Kinetics of Intramolecular Electron Transfer in Binuclear $(NC)_5Fe^{II}$–CN–Co^{III}(chelate) Complexes by Picosecond Absorption Spectroscopy

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Abstract: The rates of intramolecular electron transfer in the binuclear complexes $(NC)_5Fe^{II}$–CN–Co^{III}(chelate) (where chelate = NBETA and HEDTA) have been measured directly using picosecond absorption spectroscopy. Excitation of the Co^{III} $^1T_{1g} \leftarrow {}^1A_{1g}$ band by a 530-nm 6-ps fwhm laser pulse is followed by rapid electron transfer from Fe^{II} resulting in Fe^{III}, and Co^{II} in the ^2E state. The subsequent decay of Fe^{III} occurs with a half-life of 150 ps. Our data indicate that the Co^{II} ^2E state has ~75-ps lifetime and experiences a low-spin to high-spin intersystem crossing to form the $^4T_{1g}$ ground state. The subsequent spin-permitted electron transfer back to the Fe^{II} species occurs in ~95 ps. Curves calculated on the basis of this mechanism are in good agreement with the experimental data.

Recently, picosecond spectroscopy has been used to study electron transfer reactions between metal centers of organometallic compounds. In several of these studies the metals are bonded to porphyrins which model photosynthesis[1] or bridged by 4,4′-bipyridine (bpy) or pyrazine.[2] In particular, the reduction of $(NH_3)_5Co^{III}$bpy by $Fe^{II}(CN)_5H_2O$[3] or $Ru^{II}(NH_3)_4(SO_2)Cl$[4] is known to proceed by an inner sphere mechanism with a bypyridine bridge. The time for the completion of electron transfer is slow, presumably because of the large separation of the metals. By suitable choice of ligands the reaction $Fe^{III} + Co^{II} \rightarrow Fe^{II} + Co^{III}$ can be made to proceed essentially to completion.

Previous studies of the reduction of hexacyanoferrate ion, $Fe(CN)_6^{3-}$, by ethylenediaminetetraacetatocobaltate(II), $CoEDTA^{2-}$, have been shown to proceed via the mechanism.[5,6]

$$\begin{tikzcd}
\mathrm{Fe^{III}(CN)_6^{3-}} + \mathrm{Co^{II}EDTA^{2-}} \arrow[r, shift left, leftarrow, "K_1"] \arrow[r, shift right] \arrow[d, shift right, "\text{outer-sphere}\ k_3"'] & \mathrm{(NC)_5Fe^{III}\text{-}CN\text{-}Co^{II}EDTA^{5-}} \arrow[d, shift right, leftarrow] \arrow[d, shift left, "k_{\mathrm{et}}\ \text{inner-sphere}"] \\
\mathrm{Fe^{II}(CN)_6^{4-}} + \mathrm{Co^{III}EDTA^{-}} \arrow[u, shift right, "k_{-3}"'] & \mathrm{(NC)_5Fe^{II}\text{-}CN\text{-}Co^{III}EDTA^{5-}}
\end{tikzcd} \qquad (1)$$

Upon mixing these two reactants, a bridged intermediate, Fe^{II}–CN–Co^{III}, species forms. The reaction proceeds to final products via a slower outer-sphere pathway (k_3).

Recently, we have examined the reaction of pentadentate–EDTA derivative complexes of cobalt(II) with $Fe(CN)_6^{3-}$.[7] Two complexes, *N*-hydroxyethylethylenediaminetriacetatocobaltate(II) (Co^{II}HEDTA) and *N*-benzylethylenediaminetriacetatocobaltate(II) (Co^{II}NBETA), were prepared with $Fe(CN)_6^{3-}$ at pH 6.0, 25 °C at 0.26 M ionic strength. An immediate purple color was observed which is indicative of the Fe^{II}–CN–Co^{III}-(chelate) bridged species. No further reactions to final products were observed. The IR spectra of the corresponding silver salts indicate that the iron cyanide replaces the sixth coordination previously occupied by a water molecule on the Co(II) complex and that the three acetate carboxyl groups are equivalently bound to the cobalt.[7b,8] The binuclear bridged species can be stored at room temperature indefinitely without detectable decomposition.

Attempts to measure either the inner-sphere electron transfer rate (k_{et}) by conventional stop-flow and temperature-jump techniques of the Fe^{II}–CN–Co^{II} have been unsuccessful.[9] We present here a direct picosecond study of intramolecular electron transfer in binuclear complexes, Fe^{II}–CN–Co^{III}.

Experimental Section

Materials. $Na_3Fe(CN)_6$ and hydrated reagent $NaClO_4$ and *N*-hydroxyethylethylenediaminetriacetic acid (HEDTA) were purchased from Pfaltz and Bauer and G. F. Smith Chemical Co., respectively. The disodium salt of ethylenediaminetetraacetic acid (EDTA) was purchased from Matheson Coleman and Bell, and *N*-benzylethylenediaminetriacetic acid from LaMont Laboratories, and the cobaltous nitrate, 50% standard NaOH, methanol, NaCN, $NaNO_3$, and $AgNO_3$ were Fisher reagent grade chemicals. Ethylene glycol and glycerol were purchased from Aldrich. Filtered distilled–deionized water was used for solution preparation. All materials were used without further purification except the $NaNO_3$, which was dried in an oven at 80 °C for 2 h before use.

Solution Preparation. Stock solutions of all chemicals were prepared by weight, except for $Co(NO_3)_2$ solutions, which were standardized by titration with standard EDTA using Xylenol Orange indicator.[10] Co^{II} chelate solutions were prepared with 10% excess of the appropriate chelate. Hexacyanoferrate(III) solutions were analyzed spectrophotometrically with a molar absorbance of 1023 M^{-1} cm^{-1} at 420 nm. All solutions were prepared at pH 6.0 and I = 0.26 M with $NaClO_4$ or $NaNO_3$. No difference in the kinetic data was observed between these two ionic strength adjusters. All pH measurements were made with a Fisher Accumet Model 520 or 140 equipped with a glass microprobe electrode.

The bridged species, $(NC)_5Fe^{II}$–CN–Co^{III}NBETA and $(NC)_5Fe^{II}$–CN–Co^{III}HEDTA were prepared by addition of $Fe^{III}(CN)_6^{3-}$ to a solution containing the appropriate Co^{II} chelate (pH 6.0) until ~1% excess $Fe^{III}(CN)_6^{3-}$ was present. Under these conditions the experimental equilibrium constant for the formation of the bridged Fe^{II}–CN–Co^{III} species is approximately 10 000.[8] On mixing, an immediate color change to purple was observed which is indicative of the bridged species formation.

The oxidized species Fe^{III}–CN–Co^{III} were prepared by adding H_2O_2 to a solution of Fe^{II}–CN–Co^{III} and gently warming. Co^{III} pentadentate chelate complexes were prepared in the same manner as above. After formation, the respective solutions were readjusted to pH 6.0 with either dilute HNO_3 or $HClO_4$. The aquo ligand on the Co^{III} chelate complexes could be replaced by OH^- or CN^- with NaOH or NaCN. The bonding order was found to be $H_2O < CN^- < OH^-$.[7]

Apparatus. UV–visible spectra were recorded by Cary 15 and Varian 634 spectrometers. A similar laser system to that used in the kinetic measurements has been described in detail elsewhere.[11,12] Briefly, it

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Table I. Spectral Transitions

compound	d orbitals	λ_{max}	assigned transitions
$Fe(CN)_6{}^{4-}$	$t_{2g}{}^6$	323 nm	$^1T_{1g} \leftarrow {}^1A_{1g}$*
		270 nm	$^1T_{2g} \leftarrow {}^1A_{1g}$*
$Fe(CN)_6{}^{3-}$	$t_{2g}{}^5$	420 nm	charge-transfer band obscures $^2T_{2g}$ ground-state transition[a]
Co^{II}(chelate)	$t_{2g}{}^5\ e_g{}^2$	unresolved doublet	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$*
		480–510	$^4A_{1g} \leftarrow {}^4T_{1g}$*
Co^{III}(chelate)	$t_{2g}{}^6$	540 nm	$^1T_{1g} \leftarrow {}^1A_{1g}$*
		382 nm	$^1T_{2g} \leftarrow {}^1A_{1g}$*
Fe^{II}–CN–Co^{III}	$t_{2g}{}^6/t_{2g}{}^6$	575 nm	charge-transfer band contribution to $^1A_{1g}(Co^{III})$ ground state
Fe^{III}–CN–Co^{III}	$t_{2g}{}^5/t_{2g}{}^6$	420 nm	charge-transfer (Fe III) band
		530 nm	$^1T_{1g}(Co^{III}) \leftarrow {}^1A_{1g}$

[a] Reference 14.

consists of a passive mode locked Nd^{3+}:glass oscillator producing a train of approximately 6-ps fwhm, 1060-nm pulses, separated by approximately 9 ns. This is followed by a single pulse selecting Pockels cell. The pulse is then amplified by three Nd^{3+}:YAG amplifiers and a Nd^{3+}:glass amplifier. The amplified pulse is frequency doubled by a KDP crystal, and the resulting 530-nm light is split off for sample excitation. The remaining 1060-nm light is passed through a H_2O/D_2O cell to produce a visible light continuum. The continuum pulse is then passed through a 6-ps or 20-ps echelon and then split to reference and interrogation components. The beams are recombined and focused through a 0.25-m monochromator onto a Vidicon SIT tube interfaced into a PAR 1205 OMA (optical multichannel analyzer) and computer. The wavelengths used during this study were 420, 490, 575, 590, and 610 nm. This system examines the change in optical density (ΔOD) of a given sample at 6-ps or 20-ps intervals at one wavelength. The bandpass of the monochromator was determined to be ±8 nm. Ten segments (echelon steps) were used for each analysis.

The experimental system utilized for the measurement of the transient spectra has also been described elsewhere.[13] Briefly, it consists of a mode locked Nd^{3+}:YAG oscillator followed by a single-pulse selector and two Nd:YAG amplifiers. The 1064-nm pulse is ~25 ps fwhm. The 532-nm excitation pulse and continuum are produced by a KDP crystal and H_2O/D_2O, respectively. The reference and interrogation beams are focused onto the slit of a 0.25-m monochromator coupled to a Vidicon ISIT which is interfaced with a PAR 1215 OMA2 and Data General Eclipse s/130 minicomputer. This system measures the transient adsorption spectra at one time setting.

Kinetic Measurements. All measurements were made using a 5-mm glass sample cell. The concentration of bridged species was maintained at 4 mM, resulting in an optical density of 0.9–1.0 at 530 nm. Low-temperature studies were conducted by partial immersion of the cell in water/ice/NH_4Cl solution.

At −1 °C the following solvent systems were studied; water, 55% water/45% methanol, 55% water/45% ethylene glycol, and 55% water/45% glycerol. In all cases of mixed solvents, the sample water solution was cooled below 0 °C and the appropriate solvent slowly added with mixing. For all these mixtures, the stability of the bridged complex was affected by addition of the organic solvents producing a shift in the equilibrium constant. This resulted in the apparent production of starting materials ($Fe^{III}(CN)_6{}^{3-}$ and Co^{II}(chelate)). By working at lower temperature, we could minimize the amount of bridged species decomposition.

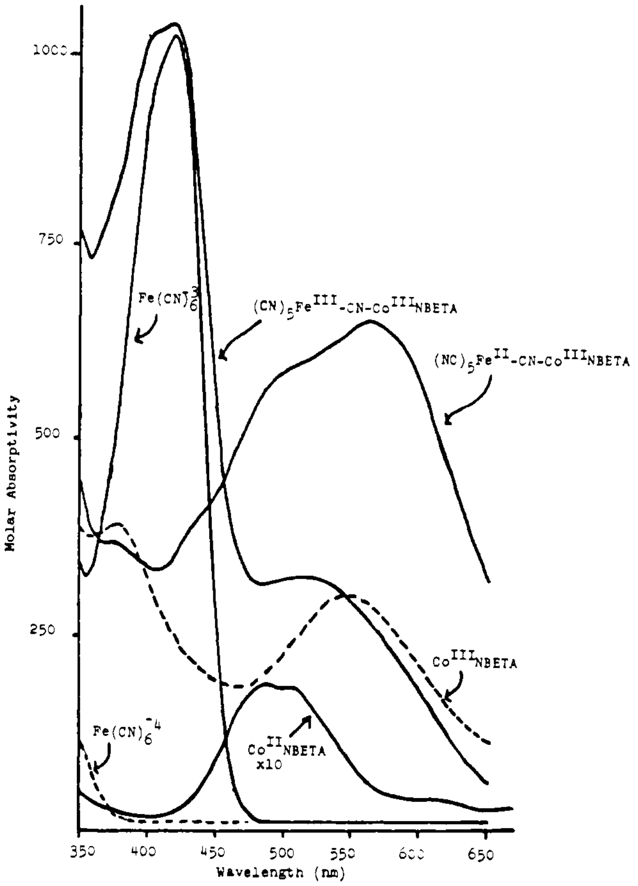

Figure 1. Visible spectra of various iron and cobalt complexes.

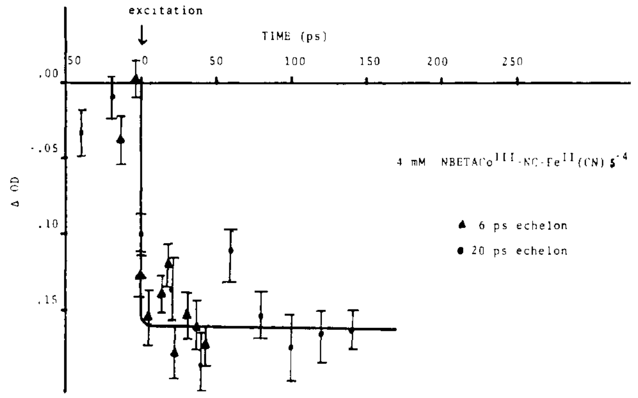

Figure 2. Experimental plot of the change in absorbance of NBETA-Co^{III}–NC–$Fe^{II}(CN)_5{}^{4-}$ excited with 530-nm 6-ps laser pulse and interrogation at 575 nm vs. time (ps). The extent of bleaching remains constant for >500 ps in the HEDTA case.

Results and Discussion

Visible absorption spectra of the NBETA compounds examined are shown in Figure 1. We found that in all cases NBETA and HEDTA complexes had very similar spectra. Table I contains the absorbance maxima and their assigned transitions.[14] It is possible that the intervalence transition occurs in the 500–600-nm band as just recently proposed by Vogler and Kisslinger,[15] however, since complete description of this assignment is not presented in their short communication and in view of the fact that the spectra of the bridged complexes are qualitatively the same as the sum of their mononuclear components, for the present we have made the same assignments to these transitions. The near-IR region 5000 to 18 000 cm^{-1} was also examined in the Fe^{II}–CN–Co^{III} compounds. No intervalence band was observed indicating this transition has ϵ_{max} of less than 5 M^{-1} cm^{-1}. The two spectral regions of greatest interest occur at the Fe^{III} absorption at 420 nm and at (Co^{II} and Co^{III} absorption) 480–610 nm. Since Fe^{II} has no visible absorption, unambiguous kinetic measurements of the formation and disappearance of Fe^{III} can be performed. However, Co^{II} and Co^{III} absorb in the same region; therefore the cobalt oxidation state may be assigned only indirectly.

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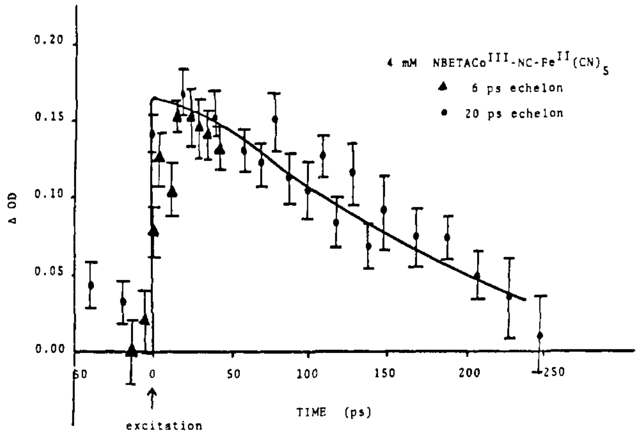

Figure 3. Experimental plot of the change in absorbance of NBETA-Co^{III}–NC–$Fe^{II}(CN)_5^{4-}$ excited with 530-nm 6-ps laser pulse and interrogation at 420 nm vs. time (ps). The solid curve corresponds to the normalized optical density calculated on the basis of the mechanism in eq 2–6.

Table II. Summary of Room Temperature Picosecond Kinetics

compound^a	interrogating wavelengths, nm	change in opt abs after 530-nm excitation
H_2O-$NaNO_3$ or $NaClO_4$	420, 575	none
$Fe^{II}(CN)_6$ + Co^{III}EDTA	420, 575	none
Co^{III}NBETA, Co^{III}HEDTA	575	none
Co^{III}(chelate)(CN)	575	none
Fe^{III}-CN-Co^{III}(chelate)	420, 575	none
Fe^{II}-CN-Co^{III}(chelate)	420	absorption increase
	575	absorption decrease

^{a} Chelate = HEDTA and NBETA.

The 530-nm, 6-ps laser pulse excites the $^1T_{1g} \leftarrow {}^1A_{1g}$ ($t_{2g}{}^5e_g \leftarrow t_{2g}{}^6$) transition in Co^{III}. The bleaching of this band as well as the 420-nm absorbance was found to have roughly linear power dependence making two-photon excitation to higher levels unlikely. In the case of the mononuclear Co^{III}(chelate) as well as the Fe^{III}–Co^{III} complexes no transient bleaching of this band is observed, indicating that relaxation back to the ground state occurs in <6 ps or the unlikely case of equal cross sections of upper excited state transitions and ground state. However, as shown in Figure 2, bleaching does occur in the $(CN)_5Fe^{II}$–CN–Co^{III}X (X = HEDTA or NBETA) and persists for >500 ps. The bleaching is not irreversible and recovers completely between laser shots (~30 s). This is accompanied with a fast (<10 ps) rise in the transient 420-nm absorption which decays nonexponentially with a half-life of ~150 ps (Figure 3). These data are summarized in Table II. The picosecond kinetic results for HEDTA and NBETA are identical within experimental error. Figure 4 shows the transient absorption difference spectra following excitation with a ~25-ps fwhm 532-nm pulse. Identical spectra were obtained at 25 and 125 ps following excitation over the wavelength range of 400–470 nm. A change in absorption maxima occurs at 420 nm with a shape similar to that of the $Fe^{III}(CN)_6$ spectrum (Figure 1) and bleaching occurs at longer wavelengths, thereby producing an isobestic point at 448 nm. The following mechanism is proposed to explain the spectra and kinetic results.

$$\mathrm{Fe^{II}\text{–}CN\text{–}Co^{III}} \xrightarrow{h\nu} \mathrm{Fe^{II}\text{–}CN\text{–}Co^{III*}} \quad \text{(excitation)} \qquad (2)$$

or

$$\mathrm{Fe^{II}\text{–}CN\text{–}Co^{III}} \xrightarrow{h\nu} \mathrm{Fe^{III}\text{–}CN\text{–}Co^{II**}} \quad \text{(excitation)}$$

$$\mathrm{Fe^{II}\text{–}CN\text{–}Co^{III*}} \rightarrow \mathrm{Fe^{III}\text{–}CN\text{–}Co^{II**}} \quad (<10\ \text{ps}) \qquad (3)$$

$$\mathrm{Fe^{III}\text{–}CN\text{–}Co^{II**}} \rightarrow \mathrm{Fe^{III}\text{–}CN\text{–}Co^{II}} \quad (\sim 75\ \text{ps}) \qquad (4)$$

$$\mathrm{Fe^{III}\text{–}CN\text{–}Co^{II}} \rightarrow \mathrm{Fe^{II}\text{–}CN\text{–}Co^{III*}} \quad (\sim 95\ \text{ps}) \qquad (5)$$

$$\mathrm{Fe^{II}\text{–}CN\text{–}Co^{III*}} \rightarrow \mathrm{Fe^{II}\text{–}CN\text{–}Co^{III}} \quad (>500\ \text{ps}) \qquad (6)$$

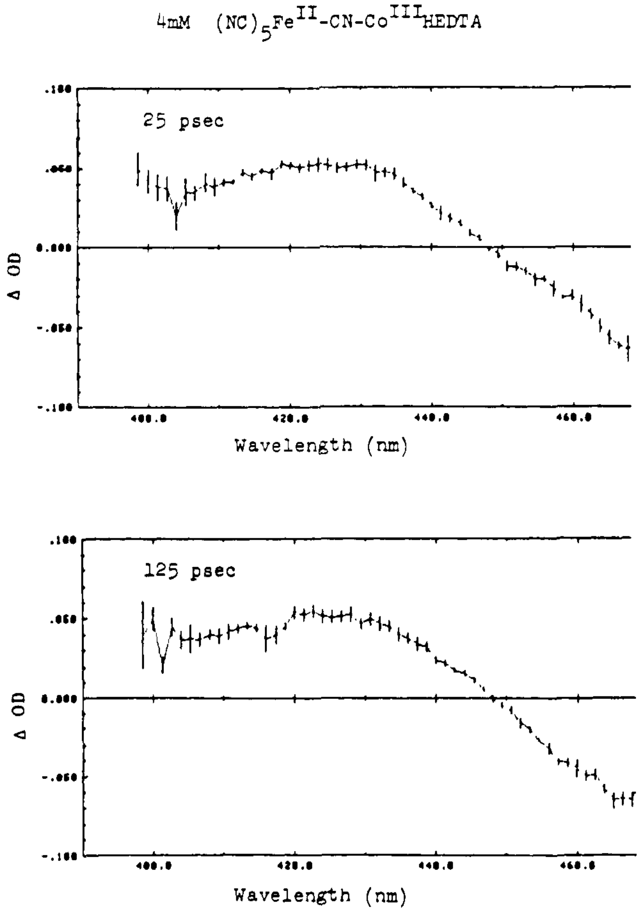

Figure 4. Transient difference spectra of HEDTACo^{III}–NC–$Fe^{II}(CN)_5^{4-}$ taken 25 ps after excitation and 125 ps after excitation. Excitation was a 532-nm ~25-ps laser pulse. Interrogation over the range of 400–480 nm.

Table III. Mixed Solvent Study

solvent mixture	−1 °C, 420 nm kinetic data	index of refraction	sp density	dielectric const
water	75 ps at max 95-ps decay	1.3333	1.000	78.54
water/45% methanol	130 ps at max 200-ps decay	1.3289	0.792	32.63
water/45% ethylene glycol	remains at max for >300 ps	1.4314	1.113	37.70
water/45% glycerol	remains at max for >300 ps	1.4729	1.261	42.50

Equation 2 corresponds to the excitation of the $^1T_{1g} \leftarrow {}^1A_{1g}$ for Co^{III}. The presence of the unfilled low-lying t_{2g} orbital increases the Co^{III} electron affinity and thereby causes the electron transfer (3) to take place.[16] Alternatively, Fe^{II}–CN–Co^{III} may be directly excited to the charge-transfer band at 530 nm, resulting in Fe^{III}–CN–Co^{II**}. This is possible assuming that the recent CT band between 500 and 600 nm observed by Vogler et al.[15] in a Ru–Ru complex is also present in the Fe^{II}–CN–Co^{III} system. This produces the Fe^{III} absorption and Co^{II} in the $^2E(t_{2g}{}^6e_g)$ state. The ground state of Co^{II} with all but the strongest field ligands is known to be high-spin[14] $^4T_{1g}$ ($t_{2g}{}^5e_g{}^2$). Equation 4 is the cobalt doublet to quartet spin flip accompanying $e_g \leftarrow t_{2g}$ transition to the ground $^4T_{1g}$ state. Our 420-nm data suggest that the ^2E ($t_{2g}{}^6e_g$) state has approximately a 75-ps lifetime and the spin-permitted electron-transfer back-reaction (eq 5) occurs in approximately 95 ps. This leaves the Co^{III} in an excited $^3T_1$ or $^3T_2$ ($t_{2g}{}^5e_g$) state which slowly

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J. Am. Chem. Soc. **1982**, *104*, 7403-7406

relaxes to the ground singlet state (eq 6). Curves calculated on the basis of this mechanism are also shown in Figure 3. In these calculations it is assumed that 420-nm ($\mathrm{Fe^{III}}$) absorption is independent of the $\mathrm{Co^{II}}$ spin state. The electron transfer from the $\mathrm{Co^{II}}\ {}^2E(t_{2g}{}^6e_g)$ is spin permitted, but these results indicate that this process is comparatively slow. Equations 5 and 6 are equivalent to the electron transfer process that occurs when $\mathrm{Fe^{III}(CN)_6{}^{3-}}$ reacts with $\mathrm{Co^{II}}$ chelate to form the paramagnetic bridged species $\mathrm{Fe^{III}}$–CN–$\mathrm{Co^{II}}$ ($t_{2g}{}^5/t_{2g}{}^5e_g{}^2$). This undergoes intramolecular electron transfer to form the $\mathrm{Fe^{II}}$–CN–$\mathrm{Co^{III}}$ ($t_{2g}{}^6/t_{2g}{}^5e_g$) product (eq 5). This product further undergoes high-spin to low-spin conversion to form the diamagnetic $\mathrm{Fe^{II}}$–CN–$\mathrm{Co^{III}}$ species that is observed[9] (eq 6). The intersystem crossing (${}^4T_1 \leftarrow {}^2E$) cannot be observed directly due to the low extinction coefficients of $\mathrm{Co^{II}}$.

This system differs from other bimetallic electron transfer complexes where it is believed the electron proceeds via resonance transfer between metal centers with some influence from the bridging ligands of the ruthenium.[2,3] The MLCT ($\mathrm{Fe^{II}} \rightarrow \mathrm{CN}$) transition occurs in the near-UV, thereby ruling out this possibility. The rate of electron transfer has been found to be dependent on the polarity of the solvent system. In less polar solvent systems the electron transfer rates were found to be lower (Table III). This is interpreted as being due to small relative changes between cobalt and iron electronic energy levels. We propose that these shifts are due to changes in charge stabilization of the respective $\mathrm{Fe^{II}}$–CN–$\mathrm{Co^{III}}$ and $\mathrm{Fe^{III}}$–CN–$\mathrm{Co^{II}}$ species.

Registry No. $\mathrm{(NC)_5Fe^{II}CNCO^{III}HEDTA}$, 83586-93-0; $\mathrm{(NC)_5Fe^{II}CNCO^{III}NBETA}$, 83586-94-1.

Small-Angle X-ray Scattering by Nonaqueous Concentrated Electrolytes: $\mathrm{LiClO_4}$ and $\mathrm{ZnBr_2}$ in Ethyl Acetate

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Abstract: Small-angle X-ray scattering has been performed on concentrated nonaqueous electrolytes (i.e., $\mathrm{LiClO_4}$– and $\mathrm{ZnBr_2}$–ethyl acetate systems) for the first time. The very dilute solutions show a monotonic scattering, revealing a low degree of association between molecules of solute. For the most concentrated solutions a well-defined maximum is observed for a scattering vector $s = (10\ \text{Å})^{-1}$ with $s = 2 \sin \theta/\lambda$. On increasing the salt concentration, the position of this maximum is shifted toward smaller angles, whereas the characteristic ring of the solvent is shifted toward higher angles, revealing structural changes.

A. Introduction

Recently X-ray and neutron scattering by concentrated aqueous solutions has had increasing experimental and theoretical attention.[1-5] Indeed, the diffraction experiments can provide extensive information about ion–solvent, ion–ion, and solvent–solvent interactions. In such aqueous systems, the scattering patterns reflect principally the ion–water interactions, whereas the ion–ion correlations are more difficult to show.[1] Nevertheless, the question of the existence of some ordered structure in concentrated electrolytes has been often raised.[1,4] The presence of a weak "prepeak" ($\boldsymbol{k} \simeq 1$ Å^{-1} with $\boldsymbol{k} = 4\pi \sin \theta/\lambda$) in the scattering patterns of aqueous systems seems to corroborate this hypothesis since it has been interpreted as due to some metal–metal interactions.[1,3,6,14] But it seems that water is not a good solvent in which to observe the ion–ion correlations. Its high dielectric constant ($\epsilon = 80$ at 293 K), principally due to numerous dipoles by unit volume, allows very strong ion–solvent interactions in the dilute range. (Indeed, water, a hydrogen-bonded solvent, has a very small size and a high dipole moment.) These interactions are still predominant on increasing the salt concentration, even though it has been shown that the dielectric constant of electrolytic solutions decreases[18] and that water undergoes important structural transformations.[8] Nevertheless, ion–ion interactions take place but often in a less important way. Thus, it seemed better to study nonaqueous solutions with a solvent of low dielectric constant (few dipoles by unit volume and large size of the molecule), allowing strong coulombic interactions. We chose ethyl acetate as solvent ($\epsilon = 6.09$ at 293 K). Indeed macroscopic data such as transport[7] and thermodynamic[8] properties of $\mathrm{LiClO_4}$– (or $\mathrm{ZnBr_2}$–) ethyl acetate solutions and microscopic data such as EXAFS[9] show that ionic clusters exist in this medium and that long-range ordered structures can be formed. In fact, the most important result of the EXAFS experiments performed on $\mathrm{ZnBr_2}$–EtOAc solutions is that these ionic clusters involve nearly 100% of the total number of $\mathrm{Zn^{2+}}$ and $\mathrm{Br^-}$ ions even in the dilute range, whereas in water, for the saturated solution, only 60% of the ions are embedded in such aggregates and this ratio decreases quickly with dilution.[10] A first qualitative evaluation of the size of these clusters for concentrated ethyl acetate solutions has given an order of $\simeq 30$ Å. If such an estimate is valuable, one would expect to observe a specific scattering at small angles, typically for vectors $\boldsymbol{s} \lesssim 9 \times 10^{-2}$ Å^{-1} ($s = 2 \sin \theta/\lambda$). For that reason, we performed small-angle X-ray-scattering experiments on these samples.

B. Experimental Section

a. Small-Angle Scattering. The absolute scattered intensity was measured with a spectrometer described elsewhere;[11] the intensity of the scattered radiation (monochromatic radiation Cu Kα, wavelength $\lambda = 1.54$ Å) was *collected* through a circular slit on a Si–Li detector protected by a beryllium window. The variation of the angle was obtained by varying the sample–detector distance, in constant steps. The thickness of the sample was controlled by various Teflon spacers; its optimum value

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