Investigation on the Electron-transfer Interaction of the Two Ferrocene Moieties Bridged by Ni^{2+} or Cu^{2+} and Its Mixed-valence Complexes

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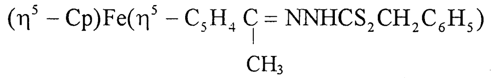
Investigation of the new mixed-valence trinuclear complexes of FcMFc (M=Ni, Cu) indicates that intramolecular long-range charge transfer for FcNiFc complex processes in timescale $1.6\bullet10^6$ s^{-1} through a long bridge including a coordinated bond at room temperature.

The intramolecular electron-transfer process may occur in mixed-valence binuclear complexes of ferrocene derivatives. To understand the structure and properties of mixed-valence iron complexes, physicists and chemists have made many considerable efforts to understand the behavior of intramolecular electron transfer in the solid state for trinuclear iron acetates[1,2] and biferrocenes.[3-5] Recently, a new compound S-benzyl-N-(ferrocenyl-1-methyl-methylidene)-dithiocarbazate,



$$(\eta^5-Cp)Fe(\eta^5-C_5H_4\underset{\underset{CH_3}{|}}{C}=NNHCS_2CH_2C_6H_5)$$

(abbreviated as FcBMMD), was synthesized.[6] Mixing this compound as a large ligand with $M(Ac)_2$ (M^{2+}=Ni^{2+} or Cu^{2+}) in ratio of 2:1 in CH_2Cl_2, the new complexes were obtained. The mixed-valence complex $[M(FcBMMD)_2]NO_3$ was prepared by adding a dichloromethane solution containing a stoichiometric amount of complex $M(FcBMMD)_2$ into a acetonitile solution of silver nitrate under continuing stirring. The purity of the new complexes was confirmed by established elemental analysis. The IR spectroscopy[7] indicates the complex M(FcBMMD) and mixed-valence cations $[M(FcBMMD)_2]^+$ have similar structure.

The structure of the complexes $Ni(FcBMMD)_2$ and $Cu(FcBMMD)_2$[7] had been determined by single crystalline *X*-ray diffraction. A representative stereoscopic molecular view for the complex $Ni(FcBMMD)_2$ is shown in Figure 1. The two Fe atoms in ferrocenes moieties have equivalent positions and with the distance is about 7.4 Å. The central Ni^{2+} of the compound $Ni(FcBMMD)_2$ is coordinated with N1, N3, S1 and S3 atoms in a plane and Cu^{2+} of $Cu(FcBMMD)_2$ in a tetrahedral coordination.

The cyclic voltammograms of the complex $M(FcBMMD)_2$ in chloromethane (1.0×10^{-3} M) were measured at a Pt wire electrodes in 0.1 M $(n\text{-}Bu)_4NClO_4$ dichloromethane, with a sweep rate 250mv/s. The ligand FcBMMD shows only one peak ($E_{1/2}$=0.688 V vs. Ag/AgCl) for its redox process as well as complex $Cu(FcBMMD)_2$ ($E_{1/2}$=0.665 V vs. Ag/AgCl). But the voltammogram of the $Ni(FcBMMD)_2$ solution (Figure 2) shows two separated peaks at $E^a{}_{1/2}$=0.765 V and $E^b{}_{1/2}$=0.809 V vs. Ag/AgCl. The behavior of the electrochemistry of the $Ni(FcBMMD)_2$ can be expressed as:

$$Fc(II)NiFc(II) - e \Leftrightarrow Fc(II)NiFc(III)$$

$$Fc(II)NiFc(III) - e \Leftrightarrow Fc(III)NiFc(III)$$

The phenomenon of the complex undergoing two reversible one-electron oxidations at close potentials means that, there is a weak interaction[8-11] between two ferrocenes through a long bridge which includes coordinated bonds. However, cyclic voltammogram of $Cu(FcBMMD)_2$ complex shows only one peak. It may be explained (1) the magnetic interaction[12,13] (as far as species with two paramagnetic centers are concerned), and (2) the nonplanarity with Cu, N1, N3, S1, S3 for $Cu(FcBMMD)_2$ complex makes larger tilt angles between the plane Cu, N1, N2, C13, S1 and plane Cu N3, N4, C33, S3.[7] The magnetic interaction of the spin state S=0 of Ni^{2+} with the neighboring Fe^{3+} site may be different from the spin state S=1/2 of Cu^{2+}. It is known that the rate of intramolecular charge transfer depends upon the tilt angle[14,15] between the planes or the orientation[16] of the protein-protein in the bridge for binuclear mixed-valence complex. The conclusion seems also to be valid for this new trinuclear Mixed-valence system.

The Mössbauer spectra for $Ni(FcBMMD)_2$ complex and its oxidized complex had been measured at room temperature. The spectra were fitted in one or two doublet splitting and were plotted in Figure 3. The Mössbauer spectra of the compound HFcBMMD as well as $Ni(FcBMMD)_2$ complex show one doublet splitting which is arised from a LS state Fe(II) site in Ferrocene of the ligand. The Mössbauer parameters (Q.S.=2.274 mm/s, I.S.=0.689 mm/s) of this doublet for ligand HFcBMMD have similar values to that of the compound $(C_5H_5)Fe[C_5H_4(CN)]$ as reported by Stukan and coworkers[17]. A new doublet appears in the spectra for mixed-valence complex of $Ni(FcBMMD)_2$. The additional Mössbauer parameters of this doublet were claimed due to the oxidized or ferricinium sites in the complex. The coexisted lines for Fe(II) and Fe(III) in Mössbauer spectrum mean that rate of intramolecular electron-transfer is less than the Mössbauer time scale $\sim10^7 s^{-1}$ at room temperature.

The UV-visible absorption spectra for $Ni(FcBMMD)_2$, mixed-valence complex $[Ni(FcBMMD)_2]^+$ and its completely oxidazed complex $[Ni(FcBMMD)_2]^{2+}$ were measured under the same conditions at room temperature. The spectra are consistent with the electronic transition of ferrocene in the range of 200 nm-600 nm. Moreover a noticeable weak peak appears significantly in about 1200 nm (ε 120) wavelength for mixed-valence complex $[Ni(FcBMMD)_2]^+$ but not for another two complexes. The peak is assigned to a photon-assisted intramolecular intervalence exchange (Fc(II)NiFc(III)⇔ Fc(III)NiFc(II)).[18] The rate of charge transfer at room temperature may be estimated as $1.6\bullet10^6$ s^{-1} by following the model of Hush.[19] This rate is less than that of Mössbauer timescale $\sim10^7 s^{-1}$.

The electron transfer for mixed-valence of the trinuclear $Ni(FcBMMD)_2$ complex at long distance (>5 Å) is demonstrated for the first time in above experiments. The intramolecular electron transfer is observed in our mixed-valence $[Ni(FcBMMD)_2]^+$ with $P2_1/n$ space group which is consistent with the conclusion of Webb[20] who discovered that the rate of electron transfer is slower than $\sim 10^6 s^{-1}$ for all temperatures in $P2_1/n$ system. The proof of electron transfer for $Cu(FcBMMD)_2$ needs further investigation.

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