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Salt effects on the electron transfer transition within the binuclear complex $[(NH_3)_5Ru^{III}(\mu\text{-}CN)Fe^{II}(CN)_5]^-$ †

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By a combination of spectroscopic and electrochemical techniques the reorganization and reaction free energies of the intramolecular electron transfer within the binuclear complex $[(NH_3)_5Ru^{III}\text{–}NC\text{–}Fe^{II}(CN)_5]^-$ in different salt solutions were obtained. It is concluded that the variations of these parameters, as well as those in the energy of the maximum of the metal-to-metal charge transter (MMCT) band, are caused by ion pairing of the binuclear complex with the ions of the electrolytes. Also demonstrated was that the static, optical and electrochemical data permit reliable obtention of the activation free energies of the thermal electron transfer reactions.

Introduction

The study of salt effects on electron transfer reactions is of interest from several points of view. Thus, in photoinduced electron transfers, if the reaction products are ions of opposite charge sign, and the product of their charges is greater than the product of the reactants' charges, improvement of the yield can be achieved by addition of electrolytes to the reaction medium.[1]

On the other hand, the study of salt effects is of interest as a part of the more general topic of solvent effects on chemical reactivity. From this point of view, the electron transfer reactions are perhaps optimal candidates as probe reactions, because for this kind of reaction there is a good theoretical framework, the Marcus–Hush treatment.[2,3] According to this treatment, as is well known, the activation free energy, $\Delta G^{\ddagger}$, depends on two parameters: the reaction free energy, $\Delta G^{\circ\prime}$, and the reorganization free energy, λ.[2] By adequate selection of the reactants, these parameters can be obtained independently.[4] Moreover, in the case of electron transfer reactions it is possible to obtain the relevant parameters ($\Delta G^{\circ\prime}$ and λ) through non-kinetic techniques.[5] This possibility arises from the fact that given a thermal electron transfer process there is always an optical electron transfer process with the same reaction and reorganization free energies.[6] This relationship is shown in Fig. 1.[7] As can be seen in the figure, $E_{op} = h\nu_{max}$ is the energy corresponding to the absorption maximum of the band produced by the optical transition. This energy is given by eqn. (1)[6] in such a way that the relationship between the energetics of the optical and thermal processes is as in eqn. (2). In fact, the band also gives the reorganization free energy. However, the obtention of λ from the band is precluded from a practical point of view because of the phenomena of inhomogeneous broadening.[8] An alternative approach, used in this work, is to employ a combination of thermodynamic (electrochemical) and spectroscopic measurements. This consists of determining the value of E_{op} from the band and the reaction free energy, $\Delta G^{\circ\prime}$, from electrochemical measurements. In this way it is possible to obtain the variations of both $\Delta G^{\circ\prime}$ and λ [(through eqn. (1)] when the reaction medium is changed by the addition of salts.[9]

$$E_{op} = \lambda + \Delta G^{\circ\prime} \qquad (1)$$

$$\Delta G^{\ddagger} = \frac{(\lambda + \Delta G^{\circ\prime})^2}{4\lambda} = \frac{E_{op}{}^2}{4(E_{op} - \Delta G^{\circ\prime})} \qquad (2)$$

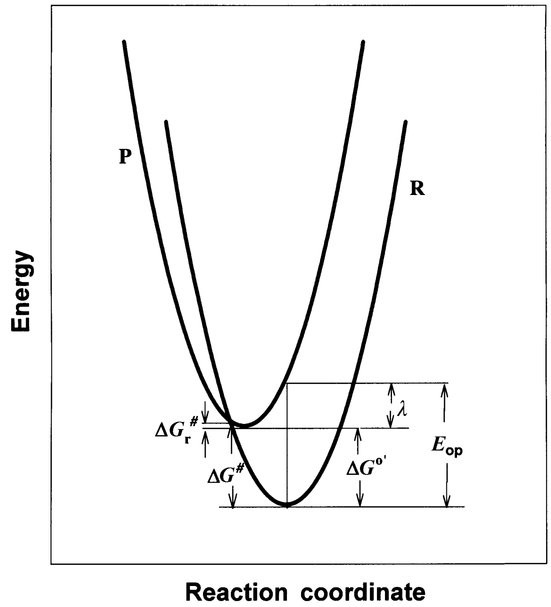

Fig. 1 Free energy surfaces (FES) for the reactant and product states showing the characteristic magnitudes for the optical (vertical transition) and thermal (movement of representative point along the reaction coordinate) electron transfers.

In the spirit of this approach, we present the results corresponding to a systematic study of salt effects on the energy of the optical electron transfer transition within the binuclear complex $[(NH_3)_5Ru^{III}(\mu\text{-}CN)Fe^{II}(CN)_5]^-$, as well as on the reaction and reorganization free energies. This complex was selected because it shows a clear metal-to-metal charge transfer (MMCT) band in water[10] and because it is a localized mixed valence compound[10b] (class II in Robin–Day classification[11]), which is essential in order to apply eqns. (1) and (2). This complex also permits us to perform electrochemical measurements on the two metallic centers, because electron transfers from or to these are reversible from an electrochemical point of view.

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† Electronic supplementary information (ESI) available: maximum band energies, redox potentials, free energy changes, reorganization free energies and activation free energies. See http://www.rsc.org/suppdata/dt/b1/b101069g/

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Thus, the two parameters appearing in eqn. (1) (E_{op} and $\Delta G^{\circ\prime}$) can be obtained directly from experiments. Indeed, cyano-bridged binuclear and polynuclear mixed valence complexes are interesting as a result of their unique structural, redox and charge transfer properties, which ensures their potential applications within the fields of solar energy conversion and molecular electronics.[12] Finally, optical and thermal electron transfer within these complexes are quite sensitive to solvent effects.[13]

The electrolytes employed in this work are $LiNO_3$, $Mg(NO_3)_2$, $La(NO_3)_3$, Na_2SO_4 and $NaClO_4$. In this way, the effects of changing the charges of the anions and cations of the salts have been studied. Some comparisons with other thermal processes have also been considered.

Results

Tables S1–S5 [see Electronic Supplementary Information (ESI)] give the experimental values of the maximum band energy, E_{op}. These tables also show the corrected values of these parameters, E_{op}^{corr} (the values to be used in the following calculations) obtained as in eqn. (3). The δ parameter in this

$$E_{op}^{corr} = E_{op} - \delta \qquad (3)$$

equation represents a correction for the spin–orbit coupling of the iron(III) center in the vibronically excited state[14] (the asterisk in eqn. (4) indicates this vibronically excited character).

$$[(NH_3)_5Ru^{III}\text{–NC–}Fe^{II}(CN)_5]^- \xrightarrow{h\nu} ([(NH_3)_5Ru^{II}\text{–NC–}Fe^{III}(CN)_5]^-)^* \qquad (4)$$

This correction is necessary because in octahedral symmetry the d^5 T state of the metal is split by spin–orbit coupling into a higher degenerate E state and a lower A state, the energy separation of these states being (3/2)δ, where δ is the spin–orbit coupling parameter. Owing to the existence of two excited states, the experimental charge transfer band is the sum of two bands, corresponding to transitions from the ground state to the E and A states. These bands are at $\delta/2$ (higher) and δ (lower) energies, respectively, than the maximum absorption observed in the composite (experimental) band, so that the transition to the *lower* excited state corresponds to the value of E_{op}^{corr} as given by eqn. (3). A value of 450 cm^{-1} = 5.4 kJ mol^{-1} for δ was used in this work.[14b] In this way E_{op}^{corr} and $\Delta G^{\circ\prime}$ (see below) correspond to the same process.

The values of this latter free energy appear in Tables S1–S5 as well as the standard formal redox potentials of both ruthenium and iron centers. These free energy changes corresponding to the forward thermal electron transfer process (5) were calculated as in eqn. (6) with $\Delta E^{\circ\prime} = E^{\circ\prime}(Ru) - E^{\circ\prime}(Fe)$, where

$$[(NH_3)_5Ru^{III}\text{–NC–}Fe^{II}(CN)_5]^- \longrightarrow [(NH_3)_5Ru^{II}\text{–NC–}Fe^{III}(CN)_5]^- \qquad (5)$$

$$\Delta G^{\circ\prime} = -F\Delta E^{\circ\prime} \qquad (6)$$

Ru represents the ruthenium ammine center and Fe is the iron cyanide center. According to the uncertainty in redox potentials, these values should have an uncertainty of about 1 kJ mol^{-1}. Now, from the data for $\Delta G^{\circ\prime}$ and E_{op}^{corr} the values of the free energies of reorganization, λ, and activation $\Delta G^{\ddagger}$, were obtained, using eqns. (1) and (2), respectively. These values are also included in Tables S1–S5.

It is important to realize that the determination of $\Delta G^{\circ\prime}$ by the preceding method implicitly assumes that the redox pontential of each center is not affected by the oxidation state of the other,[15] as in ref. 16. An idea of the uncertainty of $\Delta G^{\circ\prime}$ collected in Tables S1–S5 can be obtained by comparing the value of the reorganization free energy, λ, corresponding to water (in fact, in 0.2 mol dm^{-3} $NaClO_4$, Table S4) with the value of this parameter obtained by Walker *et al.*[10a] (53.6 kJ mol^{-1}). The difference between this value and those in the table, about 2 kJ mol^{-1}, could be considered the maximum value for the uncertainty of $\Delta G^{\circ\prime}$ values, arising from the procedure used in its determination. It is worth pointing out that the influence of the oxidation state of a center on the redox potential of the other center is a constant *independent of the solvent*. Thus, the above mentioned uncertainty would imply a *constant* shift (of about 2 kJ mol^{-1}) in the values of $\Delta G^{\circ\prime}$ (and λ) appearing in the tables. In this way the conclusions on the trends in these parameters would not change. Indeed, the uncertainty itself, 2 kJ mol^{-1}, is the same order as that originated by the experimental aleatory errors.

Discussion

(a) Salt effects on E_{op}, λ and $\Delta G^{\circ\prime}$

Considering firstly the values of E_{op}^{corr}, Tables S1–S5 show that this energy increases when the salt concentration increases for all electrolyte solutions, except in the case of $NaClO_4$ solutions. The increase in E_{op}^{corr} results from an increase of both λ and $\Delta G^{\circ\prime}$ (see Tables S1–S5). The behaviour of the latter parameters in the different electrolyte solutions can be considered, at first, the expected one.

Thus, the values of $\Delta G^{\circ\prime}$ depend on the standard formal potentials of both centers, which are given by eqn. (7) where

$$E^{\circ\prime} = E^{\circ} + \frac{RT}{F}\ln\frac{\gamma_{ox}}{\gamma_{red}} \qquad (7)$$

E° is the standard redox potential, γ_{ox} and γ_{red} are the activity coefficients of the oxidized (ox) and reduced (red) species of the redox couple.

Increasing the salt content in the solution would produce a decrease in both γ_{ox} and γ_{red} of each couple. For the ruthenium center the decrease in γ_{ox} is more marked than the decrease of γ_{red} because of the higher charge of the oxidized form of this couple. The opposite is true for the anionic (iron) center since in this case the (absolute) value of the charge is higher for the reduced form of the couple. Thus, an increase of the salt concentration would cause a diminution of the oxidant power of the ruthenium and simultaneously the iron center becomes less reducing. Consequently, the electon transfer reaction [(eqn. (5)] becomes less favourable, that is its reaction free energy increases.

However, it is interesting to consider the data corresponding to $NaClO_4$. In this case $\Delta G^{\circ\prime}$ is independent of the electrolyte concentration, see Table S4. This suggests that the effect of salts is not a simple ionic cloud effect. Moreover, although the variation of the redox potentials of the ruthenium center is in qualitative agreement with expectations based on the ionic cloud effect for the case of Na_2SO_4, the changes of these redox potentials for the other salts go in the opposite direction. This confirms the point of view that other effects different from the ones derived from the interactions of the ruthenium center in the binuclear complex with its ionic cloud are relevant. We suggest some influence of the ionic cloud around the iron center and/or of the association of this center with the cations of high charge as the origin of the *abnormal* behaviour of the redox potentials of the ruthenium center. A similar explanation of the influence of the ions associated to a center on the redox potential of the other center has been given by Piotrowiak *et al.* in the field of organic photochemistry.[17] In fact, the variations of redox potentials of the closely related $[Ru(NH_3)_5(pz)]^{3+/2+}$ couple in salt solutions show a *normal* behaviour, that is they decrease as the electrolyte concentration increases.[18]

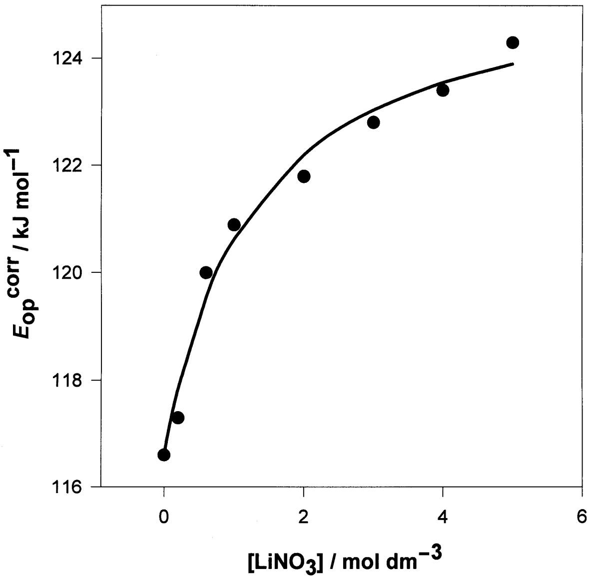

Fig. 2 Plot of E_{op}^{corr} *vs.* the concentration of the $LiNO_3$ solutions for the electron transfer reaction within the complex $[(NH_3)_5Ru^{III}$-$(\mu$-$CN)Fe^{II}(CN)_5]^-$ at 298.2 K.

As to the λ values, the trend of this parameter is similar to the observed one in other studies corresponding to salt effects on thermal[19] and optical[20] electron transfer processes in concentrated electrolyte solutions. That is, an increase in λ is observed when the salt concentration increases. This fact can be interpreted, in a qualitative form, using the Marcus treatment of salt effects on the reorganization energies[21] which predicts an increase in λ in electrolyte solutions as a consequence of the ionic cloud reorganization. However, this treatment cannot be applied to the present case in a quantitative way because it is based on a Debye–Hückel type distribution of ions in solution, which cannot be used in concentrated electrolyte solutions. Indeed, as mentioned above in relation to the discussion on reaction free energies, other effects, different from the ionic cloud effects, seem to be operative.

Some idea about this kind of effect can be obtained considering again the values of E_{op}^{corr}. These values are well fitted by eqn. (8) in which $(E_{op}^{corr})_w$ represents the (corrected) energy

$$E_{op}^{corr} = \frac{(E_{op}^{corr})_w + K[\text{salt}](E_{op}^{corr})_s}{1 + K[\text{salt}]} \qquad (8)$$

of the optical transition in water (116.6 kJ mol^{-1}) and $(E_{op}^{corr})_s$ this energy in a (hypothetical) solution of the salt at infinite concentration. In Fig. 2 the fitting for $LiNO_3$ solutions is shown. Similar results are obtained for the other salts.

We will not discuss here the values of the parameters $(E_{op}^{corr})_s$ and K found by the fitting because, as has been shown, equations like this can fit the results with various combinations of the parameters.[22] The important point here is that the possibility of fitting the data corresponding to E_{op}^{corr} by eqn. (8), with $(E_{op}^{corr})_s > (E_{op}^{corr})_w$, has been considered as a demonstration of the participation of associated forms of the absorbing species.[23] It is worth pointing out that application of eqn. (8) requires that $\Delta E_{op} = (E_{op}^{corr})_s - (E_{op}^{corr})_w$ is small in comparison with the bandwidth.[24]

Thus, it seems reasonable to conclude that the observed effects (on E_{op}^{corr}, λ and $\Delta G^{\circ\prime}$) are mostly due to an ion-pair effect, rather than to an ionic cloud effect. This idea receives further support from the fact that ionic cloud effects for salt concentrations greater than 0.5 mol dm^{-3} seem to be nearly constant.[25] Indeed, an interpretation of salt effects on electronic transitions based on ion-pairing effects, instead of the one based on ionic cloud effects, seems also to be better from a more fundamental point of view, at least in concentrated electrolyte solutions. In fact, the ionic cloud interpretation, based on the Debye–Hückel treatment, would be valid only if the interactions of the centers in the binuclear complex with the counter ions of the supporting electrolytes were small in comparison with k_BT. As these interactions (potentials) are inversely proportional to the distance and, on average, the ions will be in close contact in concentrated electrolyte solutions, this supposition cannot be mantained. Under these circumstances, that is, in the presence of tight ion pairs, the diffusion of the ions, following electron transfer as a consequence of the redistribution of the charges, has to be treated explicitly.[26,27] Moreover, the magnitude of the variations of λ and $\Delta G^{\circ\prime}$ with salt concentration also seem to support the idea of an ion-pairing origin rather than an ionic cloud effect. Thus, according to Marcus:[26] *at fixed position of the ion associated with the binuclear complex*, λ is expected to be approximately the same for associated and free binuclear complexes, in such a way that variations of E_{op}^{corr} would be caused mainly by the changes in the reaction free energy ($\Delta G^{\circ\prime}$). The fact that changes of $\Delta G^{\circ\prime}$ were for all cases nearly twice the changes of λ seems to support the interpretation based on ion-pairing.

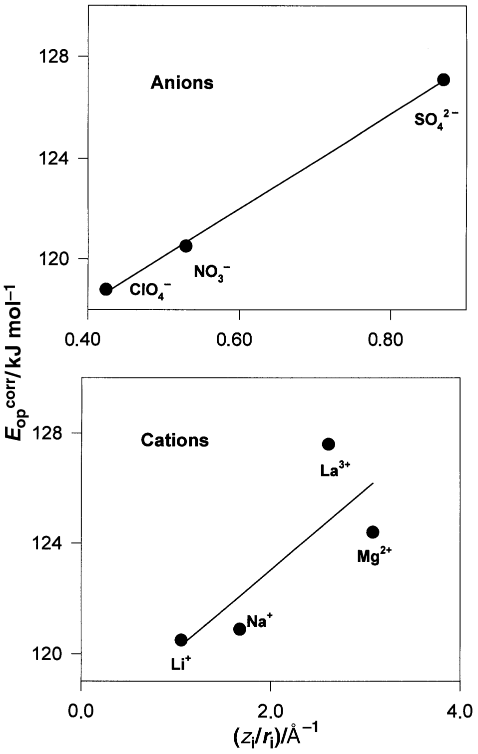

Fig. 3 Plot of E_{op}^{corr} *vs.* the charge/radius (z_i/r_i) for anions and cations. Ionic radii taken from ref. 28.

As a final argument which supports the interpretation based on ion-pairs, it is relevant to consider that for salts (at concentration 1 mol dm^{-3}) with a common anion (NO_3^-) the changes in E_{op}^{corr} increase as $Na^+ < Li^+ < Mg^{2+} < La^{3+}$ and for the case of salts with a common cation (Na^+) as $NO_3^- < ClO_4^- < SO_4^{2-}$ (the data for $NaNO_3$ solution are given in ESI Table S6). That is, the ion-pair effect on E_{op}^{corr} increases as the relation charge/radius of the ions does for the case of the anions, as shown in Fig. 3. This kind of variation can be explained, at least qualitatively, using the model of Chapman and Maroncelli[29] based on the consideration of a multistep association between the ions of the supporting electrolytes and the probe. It should be mentioned that in the case of cations the linear relationship between E_{op}^{corr} and the charge : radius ratio is not as good as for the anions (see Fig. 3), which seems to indicate that other effects are also operative in the case of the cations. Tentatively, we suggest a local hydrolysis that could give

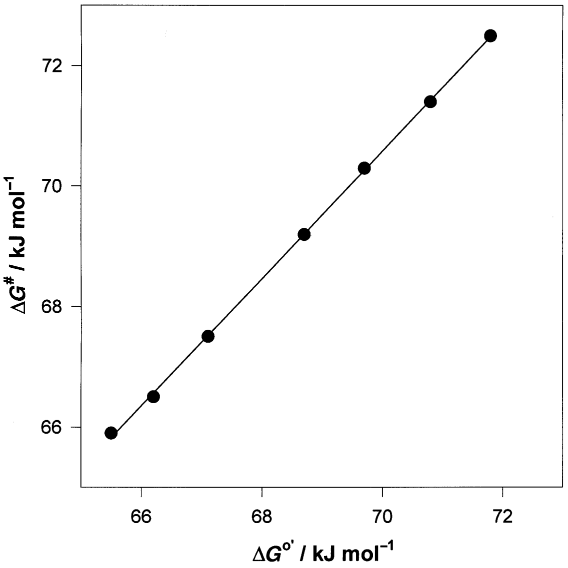

Fig. 4 Plot of the activation free energy, $\Delta G^{\ddagger}$, *vs.* the reaction free energy, $\Delta G^{\circ\prime}$, for the electron transfer reaction within the complex $[(NH_3)_5Ru^{III}(\mu\text{-}CN)Fe^{II}(CN)_5]^-$, in the presence of $La(NO_3)_3$ solutions at 298.2 K.

an additional effect of the cations associated with the iron center: a protonation of this center. As is well known, the phenomena of local hydrolysis has been invoked under similar circumstances in order to explain the *abnormal* activity coefficient of the alkali metal hydroxides, and other salts with protonable anions.[30]

This interpretation of the effects of cations and anions would imply that the anions participate as bare ions in the formation of the ion-pair with the ruthenium center. In the case of ion-pairs formed by the iron center of the binuclear complex with the cations, the latter would participate as solvated ions (at least in part). Note that in the case of anions the participation of the bare ions would permit the formation of hydrogen bonds with the ammonia ligands of the ruthenium.

(b) Prediction of the activation free energy from optical and electrochemical data

The data obtained in this work permit some additional information. Thus, from eqn. (2) it is possible to obtain the activation free energy corresponding to the thermal electron transfer reaction (5) (see Tables S1–S5). This activation free energy is a linear function of the reaction free energy, as shown in Fig. 4 for the case of $La(NO_3)_3$ solutions. Similar plots were obtained for the other electrolyte solutions. The slope of these linear plots is close to unity, which implies a transition state located near the product state along the reaction coordinate, as can be seen in Fig. 1. This circumstance is, obviously, a consequence of the λ and $\Delta G^{\circ\prime}$ values being close to each other (see Tables S1–S5) and thus the Brönsted slope, a, which for electron transfer reactions is given by eqn. (9) as follows from

$$a = \frac{1}{2} + \frac{\Delta G^{\circ\prime}}{2\lambda} \qquad (9)$$

the Marcus equation of the activation free energy [see eqn. (2)], is in the present case close to unity. This conclusion is in agreement with previous studies on this and related binuclear complexes.[31]

Finally, we will consider one of the questions mentioned in the introductory section, the possibility of obtaining reliable activation free energies for electron transfer reactions through optical and thermodynamic (electrochemical) data, that is from a kinetically independent procedure. This possibility of getting activation free energy is of interest, because if $\Delta G^{\ddagger}$ is available the determination of the rate constant through a conventional kinetic procedure permits the obtention of the preexponential term in this constant, as pointed out by Weaver[32] and Bu and Dong.[33] This term is of interest since, as is well known, it contains information on the electronic and dynamic solvent effects of the electron transfer reactions. In order to check this possibility a difficulty arises: for the forward (thermal) electron transfer there are no data and they cannot be obtained. For this reason we have compared the *variations* of the activation free energy of this process, calculated through eqn. (2), with the *measured variations* of the activation free energies for the electron transfer process (10, pz CO_2 = pyrazine carboxylate)

$$[(NH_3)_4Co^{III}(\mu\text{-}pzCO_2)Fe^{II}(CN)_5]^- \longrightarrow [(NH_3)_4Co^{II}(\mu\text{-}pzCO_2)Fe^{III}(CN)_5]^- \qquad (10)$$

which are available in some salt solutions.[19a] The latter binuclear complex is quite similar to the one considered in this work, thus both have the same charge (−1) and the peripheries of the two metallic centers are similar (in fact, identical in the case of the iron center). As the sizes of the two complexes are also similar, it seems reasonable to suppose that their interactions with the surrounding medium (the electrolyte solutions) will be almost the same. Consequently, if the calculations of the activation free energies through optical and electrochemical data are reliable, *changes* in this parameter for processes (5) and (10) should be linearly related, with the slope close to unity. Fig. 5 represents plots of the activation free energies for these processes. It can be seen that, in fact, they are linearly correlated with a slope close to unity. This result seems to support the idea of calculating activation free energies for thermal processes from optical and electrochemical data.

On the other hand, for the reverse of the electron-transfer process in eqn. (5), that is eqn. (11) the activation free energy can be obtained by using eqn. (12) because one can assume that

$$[(NH_3)_5Ru^{II}\text{–}NC\text{–}Fe^{III}(CN)_5]^- \longrightarrow [(NH_3)_5Ru^{III}\text{–}NC\text{–}Fe^{II}(CN)_5]^- \qquad (11)$$

$$\Delta G_r^{\ddagger} = \frac{(\lambda + \Delta G_r^{\circ\prime})^2}{4\lambda} \qquad (12)$$

the reorganization free energy, λ, for both forward and reverse processes have the same value. In fact, it follows from Marcus' assumption that the free energy curves of the reactant and product states are parabolas of the same curvature.[2] Thus, in order to check the values of activation free energy for reaction (11), we have estimated the value of k_{et} for this process in water (in fact, $NaClO_4$ at concentration 0.2 mol dm^{-3}): according to the model of Jortner and Bixon,[34] by employing up to the second order power of the electronic coupling, the preexponential factor of k_{et} has a value of 4.8×10^{12} s^{-1}. This would correspond to a k_{et} value of 3.2×10^{12} s^{-1}, in close agreement with that obtained in water by Walker *et al.*,[10a] by using transient pump–probe measurements (10^{12}–10^{13} s^{-1}).

Conclusion

The results in this work show that the study of the MMCT bands combined with electrochemical techniques can give interesting information on the medium effects upon electron transfer processes. In particular, the possibility of having, independently, variations of λ and $\Delta G^{\circ\prime}$ induced by the solvent permits us to gain a deeper insight into causes of changes in reactivity when the reaction medium is changed. It has also been shown that it is possible to obtain reliable values of the activation free energy from static (optical and electrochemical)

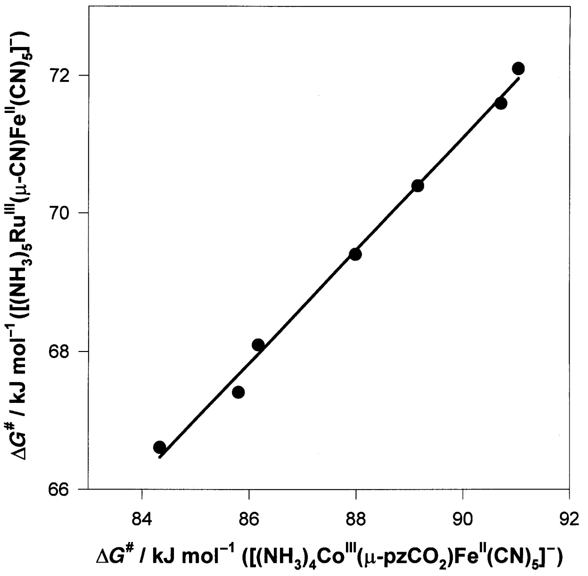

Fig. 5 Plot of $\Delta G^{\ddagger}$ for the process $[(NH_3)_5Ru^{III}(\mu\text{-}NC)Fe^{II}(CN)_5]^- \longrightarrow [(NH_3)_5Ru^{II}(\mu\text{-}NC)Fe^{III}(CN)_5]^-$ *versus* $\Delta G^{\ddagger}$ for the reaction $[(NH_3)_4Co^{III}(\mu\text{-}pzCO_2)Fe^{II}(CN)_5]^- \longrightarrow [(NH_3)_4Co^{II}(\mu\text{-}pzCO_2)Fe^{III}(CN)_5]^-$ in the presence of $Mg(NO_3)_2$ solutions at 298.2 K.

data, which would permit us to obtain the preexponential term of the electron transfer rate constant. This term is of interest because it contains information on dynamic (solvent) and electronic effects of the electron transfer processes.

Experimental

Materials

The sodium salt of the mixed valence compound $[(NH_3)_5Ru^{III}–NC–Fe^{II}(CN)_5]^-$ was prepared and purified as previously described.[10a,35] The visible spectrum shows a MMCT band with absorption maximum at 982 ± 1 nm (ε_{max} = 2988 ± 20 dm^3 mol^{-1} cm^{-1}), in water. This wavelength corresponds to a value of $E_{op} = h\nu_{max}$ of 122 kJ mol^{-1}.

Salts (p.a. quality) were purchased from Merck and used without further purification. Throughout the study, double distilled and deionized water, obtained from a Millipore Milli-Q system, with a conductivity lower than $10^{-6}\ \Omega^{-1}\ m^{-1}$, was used.

Spectra

The spectra of the binuclear complex in the different media were recorded in a Hitachi 150–20 UV-vis spectrophotometer at 298.2 K. In order to minimize the uncertainty in the absorption maximum, the derivative spectra were also recorded. Thus, the uncertainty was about ±1 nm. To check on the possible influence of the concentration of the complex on the full width at half-height and absorption maximum, a set of spectra for concentrations of the binuclear complex in the range of 0.5×10^{-4} to 6.0×10^{-4} mol dm^{-3} were recorded in pure water. Both the band maximum and the full width were independent of the concentration in the above mentioned range: constant values of λ_{max} = 982 ± 1 nm and $\Delta\nu_{1/2}$ = 4700 ± 100 cm^{-1} were found. The mixed valence compound concentration was always 5.8×10^{-4} mol dm^{-3}. In addition, a buffer was always used to avoid possible shifts of the band maximum due to pH influence.[10b] The pH was kept constant at 5.7 by using the appropriate acetic–acetate buffer ([AcO$^-$] = 0.019 mol dm^{-3}). On the other hand, neither the molar absorption coefficient at the maximum of the band, ε_{max}, nor the full width at half-height, $\Delta\nu_{1/2}$, showed significant modifications, in relation to the values of these parameters in water (ε_{max} = 2988 ± 20 dm^3 mol^{-1} cm^{-1} and $\Delta\nu_{1/2}$ = 4700 ± 100 cm^{-1}), in the different electrolyte solutions employed in this study. All spectra were recorded using a quartz cell of 1 cm path length.

Electrochemistry

The redox potentials of both ruthenium and iron centers in the binuclear complex were obtained by cyclic voltammetry techniques in all solutions. The equipment, procedure and electrodes have previously been described.[36] The temperature was kept constant at 298.2 ± 0.1 K. The concentrations of the mixed-valence compound and the buffer conditions were the same as in the experiments in which the spectra were obtained. The estimated uncertainty in redox potentials is about ±5 mV.

Acknowledgements

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7 Fig. 1 corresponds to the diabatic representation of the free energy surfaces for the electron transfer process. Also it is drawn assuming a linear response of the reaction medium and that the sufaces of the reactant and product states are parabolae of the same curvature, according to Marcus' treatment.

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