decomposition to form dioxetane **3c** as second intermediate by loss of nitrogen.[9] At −80 °C, however, the pseudorotation in **3c** occurs within the time scale of the NMR experiment. This phosphadioxetane might be responsible for the chemiluminescence similar to the case of dioxetanes.[19]

Parallel ^{31}P NMR studies were carried out for the direct observation of phospha-1,2-dioxetane which could be derived from photooxygenation of phosphonium ylides.[20] The reaction mixture of photooxygenation of [α-(methoxycarbonyl)benzylidene]triphenylphosphorane[21] (**4**, 2.4×10^{-1} M) gave a ^{31}P NMR spectrum (−107 °C) featuring pairs of singlets at −25.8 and −26.9 ppm in a ratio of 0.9:1, respectively, together with two other singlets: 25.8 (triphenylphosphine oxide) and 20.8 ppm (unreacted **4**). On
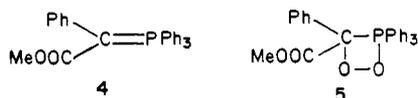
warming to 27 °C, both upfield peaks disappeared. We can assign such upfield peaks as those of the conformers of dioxetane **5**[16,23,24] similar to the case of diazine **2c**.

Acknowledgment. We thank Y. Nagai, Eisai Company Co., Ltd., for measurement of the high-field ^{31}P NMR spectra.

(19) See, for example: (a) Gunderman, K. D. "Chemiluminescence and Bioluminescence"; Plenum Press: New York, 1973. (b) Schaap, A. P.; Zaklika, K. A. "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Ed.; Academic Press: New York, 1979; p 174. (c) Schuster, G. B. *Acc. Chem. Res.* **1979**, *12*, 366.
(20) Jefford, C. W.; Barchietto, G. *Tetrahedron Lett.* **1977**, 4531.
(21) Bestman, H. J.; Schultz, H. *Justus Liebigs Ann. Chem.* **1964**, *674*, 11.
(22) When the reaction mixture was warmed to room temperature with 9,10-diphenylanthracene, a very weak light emission was observed.
(23) De'Ath, N. J.; Denny, D. Z.; Denny, D. B. *J. Chem. Soc., Chem. Commun.* **1972**, 272.
(24) An approximate value of k_c is 4×10^2 s^{-1}.[16b]

Phase Transitions Affecting Intramolecular Electron Transfer in Mixed-Valence Trinuclear Iron Acetate Complexes[1]

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In a recent paper[3] we suggested that in the solid state the ability of one of the three 4-ethylpyridine ligands of oxo-centered [Fe$_3$O(O$_2$CCH$_3$)$_6$(4-Et-py)$_3$](4-Et-py) to move between two positions as the temperature of the crystal was increased controlled

(1) A part of this paper corresponds to Contribution No. 89 from the Chemical Thermodynamics Laboratory.
(2) On sabbatical leave from the Department of Engineering Physics, The Unversity of Electro-Communications, Tokyo, Japan.
(3) Oh, S. M.; Hendrickson, D. N.; Hassett, K. L.; Davis, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 7984–7985.
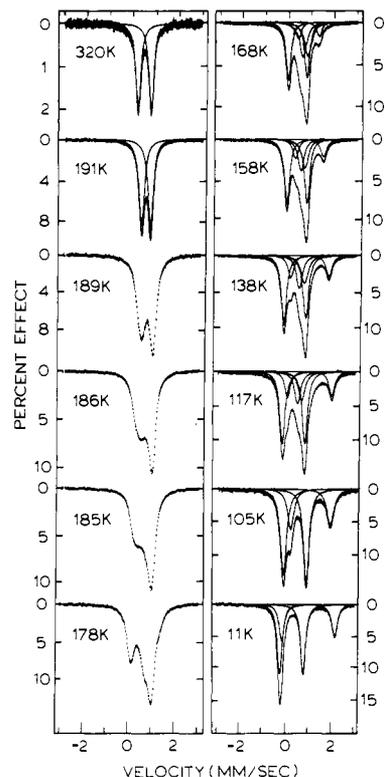
Figure 1. Variable-temperature [57]Fe Mössbauer spectra for [Fe$_3$O-(O$_2$CCH$_3$)$_6$(py)$_3$](py). Velocity scale is referenced to iron foil at room temperature.

the rate of *intra*molecular electron transfer in the mixed-valence Fe$_3$O complex. In this paper direct evidence will be presented for the presence of phase transitions in [Fe$_3$O(O$_2$CCH$_3$)$_6$(py)$_3$](py) (**1**) that affect the rate of *intra*molecular electron transfer.

Compound **1** is isostructural with the analogous manganese compound.[4,5] In the room-temperature space group R32 the Fe$_3$O triangular complexes are arranged in stacks with C_3 axes oriented down the stacks. Ongoing single-crystal X-ray work[6] shows that the pyridine solvate molecules are sandwiched between the Fe$_3$O complexes in the stacks. The plane of the solvate molecule is perpendicular to the Fe$_3$O plane. At room temperature the pyridine solvate molecules are disordered in three positions about the C_3 axis.

Variable-temperature Mössbauer spectra for **1** are shown in Figure 1. At temperatures below ~100 K, two quadrupole-split doublets are seen, one characteristic of high-spin Fe^{II} and the other of high-spin Fe^{III}. As the sample temperature is increased from 11 K, the first appreciable change in the spectrum is seen at ~117 K, where a third doublet appears. The spectrum changes dramatically as the temperature is further increased, eventually to become a single average doublet[7] at temperatures above ~190 K. It is clear that the rate of *intra*molecular electron transfer is increasing with increasing temperature. Above ~190 K it exceeds the ~10^7–10^8 s^{-1} rate which the Mössbauer technique can sense.

The heat capacity at constant pressure was measured for a 17.7794-g sample of **1** from 12 to 300 K. As can be seen in Figure 2, there are basically two phase transitions present, a first-order

(4) Baikie, A. R. E.; Hursthouse, M. B.; New, D. B.; Thornton, P. *J. Chem. Soc., Chem. Commun.* **1978**, 62.
(5) See Table III in: Catterick, J.; Thornton, P. *Adv. Chem. Radiochem.* **1977**, *20*, 291.
(6) Strouse, C. E.; Hendrickson, D. N.; Oh, S. M., unpublished results.
(7) Evidence for the fact that the single doublet seen in the 320 K spectrum is the average of the two doublets seen in the 11 K spectrum can be taken from the isomer shift data. At 320 K the single doublet has δ 0.753 (1) mm/s. At 11 K the Fe^{II} doublet has δ 1.260 (2) mm/s and the Fe^{III} doublet has δ 0.521 (1) mm/s; the average of these two doublets gives δ 0.767 mm/s.
(8) Kambara, T.; Sorai, M.; Oh, S. M.; Hendrickson, D. N., unpublished results.
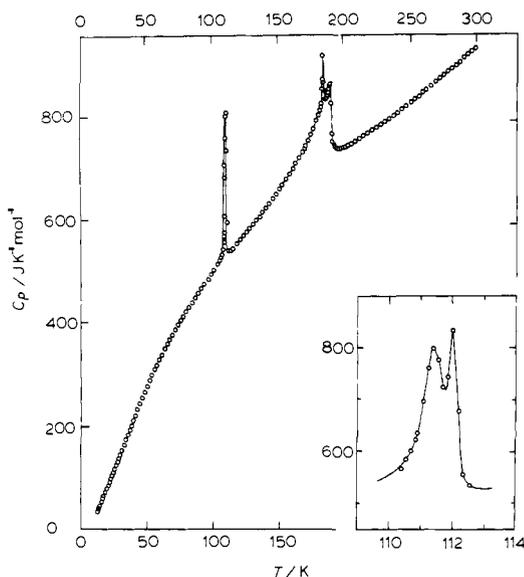
Figure 2. Plot of heat capacity at constant pressure, C_p, as a function of temperature. The inset shows an expanded view of the low-temperature heat capacity effect.

phase transition with two C_p peaks at 111.4 and 112.0 K and a higher order phase transition with two C_p peaks at 185.8 and 191.3 K. It is very interesting that the temperature of the 111–112 K phase transition occurs at the temperature where the first Mössbauer spectrum change occurs. The higher order phase transition can be seen to evolve over a large temperature range with C_p peaks at the temperature where the Mössbauer spectrum becomes a single average doublet.

It is suggested that the lower temperature phase transition is an order–disorder phase transition. At temperatures below this first phase transition the triangular complexes each have a static distortion reflecting the iron valence states. One iron is Fe^{II} and the other two are Fe^{III}. These distorted complexes are ordered in domains, e.g., homogeneous regions of crystallite where the distortions of the Fe_3O units are ordered in the same sense. At the low-temperature phase transition these domains disappear and the sense of distortion becomes randomly distributed throughout the crystallite. Cooperativity is the essence of a phase transition. The packing arrangement in **1** involves stacks of pyridine ligands with an interplanar separation of $c/3 = 3.5$ Å. The pyridine ligands from neighboring molecules experience appreciable π–π overlap and this could lead to cooperativity and the first-order phase transition at 111–112 K. In a later paper[8] it will be shown that the third doublet that appears in the Mössbauer spectrum (see Figure 1) at ~117 K is attributable to Fe_3O complexes that are electronically delocalized. The first-order phase transition at ~112 K leads to a change in the potential energy diagram such that above this temperature the zero point energies of the delocalized and localized complexes become comparable in magnitude.

The higher temperature phase transition is not first order, for it evolves over an extensive temperature range. It is likely that this phase transition involves Fe_3O molecules becoming thermally activated to change their sense of distortion combined eventually with the pyridine solvate molecules starting to rotate about the C_3 axes of the stacks of Fe_3O molecules. Preliminary single-crystal X-ray diffraction work[6] indicates that the C_3 axis disappears at ~190 K as the crystal is cooled from 300 K.

Definitive evidence for the motion of solvate molecules in the solid state has been determined for compound **2**, $[Fe_3O-(O_2CCH_3)_6(4\text{-}CH_3\text{-}py)_3](C_6D_6)$, where the solvate molecule is a deuterated benzene. Compound **2** is isostructural with **1** and shows a similar temperature dependence in its Mössbauer spectrum. A complete single-crystal ^2H NMR study has been carried out on **2** at room temperature. Rotations were carried out about three orthogonal axes. At every setting of the single crystal only a single quadrupole-split doublet is seen. It is clear that the C_6D_6

molecule is rapidly rotating about a 6-fold axis to make all deuteron sites equivalent. The principal components of the deuteron quadrupole interaction tensor were found to be -13.5 ± 0.5, -18.3 ± 0.5, and $+31.6 \pm 0.5$ kHz. These values are considerably reduced from what is expected for a C_6D_6 *fixed* in the solid in which case the axially symmetric principal components are -67 and 135 kHz. Reorientation about the C_3 axis along the molecular stacks or about a C_2 axis perpendicular to it is also present in addition to the rotation about the 6-fold axis.

Variable-temperature IR studies of **1**, isostructural $[Fe_2^{III}Co^{II}O(O_2CCH_3)_6(py)_3](py)$, and symmetric $[Fe^{III}_3O-(O_2CCH_3)_6(py)_3]ClO_4$ clearly indicate, based on the M_3O asymmetric stretch regions, that compound **1** is "valence localized" in terms of the IR experiment in the 500–800-cm^{-1} region. Thus, **1** and the $Fe^{III}_2Co^{II}$ complex each show two asymmetric stretches, whereas, the higher symmetry Fe^{III}_3 complex exhibits one such band. This same conclusion was reached by Cannon et al.[9] At or above the higher temperature phase transition the pyridine solvate molecules are rotating and the Fe_3O molecules are changing their sense of distortion much faster than can be sensed by the Mössbauer technique but slower than would average the two Fe_3O asymmetric stretching bands.

Dynamics in the solid state involving the onset of motion in a ligand, solvate molecule, or counterion at a certain temperature could in general be major factors determining whether the *intra*molecular electron transfer in a given mixed-valence complex is fast or slow. We have also detected phase transitions for the mixed-valence complex $[Fe_3O(O_2CCH_3)_6(3\text{-}CH_3\text{-}py)_3](3\text{-}CH_3\text{-}py)$,[10] which has a different solid-state structure than **1**, and for mixed-valence biferrocenium triiodide.[11]

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(10) Sorai, M.; Shiomi, Y.; Hendrickson, D. N.; Oh, S. M., unpublished results.

(11) Sorai, M.; Hendrickson, D. N.; Dong, T.-Y.; Cohn, M. J., unpublished results.

Stereoselective Synthesis of γ,δ-Epoxy-β-methyl-γ-(trimethylsilyl)alkanols. Synthesis of the C(1)–C(7) Segment of 6-Deoxyerythronolide B

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Previously, we have reported a highly enantio- and diastereoselective synthesis of *syn*- and *anti*-β-methyl-γ-(trimethylsilyl) homoallyl alcohols **1** and **2**.[1] In connection with ongoing program directed toward the utilization of these alcohols for synthesis of naturally occurring acyclic molecules such as macrolide and ionophore antibiotics, we have been interested in stereoselective synthesis of four possible diastereoisomers of γ,δ-epoxy-β-

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