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Outer-Sphere Metal–Metal Charge-Transfer Transitions in Encounter Complexes of Free Mobile Cyanometalate Ions: Direct Observation of the "Reactive Associate" of Electron-Transfer Reactions

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Outer-sphere metal–metal charge-transfer (MMCT) transitions are observed in the visible and near-infrared spectral regions for encounter complexes of free mobile hexacyanoferrate(III) and hexacyanometalate(II) (M = Fe, Os) and octacyanometalate(IV) (M = Mo, W) anions, respectively, in aqueous solution at high concentrations of the reactants. The assignment of the observed bands to MMCT transitions is supported by the similarity of both anion-dependent absorption maxima shifts and relative bandwidths when compared to the MMCT transitions in ion pairs of $[Ru(NH_3)_6]^{3+}$ with the same donor anions. Molar extinction coefficients $\epsilon_{max} = 28$ (M = Fe), 45 (Os), 13 (Mo), and 24 M^{-1} cm^{-1} (W), respectively, as well as pre-equilibrium constants $K_A = (5.5 \pm 0.6) \times 10^{-2}$ M^{-1} in each case are obtained for the $[M(CN)_x]^{4-}/Fe(CN)_6]^{3-}$ systems. The electronic coupling between the metal centers, estimated from the intensities of the MMCT absorptions, is sufficiently strong for a nearly adiabatic nature of the corresponding thermal reactions.

Introduction

Metal–metal charge-transfer (MMCT) transitions in mixed-valence bi- or polynuclear metal complexes and related ion pair systems formed by oppositely charged species are of increasing interest.[1–20] Optical absorption bands arising as a result of such transitions carry information about the elementary mechanisms of electron hopping, particularly concerning the role of the electronic and nuclear subsystems and their contributions. These systems have often been explored for the resemblance with appropriate theoretical models.[1,3–5,12–17,19,20] Comparison of the results of the optical band shape analysis with kinetic data for related thermal processes also has considerable interest.[3,8,11,14,17,18]

The above mentioned electronic transitions occur under conditions where the metal centers are more or less rigidly fixed by ligand bridges or strong electrostatic attraction. Thus, the related thermal electron-transfer reactions are "unimolecular" processes. In order to gain further insight into the more complicated bimolecular "one collision" reactions between free mobile reactants the detection of optical charge-transfer phenomena between like charged species is important. Several attempts were directed toward the detection of such kind of transitions, and few reports have appeared[21] (for reviews see e.g. refs 2 and 17). Nevertheless, either the definite structure of the complex ions involved was unknown due to the complicated compositions of the solutions used or the band shape parameters could not be determined accurately. However, the outer-sphere metal–metal charge-transfer transition between $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ ions in concentrated (0.3–0.6 M, 25–60 °C) aqueous solutions of the corresponding potassium salts was reported.[22,23] The absorption band was analyzed by employing band shape theory in order to calculate the rate constant of the corresponding self-exchange reaction.

The detection of optical transitions of the same type but in asymmetrical systems involving other cyanometalate complexes promises information on the free energy relationships within the reaction series. In the present work we report completed sets of characteristic spectroscopic data on optical MMCT transitions between easily oxidizable cyanometalate complexes, viz. $[Fe(CN)_6]^{4-}$, $[Os(CN)_6]^{4-}$, $[Mo(CN)_8]^{4-}$, and $[W(CN)_8]^{4-}$, respectively, as donor components and $[Fe(CN)_6]^{3-}$ as the acceptor in aqueous solution.

Experimental Section

$K_3[Fe(CN)_6]$ (Laborchemie Apolda) and $K_4[Fe(CN)_6]\cdot 3H_2O$ (Merck) were of analytical grade and used as purchased. $K_4[Ru(CN)_6]\cdot 3H_2O$ (Alfa) and $[Ru(NH_3)_6)]Cl_3$ (Aldrich) were recrystallized twice from methanol/water prior to use. $K_4[Mo(CN)_8]\cdot 2H_2O$,[24] $K_4[W(CN)_8]\cdot 2H_2O$,[25] and $K_4[Os(CN)_6]\cdot 3H_2O$[26] were prepared according to the literature.

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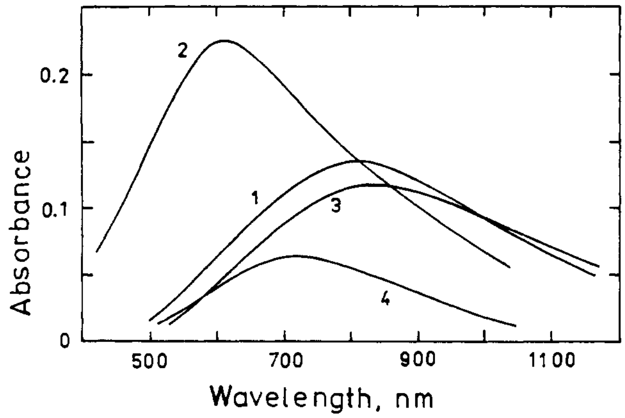

Figure 1. Vis/NIR spectra of aqueous solutions containing both 0.3 M $[Fe(CN)_6]^{3-}$ and $[M(CN)_x]^{4-}$ (M = Fe (1), Os (2), W (3), Mo (4); $[K^+]$ = 2.5 M; 25 °C, optical path length 1.00 cm).

Stock solutions (0.6 M, except otherwise indicated) for all potassium cyanometalates were prepared by weight using 0.1 M KOH in bidistilled water as solvent. The stock solution of $K_3[Fe(CN)_6]$ was additionally 0.6 M in KCl in order to keep the potassium concentration in the mixtures constant. All solutions were prepared and handled under exclusion of daylight. A 0.1 M concentration of potassium hydroxide was shwon previously to suppress sufficiently the cyanide ligand substitution from hexacyanoferrate(III) by water molecules, proceeding thermally, eventually leading to the formation of a binuclear cyanobridged species.[10,27] The latter absorb much more intensely in the spectral region close to that one of present interest, thus, if appeared, obscuring entirely the outer-sphere electron-transfer bands under investigation. At the same time, under the present experimental conditions, insignificant formation of hydroxopentacyanoferrate(III) ions was observed, leading to a slow increase of absorption in the region up to 600 nm, which, however, did not affect the detection of the new absorption bands. For several compositions of solutions studied some additional absorptions were observed distorting the low-energy tails of the bands under investigation. These absorptions are tentatively assigned to MMCT transitions in binuclear complexes formed as trace compounds (well below 10^{-5} M) probably due to longer action action of spectrophotometer light on the samples.

Phosphate buffer solutions (pH 7) containing $[Ru(NH_3)_6)]Cl_3$ and the appropriate potassium cyanometalate in variable concentrations (1–40 mM) were prepared and handled by analogy to the procedure described elsewhere.[28]

Spectroscopic measurements were performed at 25 °C on a Cary 3 (Varian) or a Lambda 19 (Perkin-Elmer) instrument. The tandem cell technique was applied when searching for new absorption bands, while 2.00-cm quartz or Infrasil cells were used for the determination of absorbances.

Results and Discussion

Band Shape Parameters and Pre-Equilibrium Constants. The new family of outer-sphere metal–metal charge-transfer bands is presented in Figure 1. For simplicity we will use in the following the abbreviations M/Fe for the $[M(CN)_x]^{4-}/[Fe(CN)_6]^{3-}$ systems. The bands are approximately Gaussian-shaped and almost perfectly resolved at least above their half-height. Characteristic parameters of these absorption bands are given in Table 1. Attempts were also made to detect the MMCT band for the Ru/Fe system, and some evidence was found that it is situated in the region of about 500 nm. Nevertheless, this band could not have been completely resolved due to the exceedingly large absorption of $[Fe(CN)_6]^{3-}$ in that region. The assignment of the observed bands to MMCT transitions is supported by the similiarity of both the anion-dependent maximum shift and relative bandwidths when compared to MMCT transitions in the ion pairs of $[Ru(NH_3)_6]^{3+}$ with the same cyanometalate ions (Table 2).

Table 1. Band-Shape Parameters and Pre-Equilibrium Constants of the $[M(CN)_x]^{4-}/[Fe(CN)_6]^{3-}$ Absorbing Species

	Fe/Fe	Os/Fe	Mo/Fe	W/Fe
λ_{max}, nm	820	610	720	840
$\bar{\nu}_{max}$, cm^{-1}	12 200	16 400	13 900	11 900
$\Delta\bar{\nu}_{1/2}$, cm^{-1}	7900	10 100	6500	7200
ϵ_{max}, M^{-1} cm^{-1}	28	45	13	24
10^2K_A, M^{-1}	5.5 ± 0.6	5.5 ± 0.6	5.5 ± 0.6	5.5 ± 0.6

Table 2. Band-Shape Parameters for MMCT in Ion Pairs $[Ru(NH_3)_6]^{3+}/[M(CN)_x]^{4-}$

	M			
	Fe	Os	Mo	W
λ_{max}, nm	730	575	660	752
$\bar{\nu}_{max}$, cm^{-1}	13 660	17 390	15 150	13 300
$\Delta\bar{\nu}_{1/2}$, cm^{-1}	6300	9000	4200	6000
ϵ_{max}, M^{-1} cm^{-1}	34	40	11	20

The molar conpositions of the absorbing species have been studied by means of Job's method,[29] Figure 2, for a total cyanometalate concentration of 0.6 M at constant (2.5 M) concentration of K^+. A 1:1 $[M(CN)_x]^{4-}$:$[Fe(CN)_6]^{3-}$ molar composition of the absorbing species was found in each case. The shapes of these plots are almost parabolic, indicating that the number of absorbing species is much lower than the total amount of present cyanometalate complexes. Otherwise Job's plot should show nearly triangular curves. This observation points to the need of a closer proximity of the reactants than the mean interreactant distance of 13–14 Å, under the prevailing conditions, for optical MMCT to occur. The absorbing species therefore may be regarded as encounter complexes. Bimolecular extinction coefficients $\epsilon^{(2)}_{max}$ = 1.54 (M = Fe), 2.48 (Os), 0.72 (Mo), and 1.32 M^{-2} cm^{-1} (W), respectively, were obtained for the M/Fe systems under the present conditions by regressional analysis. These quantities are composed from the more usual "unimolecular" extinction coefficient of the absorbing species, ϵ_{max}, and the formal pre-equilibrium formation constant, K_A. Due to the rather low value of K_A (K_A·0.6 M ≪ 1) a nonlinear regressional analysis of Job's plots failed to give reliable individual values of K_A and ϵ_{max}. Alternatively, the Benesi–Hildebrand method,[30] eq 1 (d is the optical path length; A_{max} is the absorbance at the band maximum), Figure 3, was applied to estimate the molar extinction coefficients of the absorbing species.

$$[X]_0[Y]_0d/A_{max} = 1/(K_A\epsilon_{max}) + [X]_0/\epsilon_{max} \qquad (1)$$

$$X = [Fe(CN)_6]^{3-};\ Y = [M(CN)_x]^{4-}$$

The $[M(CN)_x]^{4-}{}_0$ concentration was kept constant (0.1 M) while varying the $[Fe(CN)_6]^{3-}{}_0$ concentration in the range 0.3–0.67 M. At the same time, the potassium ion concentration was held at 2.5 M by addition of appropriate amounts of KCl.

Straight lines (slope = $1/\epsilon_{max}$) were obtained in all cases, yielding ϵ_{max} = 28 (Fe/Fe), 45 (Os/Fe), 13 (Mo/Fe), and 24 M^{-1} cm^{-1} (W/Fe), respectively. From these values and the corresponding intercepts (intercept = $1/(K_A\epsilon_{max})$) pre-equilibrium constants $K_A = (5.5 \pm 0.6) \times 10^{-2}$ M^{-1} in each case were calculated.

Free Energy Relationships. According to theory[1,14,19,31] the relationship between the observed energy of the outer-sphere MMCT transition (at $\bar{\nu}_{max}$) and various free energy parameters is given by

$$hc\,\bar{\nu}_{max} = \Delta G_0 + \lambda_{in} + \lambda_{out} + \Delta w + E_{so} \qquad (2)$$

ΔG_0 is the free energy gap between the initial and the final states of charge transfer, usually defined as the difference of the formal redox potentials E^f of the complexes involved,[17,31] $\Delta G_0 = -F(\Delta E^f)$

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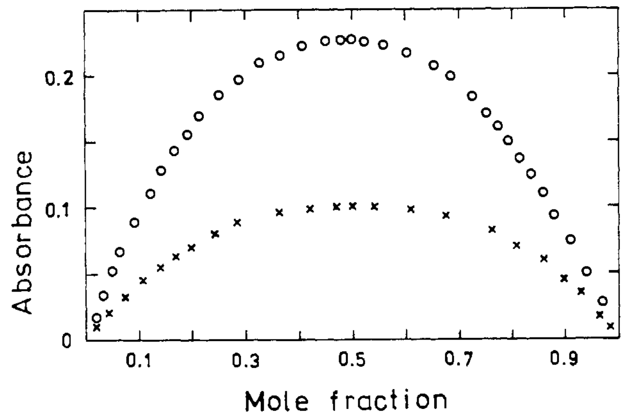

Figure 2. Job plots for the Fe/Fe (o, 700 nm) and Mo/Fe (×, 800 nm) systems (total cyanometalate concentration 0.6 M; [K+] = 2.5 M; 25 °C; optical path length 2.00 cm).

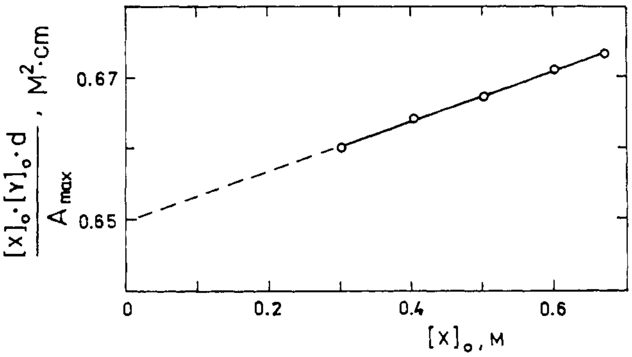

Figure 3. Benesi–Hildebrand plot for the Fe/Fe system (X = $[Fe(CN)_6]^{3-}$, Y = $[Fe(CN)_6]^{4-}$; $[Y]_0$ = 0.1 M; $[K^+]$ = 2.5 M).

(F is the Faraday constant). Δw is the difference of the work terms required to form the precursor and successor complexes of the optical charge transfer. These terms exactly cancel for the symmetrical Fe/Fe system and presumably do so for the asymmetrical M/Fe systems. λ_{in} and λ_{out} are the inner- and outer-sphere reorganization free energies. E_{so} accounts for spin–orbit splitting of the d^5 ^2T state (in octahedral symmetry) of $[Fe(CN)_6]^{3-}$ or $[Os(CN)_6]^{3-}$ formed as a result of optical charge transfer.[18,19] The corresponding transitions are rarely well-resolved.[20] As discussed elsewhere in detail,[18,19] the observed charge-transfer band is usually a composite curve of two components with maxima approximately at $\lambda_{so}/2$, where λ_{so} is the spin–orbit coupling parameter, higher and λ_{so} lower than $\bar{\nu}_{max}$. Only the lower energy transition involves the electronic ground states of reactants and products and is therefore related to both the thermal redox process and the electrochemical redox potentials. The twice as intense higher energy transition corresponds to the population of an electronically excited product state.

Spin–orbit coupling parameters λ_{so} = 460 cm^{-1} for $[Fe(CN)_6]^{3-}$ and 3000 cm^{-1} for $[Os(CN)_6]^{3-}$ have been used by Brunschwig et al.[19] in order to analyze the MMCT spectra of ion pairs $[Ru(NH_3)_5L]^{3+}$, $[M(CN)_6]^{4-}$, where L is a heterocyclic ligand. No spin–orbit coupling effects are expected for $[Mo(CN)_8]^{3-}$ and $[W(CN)_8]^{3-}$ due to the nondegenerate ground states of these d^1 species.[32]

For the Fe/Fe system, where $\Delta G_0 = 0$ and E_{so} is of minor importance, it has been shown that interionic vibrations between the complex anions and potassium counterions contribute considerably to the overall reorganization free energy, $\lambda_{in} + \lambda_{out} \approx h\nu_{max}$, of the optical transition.[22,23] In addition we observe a solvent isotope effect on the MMCT maximum of the Fe/Fe system. It shifts by about 460 cm^{-1} from 820 nm (this work) to 790 nm [23] upon replacement of H_2O by D_2O as the solvent. This increase in reorganization free energy cannot be explained by means of solvent continuum models[19,33] but indicates a specific contribution of solvent molecules present in the second coordination sphere of the complex ions.

A detailed quantitative analysis of the contributions to $\bar{\nu}_{max}$ in the asymmetrical M/Fe systems cannot yet be performed due to the lack of data for the formal redox potentials E^f of the $[M(CN)_x]^{3-/4-}$ couples under the present experimental conditions. It should be noted, however, that once spin–orbit coupling effects have been considered the maxima of the lowest-energy transitions, $\bar{\nu}_{max}' \approx \bar{\nu}_{max} - \lambda_{so}$, increase in the same order as do the standard redox potentials of the $[M(CN)_x]^{3-/4-}$ couples, E^0 = 0.356 (M = Fe),[34] 0.456 (W),[35] 0.634 (Os),[36] and 0.726 V vs NHE (Mo),[37] respectively.

Electronic Coupling. In order to elucidate the adiabaticity of the related, or reverse, thermal reactions the matrix elements of electronic coupling between the initial and the final state of electron transfer, H_{if}, were estimated from the optical band shape parameters according to Hush's equation[13] corrected for the degeneracy D of the electronic states concerned:[38]

$$H_{if} = 2.06 \times 10^{-2}(\epsilon_{max}\bar{\nu}_{max}\Delta\bar{\nu}_{1/2}/D)^{1/2}/R \qquad (3)$$

Since the distances R (in Å) between the metal centers in the absorbing species are not known, we have employed here the mean interreactant distance of ≈14 Å [23] as an upper limit, yielding lower estimates of H_{if} = 44 (M = Fe), 73 (Os), 50 (Mo), and 66 cm^{-1} (W), respectively. These values are close to the critical limit for adiabatic electron transfer, $H_{if} \approx$ 80–160 cm^{-1}.[23] Thus, the interaction between the metal centers is sufficiently strong to allow for a nearly adiabatic nature of the corresponding thermal reactions.

Conclusions

Outer-sphere MMCT transitions in a family of nonrigidly bonded systems have been documented. The kinetics of most of the related, or reverse, thermal reactions has been studied[39–43] but frequently under too different conditions (concentration, ionic strength, pH) to allow for comparison with data from optical charge transfer. Prior to exploration of these systems for resemblance with appropriate models, both electrochemical and kinetical data have to be collected under the conditions where optical MMCT is observed.

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