical properties (semiconducting, conducting, superconducting, and switching). In addition, some of the mixed valence organometallic compounds may serve as useful models in studying the short-range electron transfer, occurring during biological oxidation–reduction reactions, *via* the array of "electron carriers" located on the inner membranes of chloroplasts and mitochondria. With these goals in mind we would like to report the synthesis and properties of biferrocene[Fe(II)Fe(III)]picrate (**1**) the first of a number of mixed valence organometallic compounds currently under study.



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Biferrocene, prepared by the Ullman coupling of iodoferrocene,[2] was oxidized with an excess of benzoquinone in the presence of picric acid.[3,4] If the two chromophores are assumed[5] to be only weakly interacting, then the uv spectrum should be composed of transitions characteristic of a substituted ferrocene and a substituted ferrocenium[6] ion along with an electron-transfer transition. At least five transitions are observed in the electronic spectrum of **1** (acetonitrile solvent) in the uv to near-ir region (see Figure 1).[4] The broad band of **1** centered at 550–600 mμ (ε 1860, acetonitrile) is tentatively assigned to the substituted ferrocenium portion of **1**. The threefold increase in intensity (in comparison with the ferrocenium picrate transition), increased width, and shift to shorter wavelengths all indicate that that the two ring systems are not entirely isolated and that there is some interaction of the ferrocenium chromophore by the adjacent ferrocene ring.

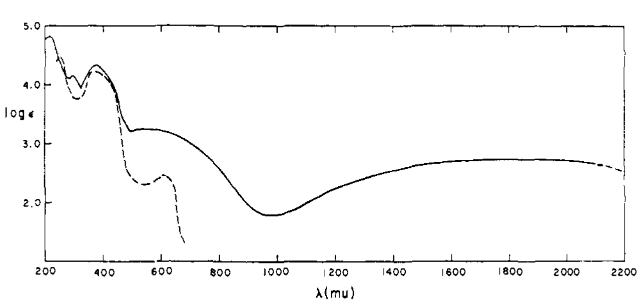

Figure 1. Visible-ultraviolet-near-infrared spectra of biferrocene-[Fe(II)Fe(III)] picrate (**1**).

In addition to the bands assigned to the substituted ferrocene and ferrocenium portions of **1** a new band is observed in the near-ir [1900 mμ (ε 551)] and is ascribed to an electron-transfer transition

$$[\mathrm{Fc(II)\text{-}Fc(III)}]^+ \xrightarrow{h\nu} [\mathrm{Fc(III)\text{-}Fc(II)}]^+$$

where Fc represents the ferrocenyl group either in oxidation state II or III.

At least in part, the width of this and other electron-transfer bands may be explained by observing that the equilibrium distance between the two metal centers (reactant and product) can vary somewhat from molecule to molecule. This gives rise to a large number of allowed Franck–Condon transitions.[7] An assignment of the 1900-mμ band to an electron-transfer transition is consistent with Taube's assignment of the 1570-mμ band in a mixed valence ruthenium complex[8] to an electron-transfer transition. The Ru(II)–Ru(III) distance in Taube's relatively rigid complex is about 6.8 Å while the Fe(II)–Fe(III) distance in **1** has been calculated from models to be from 3.8 Å (*cis* coplanar) to 5.1 Å (*trans* coplanar). If the half-width ($\Delta\bar{\nu}_{1/2}$) of the electron-transfer band does depend on the range of distances between the two metal centers,[9] then compound **1** should exhibit a broader band than the rigid ruthenium complex. The half-width of the 1900-mμ band of **1** is three times as broad as the corresponding 1570-mμ band of the ruthenium complex.

The energy associated with the near-ir electron-transfer transition ($E_{\mathrm{op}} = hc\bar{\nu}_{\mathrm{max}}$, 15.1 kcal (0.66 eV)) can be shown to be four times the activation energy for the thermal intramolecular electron transfer. This relationship was derived by Hush[9] for several model systems. If the energy barrier for the thermal intramolecular electron transfer is calculated in this manner ($hc\bar{\nu}_{\mathrm{max}}/4$ = 3.78 kcal (0.16 eV)) and this quantity is assumed equal to $\Delta G^{\ddagger}$, then an intramolecular electron-transfer rate constant can be calculated ($(kT/h) \exp[\Delta G^{\ddagger}/RT] = 1.3 \times 10^{10}$ sec^{-1}).[10] The second-order rate constant at 25° for the ferrocene–ferrocenium ion electron exchange reaction can be estimated from low-temperature experimental data to be about 3.1×10^8 M^{-1} sec^{-1}.[11] To compare the two rate constants, we calculate that a total concentration of 12 *M* is required to produce a solution where the average distance be-

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[1] M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 247 (1967); G. C. Allen and N. S. Hush, *Progr. Inorg. Chem.*, **8**, 357 (1967).

[2] M. D. Rausch, *J. Org. Chem.*, 26, 1802 (1961).

[3] G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, *J. Amer. Chem. Soc.*, 74, 2125 (1952); L. M. Epstein, *J. Chem. Phys.*, **36**, 2731 (1962).

[4] The detailed synthesis and characterization of **1** will be described in our full paper along with a number of other details.

[5] The ir spectrum of **1** supports this assumption.[4]

[6] D. R. Scott and R. S. Becker, *J. Phys. Chem.*, **69**, 3027 (1965); *J. Chem. Phys.*, **35**, 516 (1961); A. T. Armstrong, F. Smith, E. Elder, and S. P. McGlynn, *ibid.*, **46**, 4321 (1967); A. T. Armstrong, D. G. Carroll, and S. P. McGlynn, *ibid.*, **47**, 1104 (1967).

[7] This cannot be the only important factor inasmuch as Taube has recently observed that a fairly rigid mixed valence compound also gave a relatively broad band.[8] However, it should be noted that when this band is graphed in terms of $\bar{\nu}$ (cm^{-1}) instead of λ (mμ) the band appears not to be exceptionally broad.

[8] C. Creutz and H. Taube, *J. Amer. Chem. Soc.*, **91**, 3988 (1969).

[9] N. S. Hush, *Progr. Inorg. Chem.*, **8**, 391 (1967).

[10] If the $T\Delta S^{\ddagger}$ term for the electron-transfer reaction is small, then the free energy ($\Delta G^{\ddagger}$) for this reaction is approximately equal to the activation energy (E_{th}). For the ferrocene–ferrocenium ion exchange the $T\Delta S^{\ddagger}$ term is less than 7% of the total free energy.[11]

[11] D. R. Stranks, *Discussions Faraday Soc.*, **28**, 73 (1960).

tween the ions is 4.1 Å[12] (in the range of the iron–iron distance of **1**, 3.8–5.1 Å). This concentration, when multiplied by the bimolecular rate constant, gives a pseudo-first-order rate constant of about 4×10^9 sec^{-1}. This value is in very good agreement with the rate constant calculated from the near-ir transition (1.3×10^{10} sec^{-1}).

The electron-transfer transition is also observed in thin-film solid-state spectra of **1** (maximum at 1900 mμ). In addition, the relative absorptivities of the solid-state and acetonitrile solution spectra are the same. The band maximum and relative absorptivities probably indicate that very similar distances, geometries, and interactions are involved in the solid and in solution.

Conductivity measurements along the long axis of single crystals of **1** were performed in a nitrogen atmosphere using the two-probe technique.[13] The conductivity (σ) was determined, at a given temperature, from the slope of a plot of current (I) *vs.* voltage (V) or log I *vs.* log V when the current and voltage range was very large.

Compound **1** was observed to behave in an ohmic fashion ($\sigma = 2.3 \times 10^{-8}$ ohm^{-1} cm^{-1} at 298°) over a very large range of field strengths (10^{-2} to 8×10^3 V/cm). For most organic aromatic molecular solids both the dark and photoconductivity cease to be ohmic when field strengths exceed about 1000 V/cm.[14] The ohmic behavior of **1** at very high field strengths could be due to a high mobility (μ) of the carriers, a large number of carriers (n), or particularly good electrode behavior (injecting) compared to the other cases studied. Regardless of the cause, it has not been possible to observe the space-charge limited (SCL) region usually found for organic compounds.

If the conductivity is ionic and not electronic the compound should be slowly electrolyzed when current flows through the crystal. To test for ionic conduction a larger amount of charge was passed through the sample than would be allowed by Faraday's law without a drastic change in the conductivity. No conductivity change could be detected.

In addition to the measurements of current *vs.* voltage at room temperature, the conductivity as a function of temperature was determined and found to obey the following functional relationship.

$$\sigma(T) = \sigma_0 \exp[-E_a/kT]$$

From the slope of a plot of σ *vs.* $1/T$, the activation energy (E_a) for the conduction process was determined. The interpretation of the constant (σ_0) will depend upon the nature of this conduction process involved.[15] Values of σ, σ_0, and E_a are given in Table I for ferrocene, ferrocenium picrate, and biferrocene[Fe(II)Fe(III)] picrate.

The conductivity of the mixed valence compound **1** *is observed to be six orders of magnitude larger than either ferrocene or ferrocenium picrate.* The comparison of **1** and ferrocenium picrate is particularly important inasmuch as both picrates were prepared *via* the same method and subjected to identical isolation and purification procedures, and the conductivity measurements performed in the same manner. The increase in conductivity could be due to an increase in the number of charge carriers (n), an increase in the mobility (μ) of the carriers, or both ($\sigma = ne\mu$).

Table I. Conductivity of Ferrocene Compounds

Compound	σ(298°), ohm^{-1} cm^{-1}	E_a, eV	σ_0, ohm^{-1} cm^{-1}
Ferrocene[a]	1×10^{-13}	0.61	10^{-4}
Ferrocenium picrate	7.3×10^{-14}		
Biferrocene[Fe(II)Fe(III)] picrate	2.3×10^{-8}	0.43	0.4

[a] D. C. Hoesterey and G. M. Letson, *J. Chem. Phys.*, **41**, 675 (1964).

The activation energy (0.43 eV) observed for the electronic conduction in **1** is much larger than the calculated thermal activation energy (0.16 eV) for intramolecular electron transfer in **1**. This indicates that the rate-limiting process is not intramolecular electron transfer but must be related to the intermolecular carrier transfer mechanism. While we have been able to effect a very large (10^6) change in the conductivity with very minor structural modifications it would appear that in order to increase the conductivity even more, to obtain either a metal or a superconductor, will require structural or crystal changes[16] aimed at reducing intermolecular as well as intramolecular barriers. A number of mixed valence ferrocene compounds, including the analogous ferrocene polymer, are currently under investigation.

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(12) E. M. Kosower, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, p 344.

(13) L. Marton, Ed., "Methods of Experimental Physics," Vol. 6B, "Solid State Physics," Academic Press, New York, N. Y., 1959.

(14) D. R. Kearns in "Advances in Chemical Physics (VII). The Structure and Properties of Biological Systems," Interscience Publishers, New York, N. Y., 1964, p 282.

(15) F. Gutmann and L. E. Lyons, "Organic Semiconductors," John Wiley & Sons, Inc., New York, N. Y., 1967.

(16) The picrate salt was chosen as the first candidate for study inasmuch as it is known (R. C. Petterson, Ph.D. Thesis, University of California, Berkeley, Calif., 1966) that the picrate ions and ferrocenium ions stack in alternate columns. However, the crystal structure of biferrocene[Fe(II)Fe(III)] picrate has not been determined.

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(18) National Institutes of Health Predoctoral Fellow.

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Thallium-205 Nuclear Magnetic Resonance as a Probe for Studying Metal Ion Binding to Biological Macromolecules. Estimate of the Distance between the Monovalent and Divalent Activators of Pyruvate Kinase

Sir:

Recently, there has been considerable interest in applying nonproton nmr spectroscopy for studying molecular interactions of biochemical importance.[1] Thal-

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(1) (a) T. R. Stengle and J. D. Baldeschwieler, *Proc. Nat. Acad. Sci. U. S.*, **55**,1020 (1966); *J. Amer. Chem. Soc.*, **89**, 3045 (1967); (b) T. L. James and J. H. Noggle, *Proc. Nat. Acad. Sci. U. S.*, **62**, 644 (1969), and references cited therein; (c) R. G. Bryant, *J. Amer. Chem. Soc.*, **91**, 1870 (1969).