Table V

solute	concn.[a] range	atom fract. deuterium	slope perpend. field[b]	slope parallel field[b]	slope corr.[c]
glucose	0.002–0.02	0.0	164 ± 34	−123 ± 4	68.6
glucose	0.002–0.02	0.90	154 ± 26	−138 ± 21	56.8
α-methyl glucoside	0.002–0.02	0.0	594 ± 26	996 ± 157	726
α-methyl glucoside	0.002–0.02	0.93	372 ± 91	1145 ± 79	630

[a] Moles of one solute exchangeable site/moles of total exchangeable sites. [b] Slope of plot of chemical shift of exchangeable proton resonance, relative to an external reference of pure solvent, as a function of solute concentration, Hz/(moles of one solute exchangeable site/moles of total exchangeable sites). Positive values indicate upfield shifts of sample resonance relative to external reference. [c] Data corrected (using eq 2) for the difference between the magnetic susceptibilities of sample and reference solutions, Hz/(moles of one solute exchangeable site/moles of total exchangeable site).

Figure 2 shows the results of such an experiment, comparing chemical shifts obtained for glucose in two different spectrometers. In these experiments, solutions were prepared gravimetrically from α-D-glucose and transferred to the outer cell of a coaxial tube; pure solvent (H_2O or D_2O of atom fraction deuterium, n) was then added to the internal cell, and the tube was sealed with parafilm and allowed to equilibrate overnigth at 34 °C. Chemical shifts were determined relative to the external reference, first by using a Bruker WM-250 spectrometer operating at 250 MHz and 34 °C and then by using a Varian EM-390 spectrometer operating at 90 MHz and at 34 °C. For comparison of results, chemical shifts were corrected to a common operating frequency of 90 MHz. Figure 2 shows chemical shifts that were observed for exchangeable protons of glucose solutions in H_2O (closed symbols) and D_2O (open symbols). Results obtained by using a spectrometer employing a permanent magnet with a perpendicular field (circles) are quite different from those obtained with a superconducting magnet with a field parallel to the sample (triangles), indicating that magnetic susceptibility effects are pronounced. Table V compares the slopes obtained with glucose and with α-methyl glucoside, and it can be seen that magnetic susceptibility effects of these compounds differ in both a qualitative and a quantitative sense.

In principle, true fractionation factors can be computed from these results by using eq 2a and 4a. However, compounded errors in the resulting values (1.23 ± 0.28 for glucose and 1.17 ± 0.16 for α-methyl glucoside) are too great to be useful in deciding whether they differ significantly from unity. How likely does it seem that fractionation factors of individual hydroxyl groups in thes compounds differ from unity? The values above represent complex averages of values for all the exchangeable protons in these compounds, which include primary and secondary alcoholic groups and, in the case of glucose, a hemiacetal hydroxyl group. Direct measurements indicate a value of 0.99 for methanol.[58] A solvent isotope effect of 0.94 ± 0.06 on methanol addition to acetaldehyde[49] suggests a fractionation factor of 0.95 ± 0.06 for the resulting hemiacetal. Equilibria of covalent hydration of 2-acetyl-3,4-dimethylthiazolium ion[59] and of addition of one and two water molecules to pteridine[60] also indicate fractionation factors indistinguishable from unity. Slightly higher values, averaging 1.08[16-19] are calculated for the fractionation factors of protons in *gem*-diols formed from aliphatic aldehydes. With these last exceptions, it seems that NMR evidence for hydroxyl fractionation factors in excess of unity may not be well founded and that values obtained by other methods may be more reliable.

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Communications to the Editor

Valence Delocalization in Mixed-Valence 1′,6′-Diiodobiferrocenium Triiodide

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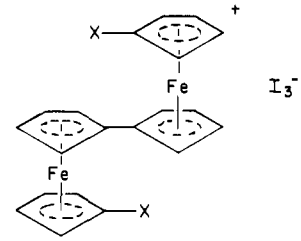
Discoveries made over the past 2 years have contributed to a much clearer understanding of factors that control intramolecular electron transfer in mixed-valence transition-metal complexes. In a very recent paper[3] it was shown that for the oxo-centered mixed-valence complex $[Fe_3O(O_2CCH_3)_6(4\text{-Et-py})_3](4\text{-Et-py})$, where 4-Et-py is 4-ethylpyridine, a transformation in the solid-state structure from statically disordered at low temperatures to dynamically disordered at high temperatures dramatically affects the intramolecular electron-transfer rate. Similar observations have now been made on several other mixed-valence trinuclear iron acetate complexes.[4] In this paper we report observations on biferrocenium triiodide (**1**), which has previously been reported[5]



1. X = H
2. X = I
3. X = Br
4. X = Cl
5. X = CH_2CH_3
6. X = $CH_2CH_2CH_3$
7. X = $CH_2CH_2CH_2CH_3$
8. X = CH_2Ph

to be valence localized at 300 K, and the X-ray structure of 1′,6′-diiodobiferrocenium triiodide (**2**), which is valence delocalized in the range 300–4.2 K.

The series of substituted biferrocenium complexes listed above will provide important information on intramolecular electron

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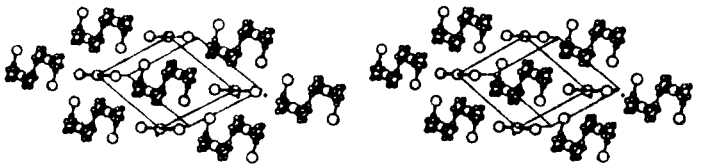

Figure 1. Stereoview showing the arrangement of 1′,6′-diiodobiferrocenium cations and triiodide anions on the mirror plane of the unit cell. The separation between the iodocyclopentadiene iodine atom and the I_3^- ion is 3.98 Å, well within twice the van der Waals radius of iodine.

transfer. Within this series **1**[5,6] and **4**[7] are valence localized at 300 K on the Mössbauer time scale, **2**[6] and **3**[7] are valence delocalized from 300 to 4.2 K, and **5**,[8] **6**,[8] **7**,[9] and **8**[9] all show a temperature dependence such that they are localized below 200 K but become delocalized above 290 K. Structural characterization of **6** has shown that the cations and anions exist in segregated "slipped stacks" in the solid state.[10] It is likely that compounds **5** and **7** have similar structures. Compound **2** has been characterized structurally at 295 K and been found to have quite a different crystal structure.[11] The 1′,6′-diiodobiferrocenium cation is centered about a site of crystallographically imposed $2/M$ symmetry in the unit cell and has the trans conformation found also for compound **6**. This symmetry requires that both iron atoms reside at environmentally equivalent positions in the unit cell. Figure 1 shows the alignment of the complex cations and I_3 anions on the crystallographic mirror plane. Close association between cations and anions was also found in the crystal structure of **6**. It is our conviction that rapid intramolecular electron transfer in **2** is supported by the symmetrical solid-state environment of both halves of the cation. Electron transfer in **2** occurs more rapidly than the Mössbauer and EPR time scales (rate $> 10^{10}$ s^{-1}) at 4.2 K, however, examination of the KBr-pellet IR spectrum of **2** and all the other salts listed above has shown that the cation is localized on the IR time scale (rate $<10^{13}$ s^{-1}).

All of the mixed-valence cations, 1–8, probably have the same trans conformation with a planar fulvalenide ligand. The magnitude of electronic coupling, i.e., the interaction of the d manifolds on the two iron ions as propagated by the fulvalenide ligand, is probably not very different from one cation to another. Furthermore, the vibronic coupling of the PKS model[12] is also probably not changing very much throughout the series. We suggest that it is the nature of the solid-state environment that determines the rate at which intramolecular electron transfer occurs. In the case of "valence localized" species the environment about the cation in the solid is not symmetric and the barrier for electron transfer is increased. If the I_3^- ion is fixed in position closer to one iron than the other, this environmental asymmetry reduces the rate of electron transfer. The Fe^{II} and Fe^{III} doublets in the Mössbauer spectra of **5**–**8** become a single average quadrupole-split doublet at temperatures of 275,[7] 245,[7] 275,[9] and 260 K,[9] respectively. At low temperatures the I_3^- ion (and substituents) are fixed in a position closer to one iron ion, but as temperature is increased the I_3^- ion becomes dynamically disordered such that on the Mössbauer and EPR time scales both metals experience equivalent environments. This motion of the I_3^- changes the potential energy curve for intramolecular electron transfer in the cation.

Two recent observations have been made which support this conclusion. We have found that the Mössbauer spectrum obtained upon heating a microcrystalline sample of **1** to 346 K consists of a single average quadrupole-split doublet. Recrystallization of microcrystalline samples of **7** and **8** by slow diffusion in CH_2Cl_2/hexane gives highly crystalline samples which exhibit one doublet at 300 K in their Mössbauer spectrum, whereas the microcrystalline samples each give a spectrum with two doublets. Two different polymorphs appear to exist in each case, one valence localized, the other delocalized on the Mossbauer time scale at 300 K. A crystallographic study[9] on delocalized crystals of **7** has shown considerable disorder of the I_3^- ion along the segregated stack of triiodide ions in the crystal structure.

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Supplementary Material Available: Tables of atomic positional and thermal parameters and observed and calculated structure factors for 1′,6′-diiodobiferrocenium triiodide (5 pages). Ordering information is given on any current masthead page.

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Metal Carbonyl Fragments as a New Class of Markers in Molecular Biology

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Although the utility of transition-metal carbonyl complexes in organic synthesis[1] and industrial catalysis[2] is now well established, their potential in biochemistry is only just being realized.[3] We report here an unprecendented use of these organometallic complexes in the important field of steroid hormone receptor assay.[4] Variations in the concentration of certain hormone receptors are clearly implicated in such cancers as breast carcinoma.[5] The

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