Specific cation–solute interactions as a major contributor to the salt effects on charge-transfer transitions

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Abstract

Metal-to-ligand charge-transfer (MLCT) absorption bands for the complexes $Fe(bpy)_3^{2+}$, $Fe(bpy)(CN)_4^{2-}$ and *cis*-$Fe(bpy)_2(CN)_2$ (bpy is 2,2'-bipyridine) are studied in several electrolyte solutions. The indirect influence of the electrolyte through changing the dielectric properties of the medium has been investigated by using the dielectric continuum theory. Results indicate that the hypsochromic shifts observed in the MLCT transition energies of the species $Fe(bpy)(CN)_4^{2-}$ and *cis*-$Fe(bpy)_2(CN)_2$ are mainly produced by specific cation–solute interactions.

Introduction

We have recently been concerned [1–4], as have others [5–23], with medium effects on charge-transfer transition energies. In the initial state, the medium is organized with its dipole oriented to interact with the ground state charge distribution of the complex. The charge distribution of the excited state will usually differ markedly from that of the ground state. Thus, the medium will no longer be favourably oriented towards the Franck–Condon (instantaneous) excited state. Depending on the nature of the medium and the change in charge distribution, the excited state may be stabilized or destabilized. In either case the energy of the transition depends on the medium. Traditionally, the solvent dependence of optical transition energies has been studied in pure solvents or in binary solvent mixtures; however, supporting electrolytes can also produce shifts in the charge-transfer bands [4, 15, 17, 18]. In the current work salt effects on metal-to-ligand (MLCT) charge-transfer transitions of the complexes $Fe(bpy)_3^{2+}$ (tris(2,2'-bipyridine)iron(II)), $Fe(bpy)(CN)_4^{2-}$ (tetra-cyano(2,2'-bipyrine)iron(II)) and *cis*-$Fe(bpy)_2(CN)_2$ (*cis*-dicyano bis(2,2'-bipyrine)iron(II)) are studied in several electrolyte solutions. We have chosen cyano-iron(II) complexes with no permanent dipole moment in the ground state ($Fe(bpy)_3^{2+}$) and with permanent dipole moment in the ground state ($Fe(bpy)(CN)_4^{2-}$ and *cis*-$Fe(bpy)_2(CN)_2$). Besides, the MLCT bands of all of them have been studied in pure solvents and in

binary solvent mixtures [1, 6, 17, 22, 23] and these previous studies can give us valuable information about the nature of these optical transitions.

Experimental

Measurements

Absorption spectra were recorded on a Hitachi 150-20 spectrophotometer at 298.2 K. The measurements were made versus an electrolyte solution blank using matched 1-cm quartz cells. Slow scan rates (0.25 nm s^{-1}) were used to maximize resolution.

Refractive index measurements were made with an Abbe refractometer, after calibration with reference solvents [24]. The measurement precision was ± 0.001.

Materials

$Fe(bpy)_3Cl_2 \cdot 6H_2O$, $K_2Fe(bpy)(CN)_4 \cdot 3H_2O$ and *cis*-$Fe(bpy)_2(CN)_2 \cdot 3H_2O$ were prepared as described elsewhere [1, 25]. Their purity was checked by CHN analysis and by comparison with published spectra. *Anal.* Calc. for $K_2Fe(bpy)(CN)_4 \cdot 3H_2O$: C, 37.5; N, 18.8; H, 3.12. Found: C, 37.1; N, 18.2; H, 3.00%. Calc. for $Fe(bpy)_2(CN)_2 \cdot 3H_2O$: C, 55.7; N, 17.8; H, 4.64. Found: C, 55.5; N, 17.6; H, 4.66%. Calc. for $Fe(bpy)_3Cl_2 \cdot 6H_2O$: C, 51.2; N, 11.9; H, 5.10. Found: C, 51.1; N, 11.3; H, 5.00%.

Alkali, alkaline earth nitrates and sodium perchlorate were obtained from Merck P. A. Lithium nitrate was obtained from Carlo Erba P. A.

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Water was obtained from a Millipore Milli-Q water system; its conductivity was less than 10^{-6} S cm^{-1}.

Results

The metal-to-ligand charge-transfer transitions studied appear in the visible region of the spectrum. In this region the absorption bands of the distinct supporting electrolytes do not interfere. The maximum of the absorption bands was determined to an accuracy of ±0.5 nm. The assignment of the bands in the absorption spectra is well established [26–28].

Table 1 summarizes the refractive index values of the electrolyte solutions used in this work at 298.2 K.

The MLCT transition energies of the species Fe(bpy)$_3^{2+}$ in several salt solutions at 298.2 K are listed in Table 2. Tables 3 and 4 summarize the MLCT transition energies of the complexes Fe(bpy)(CN)$_4^{2-}$ and cis-Fe(bpy)$_2$(CN)$_2$ in various electrolyte solutions at 298.2 K.

Discussion

The presence of an electrolyte in the medium can influence the electronic transition energy of a charge-transfer band in two different ways: indirectly, through the solvent by producing changes in the dielectric properties of the medium (which affects the solvation of the complexes), or directly through specific interactions (like ion-pairing). The indirect influence of the solvent was investigated by using eqn. (1) [14].

$$\Delta E_T = \frac{(\vec{\mu}_e - \vec{\mu}_g)^2}{b^3}\left[\frac{1 - D_{op}}{2D_{op} + 1}\right] + \frac{2\vec{\mu}_g(\vec{\mu}_e - \vec{\mu}_g)}{b^3}\left[\frac{1 - D_s}{2D_s + 1}\right] \quad (1)$$

Here the term $(\vec{\mu}_e - \vec{\mu}_g)$ is the transition dipole, which is a measure of the change in the electron dipole distribution before and after excitation and b is the radius of the species. The subscripts g and e refer to the ground and excited states, respectively. D_s and D_{op} are the static and optical (square of the refractive index) dielectric constants of the medium. The species Fe(bpy)$_3^{2+}$ (with no permanent dipole moment in the ground state) shows extremely small shifts in E_{op} with salt concentration. These shifts are barely larger than the stated error of the measurements for any of the salts used. Thus, although the data show a determinate trend, they are not worth discussing in detail.

The importance of the indirect influence of the supporting electrolyte on complexes Fe(bpy)(CN)$_4^{2-}$ and cis-Fe(bpy)$_2$(CN)$_2$ (with permanent ground state dipole moment [25]), was investigated by using eqn. (1). The static dielectric constant values of sodium nitrate, sodium perchlorate, lithium nitrate and potassium nitrate were taken from the literature [29–31]. The static dielectric constants for the nitrate of divalent cation solutions were estimated following published procedures [32]. The reliability of the estimation was tested by comparing experimental D_s values of monovalent cation nitrates with the calculated ones. Good agreement was found in all cases. With the optical and static dielectric constant values, dual parameter relations were obtained which fit the MLCT transition energies of the form E_{op} (MLCT) $= f[(1 - D_{op})/(2D_{op} + 1)] + f'[(1 - D_s)/(2D_s + 1)]$, where f and f' are the factors shown in eqn. (1), that is, $f = (\vec{\mu}_e - \vec{\mu}_g)/b^3$ and $f' = [2\vec{\mu}_g(\vec{\mu}_e - \vec{\mu}_g)]/b^3$. The dual parameter relations obtained have poor correlation coefficients. Besides, it is interesting to point out that the f factors found were negative. This result is inconsistent with eqn. (1) $(f = (\vec{\mu}_e - \vec{\mu}_g)^2)$ indicating that the supporting electrolyte influence on the MLCT transition energies of the complexes Fe(bpy)(CN)$_4^{2-}$ and cis-Fe(bpy)$_2$(CN)$_2$ is not mainly through changes in the dielectric properties of the medium. Specific interactions play an important role in the energy shifts observed.

TABLE 1. Refractive indexes of several electrolyte solutions at 298.2 K

[Salt] (mol dm^{-3})	NaNO$_3$	NaClO$_4$	LiNO$_3$	KNO$_3$	Ca(NO$_3$)$_2$	Sr(NO$_3$)$_2$	Mg(NO$_3$)$_2$
0.25	1.335	1.334	1.334	1.335	1.333	1.336	1.337
0.50	1.337	1.337	1.336	1.338	1.344	1.346	1.343
0.75	1.339	1.339	1.338	1.341	1.349	1.352	1.348
1.0	1.342	1.341	1.340	1.344	1.354	1.358	1.354
1.5				1.347	1.365	1.369	1.364
2.0	1.350	1.348	1.348	1.345	1.376	1.380	1.374
2.5				1.353	1.385	1.390	1.383
3.0	1.358	1.355	1.356		1.393	1.400	1.392
4.0	1.365	1.361	1.363				
5.0	1.372	1.367	1.370				
6.0	1.379	1.372	1.378				

n_D (pure water) = 1.3325 (taken from ref. 24).

TABLE 2. Values of the MLCT transition energy of the complex $Fe(bpy)_3^{2+}$ in various electrolyte solutions, at 298.2 K

[Salt] (mol dm^{-3})	$10^{-3}\ E_{op}$ (cm^{-1})						
	NaNO$_3$	NaClO$_4$	LiNO$_3$	KNO$_3$	Ca(NO$_3$)$_2$	Sr(NO$_3$)$_2$	Mg(NO$_3$)$_2$
0.50					19.14	19.14	19.15
1.0	19.14	19.14	19.14	19.14	19.12	19.12	19.14
1.5				19.13	19.11	19.11	19.12
2.0	19.12	19.13	19.12	19.13	19.10	19.09	19.11
2.5				19.12	19.08	19.09	19.09
3.0	19.12	19.12	19.11		19.07	19.08	19.08
4.0	19.10	19.12	19.11				
5.0	19.10	19.10	19.09				
6.0	19.08	19.10	19.08				

$10^{-3}\ E_{op}$ (pure water) = 19.15 cm^{-1}.

TABLE 3. Values of the MLCT transition energy of the complex $Fe(bpy)(CN)_4^{2-}$ in various electrolyte solutions, at 298.2 K

[Salt] (mol dm^{-3})	$10^{-3}E_{op}$ (cm^{-1})						
	NaNO$_3$	NaClO$_4$	LiNO$_3$	KNO$_3$	Ca(NO$_3$)$_2$	Sr(NO$_3$)$_2$	Mg(NO$_3$)$_2$
0.25	20.73	20.75	20.77	20.69	20.83	20.80	20.80
0.50	20.76	20.81	20.83	20.71	20.89	20.89	20.94
0.75	20.79	20.84	20.87	20.72	21.00	20.94	21.05
1.0	20.81	20.87	20.91	20.73	21.04	20.99	21.14
1.5				20.74	21.14	21.06	21.24
2.0	20.85	20.94	21.02	20.75	21.20	21.12	21.42
2.5				20.76	21.27	21.16	21.59
3.0	20.89	21.03	21.13		21.35	21.23	21.67
4.0	20.92	21.06	21.25				
5.0	20.95	21.16	21.34				
6.0	21.02	21.20	21.48				

$10^{-3}\ E_{op}$ (pure water) = 20.67 cm^{-1}.

TABLE 4. Values of the MLCT transition energy of the complex cis-Fe(bpy)$_2$(CN)$_2$ in various electrolyte solutions, at 298.2 K

[Salt] (mol dm^{-3})	$10^{-3}\ E_{op}$ (cm^{-1})						
	NaNO$_3$	NaClO$_4$	LiNO$_3$	KNO$_3$	Ca(NO$_3$)$_2$	Sr(NO$_3$)$_2$	Mg(NO$_3$)$_2$
0.25	19.23	19.24	19.24	19.24	19.26	19.25	19.25
0.50	19.23	19.25	19.25	19.24	19.27	19.28	19.29
0.75	19.24	19.26	19.25	19.24	19.29	19.29	19.30
1.0	19.24	19.27	19.30	19.24	19.31	19.31	19.33
1.5				19.24	19.34	19.33	19.39
2.0	19.25	19.30	19.32	19.24	19.38	19.35	19.44
2.5				19.24	19.41	19.36	19.50
3.0	19.27	19.33	19.33		19.44		19.55
4.0	19.27	19.36	19.38				
5.0	19.28	19.38	19.41				
6.0	19.29	19.39	19.47				

$10^{-3}\ E_{op}$ (pure water) = 19.23 cm^{-1}.

The chelate dicyano and tetracyanoferrate(II) complexes are inert to substitution reactions at room temperature. Their electronic spectra consist of two sets of absorption bands, involving the excitation of one electron from a metal d_π-orbital, to the lowest unoccupied orbitals of the aromatic diimine ligand. The configuration of the metal ion in these complexes is typically low spin, as a consequence of the strong ligand field strength of the cyanide and N-heterocyclic ligands. If the electrolyte interacts directly, the solvatochromic shifts would be expected to be principally due to the cation of the salt. This point is clear in the case of

the negatively charged species $Fe(bpy)(CN)_4^{2-}$. The neutral complex cis-$Fe(bpy)_2(CN)_2$ has a dipolar nature. On the other hand, its basic character is shown by its acid affinity [33] (presumably the site of protonation is at the nitrogen atom of the cyanide groups) and therefore a substantial interaction with the cations of the salts would also be expected for this species. Tables 3 and 4 show differences between the energy shifts produced by the presence of sodium nitrate and sodium perchlorate. This could be related to a higher dissociation degree of the perchlorate salt [32], which would cause a greater effective concentration of sodium ions in these media with respect to those of sodium nitrate. In fact, the influence of sodium chloride on the MLCT energies is similar to that of sodium perchlorate. Nonetheless, a possible specific effect of anions cannot be excluded.

Considering a direct cation influence, the site of the cation interaction may be conceivably at the lone pairs of the coordinated cyanide ligands. Both iron(II) complexes in its lowest lying MLCT state have an electron largely transferred from the Fe(II) center out to one of the bpy rings [18]. The drop in electron density at the cyano nitrogens compared to the ground state is profound. For example, for the analogue species $Ru^{II}(bpy)_2(CN)_2$ the K_a of the protonated complex has been shown to increase by nearly six orders of magnitude in the excited state relative to the ground state [34]. Thus, since the molecules around the complex cannot change their orientation during the electronic transition, a greater cation interaction at the cyanide ligands for the ground state than that of the excited state in $Fe(bpy)(CN)_4^{2-}$ and cis-$Fe(bpy)_2(CN)_2$ complexes is expected and therefore a MLCT hypsochromic energy shift with increasing salt concentration, as in fact is observed. However, when the cation introduced in the medium was $(CH_3)_4N^+$, the position of the peak maximum for both iron(II) complexes shifted to lower energy. Nearly saturated solutions of this cation as chloride salt shifted the MLCT band energy of $Fe(bpy)(CN)_4^{2-}$ to 20.45×10^3 cm^{-1}. This could help us to explain the way in which the cations influence the MLCT band energies. The mode of action of the $(CH_3)_4N^+$ cation and the rest of the monovalent cations had to be different. The latter may interact directly via the lone pairs of the coordinated cyanide ligands by displacement of solvent molecules. The $(CH_3)_4N^+$ cation would probably prefer to interact near to the more hydrophobic regions of the bpy ligands. This hypothesis could explain the bathochromic shift in the presence of $(CH_3)_4N^+$ salt since the charge density at the bpy ligand is larger in the excited state than in the ground state.

The sensitivity of the energy shift per mole of M^{n+} follows for both iron(II) complexes the trend

$Mg^{2+} > Ca^{2+} > Sr^{2+}$; $Li^+ > Na^+ > K^+$ (plots of E_{op} against salt concentration are good straight lines for all the electrolytes used). This was also the trend found by Warner et al. [17] in the study of the shifts of the LMCT transition energies of complexes of the $Fe^{III}(CN)_5L^{2-}$ type in several electrolyte solutions. The authors observed that the presence of the salts produced a bathochromic shift, which increases by increasing salt concentration. These changes were explained on the basis of ion-pair formation between the iron(III) complex and the cations present in the medium. The field strength originated by an ion (and then its electrostatic interactions with other molecules) increases by increasing the term q/r (called polarization power), where q is the charge of the ion and r its radius. From Fig. 1(a) and 1(b) one can see that a good correspondence exists between the optical energy shift per mole of electrolyte and the polarization power of the cation present in the medium for the species $Fe(bpy)(CN)_4^{2-}$ and cis-$Fe(bpy)_2(CN)_2$, respectively. Figure 2 shows that a similar correspondence exists in the case of the species $Fe(CN)_5(dmapy)^{2-}$ (dmapy is 4-(dimethylamino)pyridine). These data were taken from ref. 17. Values corresponding to trivalent cations are included in Fig. 2. We have tried to study the influence of Al^{3+} on the MLCT band energies of both iron(II) complexes. However, in order to suppress any potential hydrolysis problem, the cation influence had to be examined in the presence of 0.01 mol dm^{-3} HNO$_3$. In a previous work Schilt [33] found that due to the basic character of the complexes $Fe(bpy)(CN)_4^{2-}$ and cis-$Fe(bpy)_2(CN)_2$, a hypsochromic shift of their MLCT band energies is found by increasing the acidity of the medium. This hypsochromic shift is reversible by adding sodium hydroxide to the medium and therefore is not produced by a change in the oxidation state of the iron center (like in the case of $Fe(bpy)_3^{2+}$ in concentrated acid solutions [33]). In fact, formation equilibrium constants of the protonated complexes can be obtained spectrophotometrically [33]. In a separate experiment with 0.01 mol dm^{-3} HNO$_3$ alone a large hypsochromic shift of the MLCT band of the species $Fe(bpy)(CN)_4^{2-}$ was found relative to water. In the case of the MLCT transition of the complex cis-$Fe(bpy)_2(CN)_2$ a small hypsochromic shift was observed. For this reason we cannot study the influence of Al^{3+}.

Figures 1 and 2 show similar good correlations for the species $Fe^{II}(bpy)(CN)_4^{2-}$, cis-$Fe^{II}(bpy)_2(CN)_2$ and $Fe^{III}(CN)_5(dmapy)^{2-}$. This can be taken as evidence that the same type of interactions are operative in the three cases; that is, supporting electrolyte influence on the optical transition energies of the above species is mainly through specific cation–solute interactions.

The results of this study could be useful for explaining kinetic salt effects observed on redox reactions which
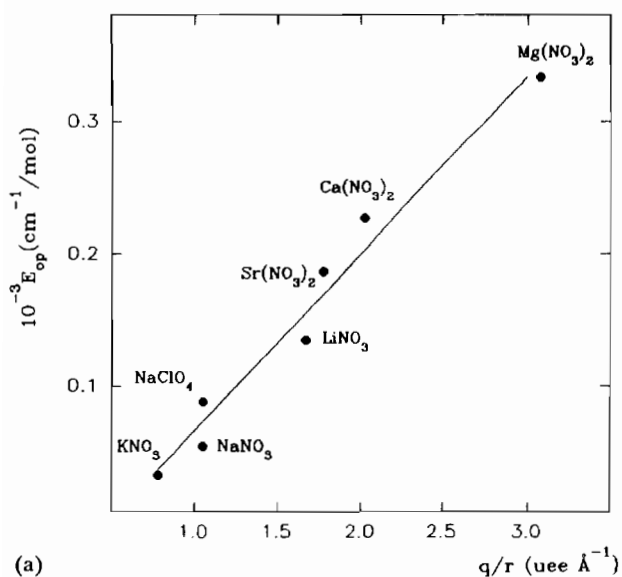
(a)
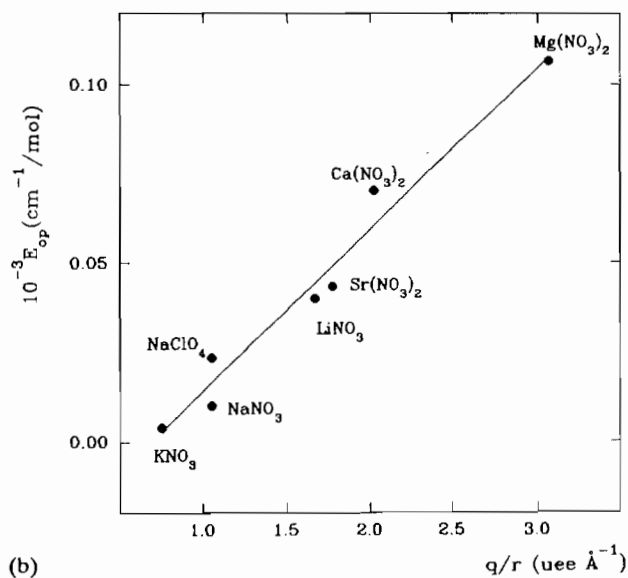
(b)

Fig. 1. Plots of the increments of electronic MLCT transition energies per mole of electrolyte against the polarization power of the cations present in the medium. $T=298.2$ K. (a) $Fe(bpy)(CN)_4^{2-}$; (b) cis-$Fe(bpy)_2(CN)_2$.

Fig. 2. Plot of the increments of the electronic LMCT transition energy of the complex $Fe(CN)_5(dmapy)^{2-}$ per mole of electrolyte against the polarization power of the cations present in the medium. $T=298.2$ K.

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involve cyanide complexes. The electron-transfer self-exchange process for the $Fe(CN)_6^{4-/3-}$ pair is accelerated by the presence of cations in the medium [35], following the trend $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$; $Sr^{2+} > Ca^{2+} > Mg^{2+}$. This was also the trend observed in the study of the redox reactions $Fe(CN)_6^{4-}/S_2O_8^{2-}$ [36] and $Mo(CN)_8^{4-}/S_2O_8^{2-}$ [37] in concentrated nitrate salt solutions. These results could be explained by considering that the electron transfer process occurs via cation-bridged ion pairs. Hence, the study of salt effects on charge-transfer transitions gives additional informations which can help explain kinetic salt effects.
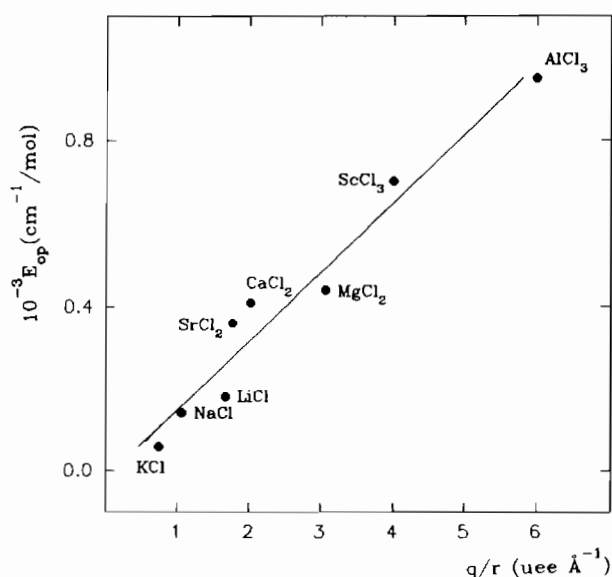
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