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Electronic Structure of the Triiodide Salt of the Asymmetric, Mixed-Valence Cation (3-Acetylfulvalene)(fulvalene)diiron(1+)

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Received June 4, 1984

The extent of delocalization is studied in the triiodide salt of the mixed-valence cation (3-acetylfulvalene)(fulvalene)diiron(1+). A single quadrupole-split doublet is seen in the 4.5 K Mössbauer spectrum of this salt. A relatively (for mixed-valence biferrocenes) isotropic EPR signal with g values of 2.340, 2.000, and 1.915 is seen for this solid at 77 K. An IT band at 7140 cm^{-1} (ϵ = 1740 M^{-1} cm^{-1}) is evident in the electronic absorption spectrum. The IR spectrum also indicates a delocalized electronic structure with a C–H ring-bending band at 840 cm^{-1}. There is no potential energy barrier for electron transfer in the bis(fulvalene)diiron(1+) mixed-valence ion. The addition of a single electron-withdrawing acetyl substituent does not seem to change this situation.

Introduction

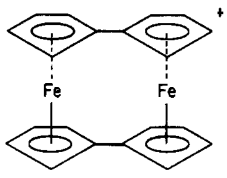
Mixed-valence transition-metal complexes have proved useful in the study of electron transfer between distant metal ions.[1-3] Very recently the Creutz–Taube (C–T) complex, $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$, has been reexamined with a battery of physical techniques.[4] It was still *not* possible to decide whether the odd electron in the C–T ion is trapped on one ruthenium ion or delocalized over both.

The introduction of asymmetry into the C–T ion by replacing the five NH_3 ligands on one of the ruthenium ions by one Cl^- and two bpy ligands has a dramatic effect.[3] The intervalence-transfer (IT) electronic absorption band in the near-IR moves from 8.8 × 10^3 cm^{-1} (ϵ = 5,500 M^{-1} cm^{-1}) for the C–T ion to 14.4 × 10^3 cm^{-1} (ϵ = 530 M^{-1} cm^{-1}) for $[(bpy)_2ClRu(pz)Ru(NH_3)_5]^{4+}$. This latter ion clearly has a weaker electronic interaction between the two different ruthenium ions than is present in the C–T ion, which results in a class II description and the presence of $Ru^{III}(NH_3)_5$ and $Ru^{II}(bpy)_2Cl$ moieties.[5] Several other asymmetric, mixed-valence ruthenium complexes have been studied.[3] However, there is no *direct* information about the electron-transfer rate in these or, for that matter, any mixed-valence ruthenium complex. The electron-transfer rate has only been indirectly characterized by analyzing the IT band.

Recently a series of binuclear mixed-valence $Cu^{II}Cu^{I}$ complexes with seven different, but related, binucleating macrocyclic ligands was reported.[6] Variable-temperature EPR data were used relatively directly to characterize the *intra*molecular electron-transfer rate for solutions of these complexes. It was found that the introduction of even an apparently small amount of asymmetry in these $Cu^{II}Cu^{I}$ complexes (with the two copper coordination sites different) affected the electron-transfer rate.

Cowan et al.[7] have probed the effects of asymmetric substitution on the mixed-valence monocation of biferrocene. Biferrocenes were investigated that had a single substituent either at the 2-position of the fulvalenide ligand or on one of the cyclopentadienide ligands. Mixed-valence ions were generated electrochemically to determine the IT band. The decrease in intensity and movement to higher energy of the IT band for the mixed-valence biferrocene with a single substituent compared to the IT band for unsubstituted mixed-valence biferrocene *suggested* that the asymmetry in the complex reduced the electron-transfer rate.

In this paper a variety of physical techniques has been used to determine directly if there is any change in the electron-transfer rate resultant upon adding a single acetyl substituent in the 3-position to the mixed-valence bis(fulvalene)diiron monocation, 1. The extents of valence delocalization have been investigated for I_3^- salts of 1 and 2 in the solid state. Physical techniques such as ^{57}Fe Mössbauer and EPR have proven to be very useful to characterize mixed-valence ferrocenes,[8] in contrast to the case for mixed-valence ruthenium complexes.



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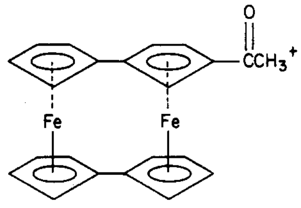

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Experimental Section

Physical Measurements. EPR spectra of powdered samples were recorded on a Varian E-9 X-band spectrometer. A quartz direct-immersion Dewar was employed to establish a sample temperature of 77 K. Powdered-sample EPR spectra were simulated with a previously reported[9] computer program.

Infrared spectra were obtained with Nicolet Model 7199 FTIR spectrometer equipped with a HgCdTe detector. All samples were prepared as 13-mm KBr pellets with 2–5 mg of compound mixed well with 150 mg of KBr.

Electronic absorption spectra were measured at room temperature with a Cary Model 14 spectrophotometer.

Iron-57 Mössbauer spectra were obtained with a constant-acceleration spectrometer that has been described.[10] Least-squares fitting of the powdered-sample Mössbauer spectra with Lorentzian lines was carried out with a modified version of a previously reported computer program.[11]

Compound Preparation. Elemental analyses were performed in the Microanalytical Laboratory of the School of Chemical Sciences.

Samples of bis(fulvalene)diiron and (3-acetylfulvalene)(fulvalene)diiron were prepared according to literature procedures.[12] Both compounds were characterized with electron-impact mass spectrometry with parent peaks of 368 and 410, respectively, seen for the two metallocenes. (3-Acetylfulvalene)(fulvalene)diiron was further characterized with a ^{1}H 360-MHz NMR spectrum ($CDCl_3$ solution) that had the same characteristics as the spectrum previously reported.[12] An IR spectrum for this same compound in a KBr pellet showed a very strong C–O band at 1666 cm^{-1}.

The triiodide salt of cation 2, $[Fe(\eta^{10}\text{-}C_{10}H_8)Fe(\eta^{10}\text{-}C_{10}H_8COCH_3)]I_3\cdot{}^1/_4I_2$, was prepared by dissolving 50 mg (0.197 mmol) of iodine in 40 mL of benzene. This solution was added to a stirred

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Table I. Parameters Resultant from Least-Squares Fitting of ^{57}Fe Mössbauer Spectra[a]

compd	*T*, K	ΔE_Q	δ[b]	Γ[c]	
(3-acetylfulvalene)(fulvalene)diiron	4.5	2.281 (2)	0.386 (1)	0.159 (2)	0.174 (2)
(3-acetylfulvalene)(fulvalene)diiron (1+) ($I_3^{-}\cdot{}^1/_4I_2$ salt)	4.5	1.667 (2)	0.396 (1)	0.147 (2)	0.148 (2)
bis(fulvalene)diiron (1+) (I_3^- salt)	4.7	1.754 (3)	0.404 (2)	0.177 (3)	0.180 (3)

[a] ΔE_Q and δ values are in mm/s; the estimated errors in the least-significant figures are given in parentheses. [b] Isomer shift relative to iron metal. [c] Full width at half-height taken from the Lorentzian fitting program. The width for the line at more negative velocity is listed first.

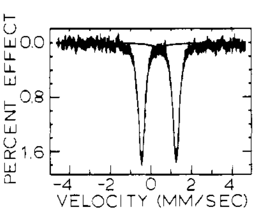

Figure 1. 4.5 K ^{57}Fe Mossbauer spectrum for (3-acetylfulvalene)(fulvalene)diiron(1+) ($I_3^{-}\cdot{}^1/_4I_2$ salt). The velocity scale is referenced to iron metal.

solution of 50 mg (0.122 mmol) of (3-acetylfulvalene)(fulvalene)diiron in 30 mL of benzene. The green precipitate that formed was filtered and washed repeatedly with anhydrous ether. Anal. Calcd for $C_{22}H_{20}OFe_2I_{3.5}$: C, 30.85; H, 2.35. Found: C, 31.16; H, 2.02.

A sample of the I_3^- salt of cation **1** was prepared as reported before.

Results

Mössbauer Spectroscopy. ^{57}Fe Mössbauer spectra were run for the triiodide salts of cations **1** and **2** at liquid-helium temperature. Only one quadrupole-split doublet is seen in the spectra of these two mixed-valence compounds (see Figure 1 for an illustration of the spectrum of the triiodide salt of **2**). In each case, the spectrum was least-squares fit with Lorentzian line shapes to obtain the parameters given in Table I. The two spectra are quite similar; however, the quadrupole splitting (ΔE_Q) for the salt of **2** (1.667 (2) mm/s) is somewhat smaller than that for the salt of **1**. Mössbauer data are also included in Table I for the unoxidized, neutral form of **2**.

Electron Paramagnetic Resonance. EPR spectra were run for 77 K polycrystalline samples of the triiodide salts of **1** and **2**; these two spectra are illustrated in Figure 2 (tracing B is for the salt of **2** and tracing C for the salt of **1**). As can be seen the two EPR spectra are also quite similar. The spectrum for the triiodide salt of **2** was simulated with a computer program employing a rhombic **g** tensor with *g* values of 2.340, 2.000, and 1.915. This simulated polycrystalline-sample spectrum is shown as tracing A in Figure 2.

Electronic Absorption Spectroscopy. The electronic absorption spectrum obtained for a room-temperature CH_3CN solution of the triiodide salt of **2** is shown in Figure 3. A relatively intense (ϵ = 1740 M^{-1} cm^{-1}) intervalence-transfer (IT) band is observed at 7140 cm^{-1}. This band is shifted to higher energy by 340 cm^{-1} compared to the IT band seen for the triiodide salt of **1** in CH_3CN (6800 cm^{-1}; ϵ = 1710 M^{-1} cm^{-1}). The band widths at half-height for the IT bands observed for the CH_3CN solutions of **1** and **2** are 3250 and 4000 cm^{-1}, respectively.

Infrared Spectroscopy. It has been shown that the perpendicular, cyclopentadienyl C–H bending modes observed in the 800–850 cm^{-1} region for mixed-valence ferrocenes reflect the oxidation state of the iron ions.[13] This band is seen at 815 cm^{-1} for ferrocene, whereas, for ferrocenium triiodide the C–H bending mode appears at 851 cm^{-1}.

Infrared spectra in the C–H bending region are illustrated in Figure 4 for a KBr pellet of the unoxidized Fe_2^{II} form of cation **2** (upper tracing) and for a KBr pellet of the triiodide salt of **2** (lower tracing). There is one strong band seen at 806 cm^{-1} for the unoxidized compound. This is typical for iron(II) metallocenes. Only one absorption band at 840 cm^{-1} is seen for the triiodide salt of **2**. The perpendicular C–H bending band observed for a variety of ferrocenium salts occurs in the 850–860 cm^{-1} region. Thus, the 840-cm^{-1} band seen for the triiodide salt of **2** is intermediate in value between what is seen for the unoxidized form of **2** and for iron(III) metallocenes. It is clear that the mixed-valence cation in the triiodide salt of **2** is delocalized on the IR time scale.

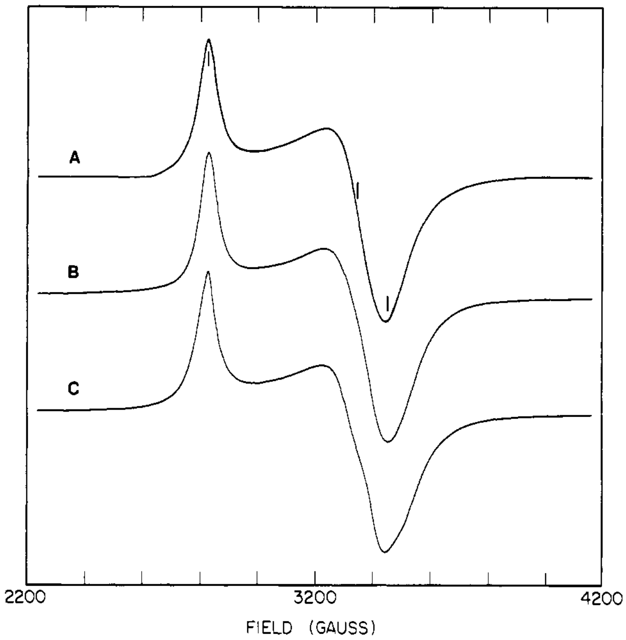

Figure 2. X-Band EPR spectra: (A) computer simulation of the spectrum obtained on the triiodide cation of **2**; (B) 77 K powder spectrum for (3-acetylfulvalene)(fulvalene)diiron(1+) ($I_3^{-}\cdot{}^1/_4I_2$ salt); (C) 77 K powder spectrum for bis(fulvalene)diiron(1+) (I_5^- salt).

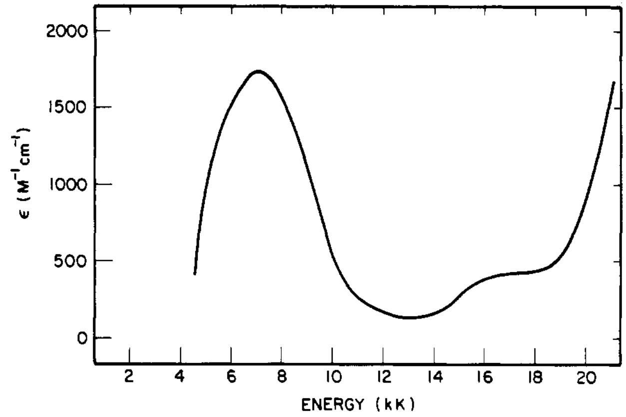

Figure 3. Electronic absorption spectrum at room temperature for the mixed-valence cation of **2** in acetonitrile.

Discussion

At the outset of this study it was thought there was some probability that the introduction of a single acetyl substituent on the mixed-valence bis(fulvalene)diiron cation would lead to an appreciable change in the potential energy barrier for electron transfer. Previous to this study it was known that cation **1** has a completely delocalized ground state with no electron-transfer barrier present. The acetyl substituent acts as an electron-with-

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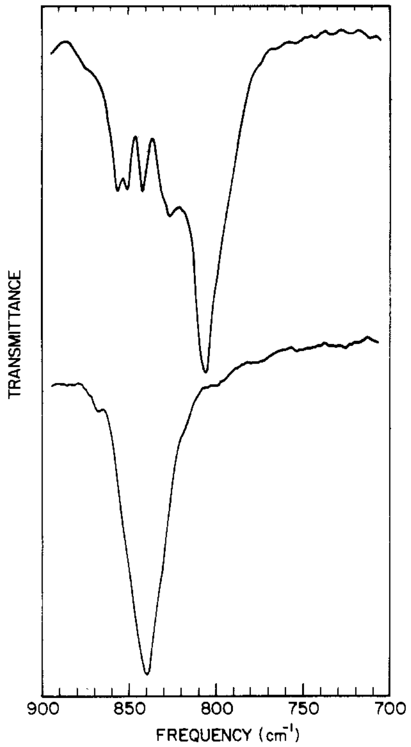

Figure 4. Infrared spectra of the perpendicular C–H bending region obtained at room temperature on KBr pellets of unoxidized neutral form of **2** (top) and the triiodide salt of **2** (bottom).

drawing group, increasing the oxidation potential of a ferrocene. For example, the oxidation potential of acetylferrocene is 0.790 V (vs. SCE) compared to 0.540 V for unsubstituted ferrocene.[7] The introduction of a single acetyl substituent on **1** to give **2** could lead to an appreciable zero-point energy difference between the two different vibronic states for **2**.

Contrary to our simple expectations, we found that the mixed-valence cation **2** has a delocalized ground state. A single quadrupole-split doublet is seen at 4.5 K in the Mössbauer spectrum for the triiodide salt of **2**. The EPR spectra for the triiodide salts of **1** and **2** look very similar, but quite different from the EPR spectra seen for EPR-localized mixed-valence biferrocenes. The IR spectrum and intensity of IT band for the triiodide salt of **2** also point to a delocalized ground electronic state for **2**.

The observation that the single unpaired electron in cation **2** is delocalized over both halves of the molecule indicates that the electron-withdrawing nature of the acetyl substituent has had little effect on the electronic structure of the bis(fulvalene)diiron cation. This very likely results from the fact that there is a strong electronic coupling between the electronic manifolds of the two iron ions in both **1** and **2**. There is no barrier for electron transfer. The single unpaired electron in **2** is located in a molecular orbital that has comparable contributions from both metallocene moieties.

In fact, the very recent report by Hillman and Kvick[14] of the X-ray structure of the picrate hemihydroquinone salt of **1** indicates the nature of the strong Fe–Fe electronic coupling in **1** and **2**. They found that the Fe–Fe distance (3.636 (1) Å) in mixed-valence **1** is 0.35 Å shorter than in the corresponding neutral Fe_2^{II} complex. The bis(fulvalene)diiron framework distorts upon oxidation to **1** so as to increase the direct Fe–Fe interaction in the mixed-valence cation. Such a direct Fe–Fe interaction had previously been suggested[8] as the explanation for the diamagnetism of the dioxidized Fe_2^{III} analogue of **1**. Apparently a direct Fe–Fe interaction is maintained in **2**, and this explains why the acetyl substituent does not have much effect on the extent of delocalization.

Acknowledgment. We are grateful for support from NIH Grant HL13652.

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Matrix-Isolation Study of Oxide-Transfer Reactions to Halogen-Containing Lewis Acids: Synthesis of the $CO_2F_2^{2-}$ Anion and Attempted Synthesis of the BF_3O^{2-} Anion

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Received July 24, 1984

The oxide-transfer technique has been coupled with matrix isolation in an attempt to synthesize and characterize the BF_3O^{2-} and $CO_2F_2^{2-}$ anions, through the reaction of Tl_2O with either BF_3 or COF_2. In the latter experiments, two sets of product bands were observed; one agreed well with the absorptions of the known CO_2F^- anion. The second set has been assigned to the $CO_2F_2^{2-}$ anion in the matrix-isolated $Tl^+{}_2CO_2F_2^{2-}$ triple ion, which rapidly eliminated TlF upon warming to form the $Tl^+CO_2F^-$ anion. Attempts to synthesize the BF_3O^{2-} anion in a similar fashion were not successful, suggesting that previous reports of the room-temperature synthesis of this anion are incorrect.

Introduction

The salt/molecule technique[1] was developed 10 years ago for the synthesis of unusual and highly reactive anions in inert matrices. This technique was initially employed for the transfer of a halide anion to a variety of Lewis acids to form the desired anion in a matrix-isolated ion pair.[2-6] Recently, the oxide-transfer technique[7] was developed in which an oxide anion O^{2-} is transferred from Tl_2O to a suitable acceptor, to form an oxyanion in a matrix-isolated triple ion. Species that have been formed in this manner[7-9] include CO_3^{2-}, CO_2S^{2-}, COS_2^{2-}, SO_3^{2-}, and $S_2O_5^{2-}$. A direct, and important, extension of this technique would be to the reaction of Tl_2O with halogen-containing Lewis acids such as BF_3 and COF_2. For these systems, not only is the addition reaction feasible to form the product oxyanion, but a variety of elimination reactions may occur to form further products.

The synthesis of the BF_3O^{2-} anion was the first reported in the late 1950s, and spectroscopic characterization followed thereafter.[10-14] However, since that time researchers have demon-

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