Effect of structural modifications on electron delocalization of mixed-valence biferrocnium systems

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Deviations of the cyclopentadienyl ring from the parallel positions were found to correlate quite well with the critical temperatures of delocalization–localization transition for mixed-valence biferrocnium cation salts on Mössbauer time scale. The observations can be rationalized by examining the variations of HOMO–LUMO gap of the Cp–Fe–Cp monomer unit as the angle of \( \angle \text{Cp–Fe–Cp} \) changes induced via ligand substitutions on the terminal Cp rings.

1. Introduction

Nature of the bridging ligand has been long viewed as one of the important factors influencing the electron delocalizations in the bridge-ligand mediated mixed-valence systems [1]. Modifications of the nature of bridge ligands have been the focus of a lot of research efforts [2]. Experimentally, such modifications are conventionally achieved by introducing ligands with \( \sigma \) or \( \pi \) characters [3] or substituting varying identities of ancillary ligands on the bridge ligands [4–6]. In this Letter, we report a structural modification induced by the substituents on terminal Cp rings for a series of mixed-valence biferrocnium cations which lead to the observation of a clear demonstration between delocalization temperatures on Mössbauer time scale and the \( \angle \text{Cp–Fe–Cp} \) angles.

Considerable progress has been made in understanding factors which control the rate of intramolecular electron transfer for mixed-valence compounds in the solid state environment [2,4,7,8]. For binuclear mixed-valence biferrocnium cations [9–20], it has been found that the nature of the solid state surrounding of a mixed-valence cation might have a dramatic effect on the rate of intramolecular electron transfer. For instance, Hendrickson and co-workers have addressed on solid-state environmental effect [18,21], counterion effect [16,17,19] and other effects on intramolecular electron transfer rates of biferrocnium salts. Dong et al. have also studied the substitution effect [22,23], effect of zero-point energy difference and anion dependence [24] on intramolecular electron transfer rates of similar systems. There has also been substantial work done by Hupp and co-workers [25] on the effect of modifications of ligands on bimolecular charge transfer. Substituents on terminal Cp rings of biferrocnium compounds were found to modify the structural characteristics, i.e. the parallel relation between two Cp rings around a metal ion [26,27]. It is interesting to see the consequence of such structural modification on intramolecular electron transfer rates. As we know, the above mentioned structural distortion is basically caused by bending motion along \( \angle \text{Cp–Fe–Cp} \) and would lead to larger extent of metal–ligand interactions. HOMO–LUMO gap of the Cp–Fe–Cp monomer unit would be a proper index to reflect this structural modification. In order to see the correlation between HOMO–LUMO gap and the intramolecular electron transfer rates of biferrocnium cations, we performed extended Hückel calculations on ferrocnium unit at different \( \angle \text{Cp–Fe–Cp} \) ranging from 160° to 180°. The atomic parameters used in the extended Hückel calculations were taken from ref. [28] and were listed in table 1.

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Table 1  
Extended Hückel Coulomb integral \( \( H_{\alpha} \) \) and Slater exponents

<table>
<thead>
<tr>
<th>( H_{\alpha} ) (eV)</th>
<th>( \zeta_1 )</th>
<th>( \zeta_2 )</th>
<th>( \zeta_3 )</th>
<th>( \zeta_4 )</th>
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</thead>
<tbody>
<tr>
<td>C 2s</td>
<td>-21.4</td>
<td>1.625</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C 2p</td>
<td>-11.4</td>
<td>1.625</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H 1s</td>
<td>-13.6</td>
<td>1.300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe 3d</td>
<td>-12.6</td>
<td>5.350</td>
<td>2.000</td>
<td>0.5505</td>
</tr>
<tr>
<td>Fe 4s</td>
<td>-9.1</td>
<td>1.900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe 4p</td>
<td>-5.32</td>
<td>1.900</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Theoretical explanations of the various facts about intramolecular electron transfer of biferrocenium cations were mostly based on PKS vibronic model [29] where the magnitude of the vibronic coupling plays an essential role. Taking into account the lattice dynamics, a micromodulation mechanism was proposed to describe the electron transfer assisted by the collective motion which was composed of local breathing mode of each monomer unit [19]. Obviously, this mechanism could not agree satisfactorily with the observed tilt angles, defined as \( \theta \) - Cp–Fe–Cp, and needs to be reexamined.

This Letter is composed as follows. Experimental setup and observations will be reported in section 2. The results of extended Hückel calculations will be discussed in section 3. Also, a refinement of the micromodulating mechanism is proposed and discussed in section 3. Conclusions are given in section 4.

2. Experimental

The preparation of compounds 1–5 (see scheme 1) were reported elsewhere [24]. The electron transfer dynamics were then determined by physical methods including Mössbauer technique, \(^{1}H\) NMR spectra, polarographic measurements, along with the structural determination using X-ray diffraction. For convenience, it would be useful to introduce the setup of the \(^{57}\)Fe Mössbauer measurement at the Academia Sinica. The instrument is of constant-acceleration type with the source, which originally consisted of 40 mCi of \(^{57}\)Co diffused into a 12 \( \mu \)m rhodium matrix, connected to a Ranger Scientific model VT-900 velocity transducer. An Ortec model 5600 multichannel analyzer, scanned over 1024 channels, receives the logic pulses from the single-channel analyzer. Computer fitting of the \(^{57}\)Fe Mössbauer data to Lorentzian line shapes were carried out using a modified version of a previously reported program [30]. Velocity calibrations were made using a 99.99% pure 10 \( \mu \)m iron foil. Typical linewidths for all three pairs of iron lines fell in the range of 0.28–0.30 mm/s. Isomer shifts are reported with respect to the thickness of iron foil at 300 K. By varying the temperature, we could determine from the observed Mössbauer spectra the critical temperature, \( T_c \), where the two doublets move together to become a single “average-valence” doublet. In other words, the intramolecular electron-transfer rate at the critical temperature is greater than the Mössbauer time scale \( (\approx 10^7 \text{ s}^{-1}) \). A typical temperature-dependent Mössbauer spectrum is shown in fig. 1.

3. Results and discussions

In fig. 2, we present the critical temperatures, \( T_c \), obtained from the temperature-dependent Mössbauer spectra and the tilt angles, \( \alpha \), derived from X-ray data [12,20,21,24] of compounds 1–5. It can be easily seen that the decreases of the critical temperatures for the delocalization–localization transition in these systems were accompanied by the increases of the tilt angles. Compound 5 is delocalized on the Mössbauer time scale at the temperature of liquid nitrogen, i.e. 77 K. The tilt angle of 5 is not known yet and assumably taken to be 13.7° from the cor-

Scheme 1.
responding monomer unit [31]. Compound 4 is found to be delocalized even at temperature of liquid helium, i.e. 4.2 K. The tilt angle of 4 is 15.6° and the largest so far according to our knowledge.

Qualitative understanding of the tilting of Cp ring in the MCP$_2$ fragment were illustrated using the Walsh diagram in Albright’s paper [32]. The key feature of this diagram is the uplifting of the $a_{1g}$ and $e_{2g}$ orbitals accompanied by the lowering of the $e_{1g}$ orbitals as the tilting angle increases. For detailed informations concerning the reactivities and general features of MCP$_2$ fragments, one should refer to the original works of Lauher and Hoffmann [33].

For the study of the electron delocalization in the biferrocenium cations 1–5, we perform extended Hückel calculation for tilt angles varying from 0° to 20° to see how HOMO–LUMO gap, i.e. $E(e_{1g}) - E(a_{1g})$, correlate to the tilt angles. In fig. 2, we also present the HOMO–LUMO gap of FeCp$_2$ unit as function of tilt angle. As can be seen from fig. 2, the HOMO–LUMO gap decreases as the tilt angle increases. Note that the tilting from the parallel Cp-ring position is caused by the substituent on the terminal Cp ring of the biferrocenium cation. Therefore, the substituent on the terminal ring of biferrocenium cation could modify the local structure of FeCp$_2$ unit.
and leads to stronger metal–ligand interactions, i.e. smaller HOMO–LUMO gap, which eventually render the intramolecular electron transfer much more feasible.

In their series of study, Dong, Hendrickson and co-workers [16,17,19] usually adopted a micromodulating picture which was composed of local breathing mode around each Fe ion. They also explained the unusual temperature-dependent Mössbauer spectra in a similar argument [12]. The argument is quite elegant so far in view of the rationale it provides for the bunch of data. However, the collective breathing mode could not give a net tilting angle. In order to fit the X-ray data, the bending mode should be coupled into the breathing mode in the original micromodulating picture. The effect of such a difference on the dynamics of intramolecular electron transfer in biferrocenium systems needs to be closely investigated.

4. Conclusion

The structural modification of local FeCp₂ unit induced by the substituent on terminal Cp ring of biferrocenium cation is found to play an important role in dynamics of the intramolecular electron transfer. The observed tilt angles and the critical temperatures for delocalization to localization transition demonstrate a clear-cut correlation. The conventional micromodulating picture derived from the collective breathing mode could not lead to net tilting. Coupling of the bending mode to original micromodulating mechanism needs to be closely investigated.

Theoretical calculations were performed to investigate the effect of tilting. As the tilt angle increases, the metal nonbonding orbital a₁₈ starts to interact with the ligand π orbitals. This interaction leads to uplifting of a₁₈ orbital and thus the decrease of the HOMO–LUMO gap. For the ligand-assisted mixed-valence systems, the stronger the metal–ligand interaction, the faster the electron-transfer rate. Our discussion shed some light into the understanding of the nature of intramolecular electron transfer in the biferrocenium cation.

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References


