tropic non-hydrogen atoms and isotropic hydrogens have converged to a standard crystallographic residual of 0.058 for the observed reflections. Additional crystallographic details are available and are described in the supplementary material.

Figure 1 is a computer-generated perspective drawing of the final X-ray model of zoanthamine. Hydrogens are omitted for clarity, and, since the absolute configuration was not determined, the enantiomer shown is an arbitrary choice.

The spectral data for zoanthamine (**1**)[3] are all compatible with the proposed structure. The ^{1}H NMR spectrum was assigned from decoupling data as follows: δ 0.92 (d, 3 H, J = 7 Hz, C-30), 0.98, 1.00, 1.20 (all s, 3 H, C-25, C-28, C-29), 1.10 (t, 1 H, J = 13 Hz, C-5), 1.17 (d, 3 H, J = 7 Hz, C-26), 1.48 (ddd, 1 H, J = 13, 12, 2 Hz, C-3), 1.56 (br, dd, 1 H, J = 12, 4 Hz, C-3), 1.55–1.90 (m, 4 H, C-7, C-8), 1.92 (d, 1 H, J = 14 Hz, C-11), 2.01 (s, 3 H, C-27), 2.10 (dd, 1 H, J = 13, 4 Hz, C-5), 2.17 (d, 1 H, J = 14 Hz, C-11), 2.23 (m, 2 H, C-14), 2.27 (m, 1 H, C-4), 2.37 (d, 1 H, J = 20 Hz, C-23), 2.42 (m, 1 H, C-13), 2.66 (dd, 1 H, J = 13, 5 Hz, C-18), 3.02 (qd, 1 H, J = 7, 5 Hz, C-19), 3.22 (s, 1 H, C-21), 3.24 (dd, 1 H, J = 7, 6 Hz, C-1), 3.29 (br d, 1 H, J = 7 Hz, C-1), 3.67 (d, 1 H, J = 20 Hz, C-23), 4.56 (m, 1 H, C-2), 5.92 (s, 1 H, C-16).

Zoanthamine (**1**) is the first example of a new class of alkaloids of unknown biosynthetic origin. Although there are some elements that suggest a triterpenoid origin, the carbon skeleton is far from a normal polyisoprenoid system. Two related metabolites have been isolated from the same organism and will be described in a future paper.[6]

Acknowledgment. This research was generously funded by grants from the University Grants Commission, New Delhi, the National Institutes of Health (CA24487 and AI11969), and the New York State and California Sea Grant Programs.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances, bond angles, and torsional angles for zoanthamine (**1**) (8 pages). Ordering information is given on any current masthead page.

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(6) Zoanthamine was inactive as a skin irritant[7] and is being reisolated for screening as an eye irritant.

(7) We thank Dr. Robert S. Jacobs, U. C. Santa Barbara, for these data.

Electron Transfer in Mixed-Valence, Oxo-Centered, Trinuclear Iron Acetate Complexes: Effect of Statically Disordered to Dynamically Disordered Transformation in the Solid State

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Received June 29, 1984

During the last decade there has been considerable interest in mixed-valence transition-metal complexes.[1,2] In the case of many such complexes the electron-transfer rate for a *solution-state* species has been determined indirectly and to some degree qualitatively by analyzing the energy and line shape of the intervalence-transfer (IT) electronic absorption band in the near-IR. For certain mixed-valence complexes such as mixed-valence biferrocenes[3-7] the electron-transfer rate in the *solid state* has been characterized relatively directly with various spectroscopic and physical techniques. In this communication we report several observations that strongly suggest that electron-transfer rates for mixed-valence complexes in the *solid state* are determined, at least in part, by dynamic disorder of coordinated ligands or solvate molecules.

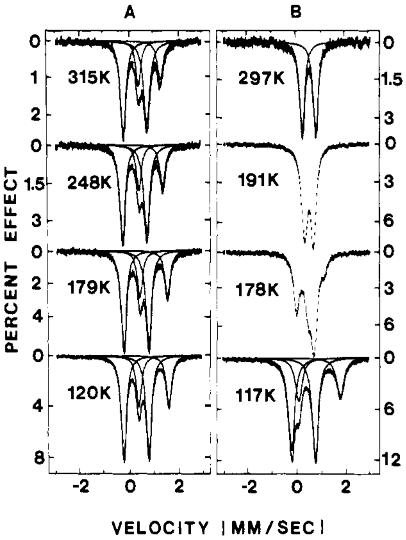

Figure 1. Variable-temperature ^{57}Fe Mössbauer spectra for $[Fe_3O(O_2CCH_3)_6(py)_3]$ (left panel) and $[Fe_3O(O_2CCH_3)_6(py)_3](py)$ (right panel).

The mixed-valence, oxo-centered, basic iron acetates with general composition $[Fe_3O(O_2CR)_6(base)_3]\cdot(solvate)$ have been characterized[8,9] to have appreciable electron-transfer rates in spite of weak antiferromagnetic exchange interactions. Our observations on these complexes and the results of single-crystal X-ray structures of $[Fe_3O(O_2CCH_3)_6(4\text{-}Etpy)_3](4\text{-}Etpy)$ (**1**) at 163 and 298 K are summarized herein.

One of the two main discoveries that we made concerning the basic iron acetates is that the solvate molecule has a dramatic effect on the electron-transfer rate for a given mixed-valence complex. Several new series (different substituted pyridines used for each series) of trinuclear iron acetates have been prepared in which only the solvate molecule differs. For example, in the series $[Fe_3O(O_2CCH_3)_6(py)_3](solvate)$, the solvate molecule can be pyridine (py), benzene, or nothing. As can be seen in Figure 1, the variable-temperature ^{57}Fe Mössbauer characteristics of $[Fe_3O(O_2CCH_3)_6(py)_3]$ and $[Fe_3O(O_2CCH_3)_6(py)_3](py)$ are different. All of the mixed-valence iron acetates give a Mössbauer spectrum at temperatures of ~100 K or lower that is characteristic of a localized electronic structure with one Fe^{II} ion and two Fe^{III} ions. The nonsolvated complex does *not* show any evidence of a change in the electron-transfer rate as the temperature is increased to 315 K. On the other hand, in the case of the pyridine solvate complex the electron-transfer rate increases as the tem-

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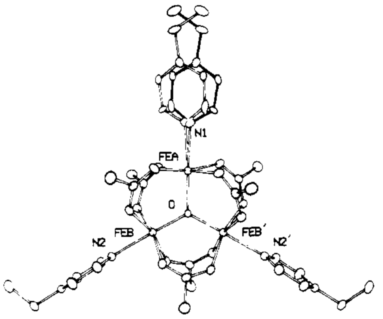

Figure 2. Molecular structure at 163 K of the mixed-valence Fe_3O complex in Figure 1. The two positions of the disordered 4-Etpy ligand at the unique iron ion (FeA) are shown.

perature is increased. Above 200 K only one average quadrupole-split doublet is seen and the electron-transfer rate is greater than ~10^8 s^{-1}. If the solvate is benzene, a different temperature dependence is observed.

The significance of our second major observation on the mixed-valence iron complexes is more subtle. We have found for many of the mixed-valence complexes exhibiting temperature-dependent Mössbauer spectra that there is no evidence of line broadening. The "Fe^{II}" and "Fe^{III}" doublets gradually move together without broadening, giving an average doublet as the sample temperature is increased, eventually becoming a single doublet. The dynamic process that leads to the averaging of the Fe^{II} and Fe^{III} doublets is always occurring faster than the Mössbauer technique can sense.

We propose that it is a transformation in certain ligands and/or solvate molecules from a statically disordered to a dynamically disordered state that indirectly controls the rate of electron transfer in these solid-state, mixed-valence complexes. At low temperatures the solid is statically disordered, and the environment about the mixed-valence core is probably asymmetric. We suggest that solvate and/or certain parts of ligands become dynamically disordered as the temperature of the solid is increased. This dynamic disorder would tend to symmetrize the environment of the mixed-valence complex. In effect, if the intermetal electronic coupling were constant as a function of temperature, the symmetrizing effect of the dynamic disorder reduces the potential barrier for electron transfer and the electron-transfer rate would be increased dramatically. No Mössbauer line broadening would be expected because the librations (phonons) operative in the dynamic disorder could well be occurring at a frequency greatly in excess of 10^8 s^{-1}.

The molecular and solid-state structures of **1** have been determined at 163 and 298 K by single-crystal X-ray diffraction techniques.[12] An oxo-centered triangular arrangement of three iron ions is present (Figure 2). The space group does *not* change from 298 to 163 K. There are two elements of disorder in the solid. The 4-Etpy solvate molecule is disordered about a center of inversion. There is a 2-fold axis of symmetry in the Fe_3O plane and the 4-Etpy ligand bonded to the unique iron ion is disordered about this axis. Large thermal parameters associated with the atoms of this disordered ligand are consistent with dynamic disorder. The ordered 4-Etpy ligands are firmly held (four intermolecular non-H contacts less than 3.5 Å), while the disordered ligand is loosely surrounded (shortest non-H contact greater than 3.7 Å, to solvate). Significantly, the Fe_3 triangle becomes more equilateral as the crystal is heated from 163 to 298 K. At 163 K the bond distances to the central oxide ion are Fe^{II}–O = 2.011 (4) and Fe^{III}–O = 1.856 (1) Å, whereas at 298 K they become "Fe^{II}"–O = 1.954 (5) and "Fe^{III}"–O = 1.880 (1) Å.

At 298 K the two Mössbauer doublets for **1** are close to, but still have not become, a single average doublet. Additional convincing evidence for the presence of dynamic disorder comes from the areas (recoilless fractions) of these doublets. At temperatures below ~100 K the area ratio of the two doublets is 2:1, in keeping with the ratio of Fe^{III} and Fe^{II} ions in the molecule. As the sample, temperature is increased above ~100 K, the Fe^{III}/Fe^{II} doublet area ratio increases until at 298 K it is 3.5:1. In order words, the dynamic disorder of the 4-Etpy ligand bonded to the "Fe^{II}" ion reduces the recoilless fraction of this iron site.

Acknowledgment. We thank the National Institutes of Health for support of the work at the University of Illinois through Grant HL13652 to D.N.H. and the Robert A. Welch Foundation for support of the work at the University of Texas at Austin through Grant F-233 to R.E.D.

Supplementary Material Available: Crystallographic summaries, listings of atomic positional parameters and thermal parameters, and selected bond lengths and angles for both structure determinations of **1** (7 pages). Ordering information is given on any current masthead page.

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[12] Monoclinic, $C2/c$, $Z = 4$: at 163 K, $a = 17.060$ (6) Å, $b = 16.934$ (7) Å, $c = 16.183$ (8) Å, $\beta = 104.49$ (4)°, $V = 4526.6$ Å^3, $D_{calcd} = 1.418$, $R = 0.045$, $R_w = 0.042$ for 2847 observed reflections ($|F_o| \geq 6.0\sigma|F_o|$); at 298 K, $a = 17.142$ (3) Å, $b = 17.004$ (1) Å, $c = 16.571$ (4) Å, $\beta = 104.27$ (2)°, $V = 4681.1$ Å^3, $D_{calcd} = 1.371$, $R = 0.052$, $R_w = 0.055$ for 2809 observed reflections ($|F_o| \geq 6.0\sigma|F_o|$).

First Stable Compound with a Protonated Phosphorus-Bound Nitrogen Atom

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Received July 27, 1984

Compounds containing quaternarized, phosphorus-bound nitrogen atoms are scarce[1–5] and no example of a compound with a protonated nitrogen of this type appears to have been isolated so far. As a rule, the haloacids readily cleave the P–N "single" bond of aminophosphanes, phosphine oxides, and related compounds, to give the corresponding halophosphine derivatives and ammonium halides. This well-documented reaction is rapid and complete at or below room temperature.[6–8] It has been extensively used as a commodious, smooth access to mixed halophosphanes and to many of their derivatives, which often cannot be isolated conveniently by other routes.[7] Coordination of the phosphorus atom to transition metals does not alter the issue of the reaction, which has also provided routes to new adducts of mixed P(III) ligands, many of which are not accessible through direct substitution.[8] Protonation of the nitrogen atom with preservation of the P–N bond seems never to have been achieved. Although such species have been postulated as reaction intermediates,[9] no direct

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[1] They consist essentially of two phosphatranes,[2] some borane aminophosphane or phosphorane adducts[3] and some transition-metal phosphoranides.[4] Evidence has also been presented for $SP(\overline{NCH_2C}H_2)_3{\cdot}BH_3$ in which at least one of the BH_3 groups is expected to be bonded to a nitrogen.[5]

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