## Lattice Engineered Micromodulation of Intramolecular Electron Transfer Rates in Trinuclear Mixed-Valence Iron Carboxylate Complexes

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The study of electron transfer events of mixed-valence transition metal complexes [1] can give insight into which factors determine the rate of electron transfer between well-separated metal sites through variation of the bridge between the metal centers. However, the influence of the environment on the rate of electron transfer in mixed-valence complexes has not been well characterized. Recently, mixed-valence biferrocenes [2] and trinuclear iron acetate complexes [3] in the solid state have been used in understanding how the environment affects the rate of intramolecular electron transfer.

For trinuclear mixed-valence complexes of composition  $[Fe_3O(O_2CCH_3)_6(L)_3]S$ , where L is a ligand and S is a solvate molecule, it has been found [3] that the onset of intramolecular electron transfer is coupled with a phase transition that involves the onset of dynamic disorder of the ligand and/or solvate molecules. At the outset it should be noted that IR studies [4] have shown that the mixed-valence Fe<sub>3</sub>O complexes are trapped on the vibrational time scale and, therefore, have potential energy barriers for electron transfer. Several theoretical models [5] have been developed to explain the nature of the phase transitions in the Fe<sub>3</sub>O complexes.

It has been found in this study [6] that systematic changes in the lattice can be made by the solvate molecule in a series of the isostructural (R32 space group) mixed-valence [Fe<sub>3</sub>O(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(4-Me-Py)<sub>3</sub>] ·S complexes, where 4-Me-Py is 4-methylpyridine and S is a solvate molecule such as benzene, CHCl<sub>3</sub>, CH3CCl3, or CH3CHCl2. These systematic changes of solvate molecules have a pronounced impact on the phase transitions at which a given complex valence detraps. This sensitivity is a reflection of the fact that the lowest energy electronic states of Fe<sub>3</sub>O complexes are vibronic and as a result these complexes are very sensitive to their environment. Heat capacity studies [7,8] of the CHCl3 complex show that it undergoes an abrupt phase transition at very low temperature (95K) and DTA data [8] show the CH3CCl3 solvate complex exhibits a phase transition at 125K. Interestingly, <sup>57</sup>Fe Mössbauer spectra of the CHCl<sub>3</sub> solvate complex show that this complex valence detraps at ~95K. However, the complex with the less symmetric CH3CHCl2 solvate molecule becomes valence-detrapped at ~45 degrees higher than for the CH<sub>3</sub>CCl<sub>3</sub> solvate complex and ~75 degrees higher than for the CHCl3 solvate complex. Changing the solvate molecules leads to changes in the intermolecular interactions propagated via the pyridine-pyridine overlaps between neighboring Fe30 molecules. Presumably, the introduction of the bulky solvate molecule (CH<sub>3</sub>CCl<sub>3</sub>) and less symmetric solvate molecule (CH<sub>3</sub>CHCl<sub>2</sub>) weakens the intermolecular interactions between neighboring Fe3O molecules and, consequently, gives higher transition temperature than that of the C3 symmetry CHCl<sub>3</sub> solvate. In fact, the results of CNDO/2 molecular orbital calculations show that an important factor is the intermolecular interaction between the Py...Py ligands for controlling the intramolecular electron transfer rate in addition to the onset of solvate molecules dynamic motion.

Interestingly, solid-state <sup>2</sup>H NMR studies [6,7] of  $[Fe_3O(O_2CCH_3)_6(Py)_3](CDCl_3)$  and  $[Fe_3O(O_2CCH_3)_6(4-Me-Py)_3](CDCl_3)$  show that even a solvate molecule such as the C<sub>3</sub> symmetry CHCl<sub>3</sub> molecule seemingly moves

synchronously with the changes of the vibronic coordinates of neighboring Fe<sub>3</sub>O molecules in the lattice. In the case of  $[Fe_3O(O_2CCH_3)_6(Py)_3](CDCl_3)$ , it is suggested that the C-D vector jumps rapidly between four positions with equal probability through the phase transition (208K). Three of these four positions are found to be off the crystallographic C<sub>3</sub> axis ( $\alpha$ =24.7°) which are consistent with the results of the single-crystal X-ray structure determination. The fourth position is where the C-D vector is along the C<sub>3</sub> axis ( $\alpha$ =0°). However, in the case of  $[Fe_3O(O_2CCH_3)_6(4-Me-Py)_3](CDCl_3)$ , it is found [7] from <sup>2</sup>H NMR and heat capacity results that the CDCl<sub>3</sub> solvate molecules only jump head to tail through the phase transition temperature (95K) and the C-D vectors do not cooperatively jump to sites off the C<sub>3</sub> axis. Furthermore, in recent study of  $[Mn_3O(O_2CCH_3)_6(Py)_3](Py)_3](Py)$  [9,10], it is found that the pyridine solvate molecules undergo abrupt dynamic motion wherein they also jump to sites off the C<sub>3</sub> axis in addition to local C<sub>6</sub> axis and C<sub>3</sub> axis rotations.

Thus, the above results strongly suggest that another important factor in controlling the rate of intramolecular electron transfer may be the van der Waals interactions between a solvate molecule and neighboring Fe<sub>3</sub>O complexes. The van der Waals interactions between a solvate molecule S which is positioned asymmetrically relative to the C<sub>3</sub> axis of a nearby Fe<sub>3</sub>O complex may lead to an interaction energy of only 10-100 cm<sup>-1</sup> per solvate molecule. However, this amount of Fe<sub>3</sub>O····S interaction may be large enough to modify the ground state potential-energy surface for a Fe<sub>3</sub>O complex and may appreciably affect the rate at which such a complex can tunnel from one vibronic minimum to another.

We have studied how the size of the carboxylate bridging ligand affects the intermolecular interactions between the neighboring Fe<sub>3</sub>O molecules and the rate of intramolecular electron transfer. The new mixed-valence complex with a bulky butyrate bridge,  $[Fe_3O(O_2CC_3H_7)_6(Py)_3](Py)$ , shows temperaturedependent Mössbauer behavior and valence-detrapping at the relatively high temperature (245K). In addition, DTA thermograms show only one thermal anomaly at 246K, which is at a higher transition temperature than that (191K) of the analogous acetate complex. Thus, we can suggest that bulky bridging ligands also have a pronounced impact on the rate of intramolecular electron transfer in the Fe<sub>3</sub>O complexes by breaking down the intermolecular interactions between neighboring Fe<sub>3</sub>O molecules [11].

Finally, we have discovered [11] the first trinuclear iron acetate complex  $[Fe_3O(O_2CCH_3)_6(3-Et-Py)_3](C_7H_8)_{0.5}$  which exhibits an isosceles  $Fe_3O$ triangular plane at room temperature, i.e., completely valence-traped on the X-ray time scale. However, the analogous mixed-valence  $[Fe_3O(O_2CCH_3)_6(3-Et-Py)_3](CH_3CCl_3)$  shows a valence detrapping phenomenon due to the adoption of a symmetric solvate molecule configuration. Thus, one really can turn on and off the intramolecular electron transfer in the mixed-valence complexes by controlling lattice environments.

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2

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3.