

Electron Transfer in Oxo-Centered, Trinuclear,
Mixed-Valence Iron Acetate Complexes

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Final Seminar

December 19, 1985

The general goal in the study of mixed-valence transition metal complexes has been to understand what factors determine the rate of electron transfer between well-separated metal sites through variation of the bridge between the metal centers [1]. It is frequently implicitly assumed for a symmetric mixed-valence complex that the electronic interaction and the vibronic coupling are the most important factor [2]. In most studies the environment about a mixed-valence complex in the solid state has not been implicated as an important factor controlling the rate of electron transfer.

The electron transfer properties in a series of complexes $[\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{L})_3](\text{S})$ were studied in the solid state where L is an axial ligand such as pyridine or substituted pyridines and S is a solvate molecule such as the corresponding pyridines, C_6H_6 , CHCl_3 or CH_3CN . It was found in this study that the three-dimensional packing arrangement of the crystalline complexes is the more critical factor for determining the rate of intramolecular electron transfer [3]. This lattice-dependent electron transfer property is believed to be from the fact that the ground state potential energy profile of the mixed-valence system is determined by the solid state packing arrangement. A complex having a more symmetric lattice shows a faster electron transfer rate, which might be due to a smaller difference between the zero-point energy levels of the corresponding nuclear configurations.

Variable-temperature single-crystal X-ray structural results on some of the complexes indicate that there are structural changes in the Fe_3O triangular framework as the sample temperature is varied [3]. It is suggested that the valence-equivalency seen in the Mössbauer spectra of those complexes at higher temperatures is the result of the structural change, rather than a simple thermal activation over the potential energy barrier.

Structural phase transitions have been detected by heat capacity measurements on some of the complexes [4]. In the mixed-valence complex $[\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{py})_3](\text{py})$ (1), four phase transitions have been identified. Interestingly, the Mössbauer spectra and the ^2H -NMR spectra of the sample, in which only the methyl group on the acetate bridge is deuterated, are changed drastically at the phase transition temperatures. In the Mössbauer spectra a third doublet, which is characteristic of the average oxidation state, appears at the low-temperature phase transition (~112 K). The valences of the three iron ions become equivalent in the Mössbauer spectrum at the high-temperature transition (185-190 K). The variable-temperature single-crystal X-ray diffraction study of this same compound indicates that the Fe_3O molecule has a C_3 axis perpendicular to the Fe_3O triangular unit above the HT-transition point (i.e., three iron atoms are structurally equivalent), but the C_3 axis disappears at the HT-transition point as the crystal is cooled down. It is clear from these results that there is a direct relationship between the phase transitions and the electron transfer properties of complex 1.

The nature of the phase transitions in complex 1 has been assigned to the three contributions: (1) An electronic transition from a localized to a delocalized state; (2) An order-disorder transition of the pyridine solvate molecule; and (3) An order-disorder transition in the direction of the electronically localized molecular distortion. A ^2H -NMR study on the pyridine- d_5 analogue of complex 1 indicates an order-disorder transition of the pyridine solvate molecules at the HT-transition point. A theoretical model [5] concerning the possible phase transitions in these mixed-valence complexes has been proposed and the LT-phase transition was explained with this model. It is suggested that the driving force for the ordering of the distorted Fe_3O molecules below the LT-phase transition to be from π - π overlapping between the pyridine ligands which belong to the nearest neighboring Fe_3O molecules.

In the closely related complex $[\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_3)_6(4\text{-Me-py})_3](\text{C}_6\text{H}_6)$ (2), which has the identical structure and similar Mössbauer spectra to complex 1, the dynamic disorder of the benzene solvate molecules was clearly identified by the single-crystal ^2H -NMR study [6]. It was found that the benzene molecules rotate about a local C_6 axis as well as about the C_3 axis (crystallographic c axis). This was done by measuring the residual quadrupolar coupling constant and the quadrupolar and dipolar tensors of the benzene deuterons. The faster electron transfer in complex 2 than in complex 1 can be explained by the fact that the π - π overlapping between the 4-Me-py ligands is smaller than that for the pyridine ligands in complex 1 and relatively easier rotation of the benzene solvate molecules than the pyridine solvate molecules in complex 1.

References

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