Correlations between Optical Charge Transfer Energies and Electrochemical Data: The Iron(III)–Catecholato System

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The electronic spectra of the $Fe(CTH)(Cat)^+$ complexes (CTH = tetraazamacrocycle; Cat = 3,5-di-*tert*-butylcatecholato, tetrachlorocatecholato) are characterized by LMCT transitions having solvatochromic character. In order to correlate the optical energies of these transitions with the electrochemical data, the free energy, enthalpy, and entropy changes associated with the redox couple $Fe^{III}(CTH)(Cat)/Fe^{II}(CTH)(Cat)$ vs Fc^+/Fc have been determined in four different solvents by cyclic voltammetry experiments at various temperatures. Following an analogous procedure, the same quantities have been obtained for the redox couples $M^{II}(CTH)(SQ)/M^{II}(CTH)(Cat)$ vs Fc^+/Fc (M = Ni, Zn; SQ = semiquinonato). By assuming that the latter quantities also characterize the the experimentally undetectable equilibrium $Fe^{II}(CTH)(SQ)/Fe^{II}(CTH)(Cat)$, the thermodynamic parameters asssociated with the LMCT equilibrium $Fe^{III}(CTH)(Cat)/Fe^{II}(CTH)(SQ)$ can be calculated and the enthalpy changes compared with the optical energies obtained from spectroscopic data. This comparison suggests that the observed solvatochromism of these iron(III)–catecholato chromophores is basically due to the difference in solvation enthalpies of the two electronic isomers $Fe^{III}(CTH)(Cat)^+$ and $Fe^{II}(CTH)(SQ)^+$ in their states of vibrational equilibrium. The effects of the solvent reorganization energies do not appear to be relevant.

Introduction

There are several examples in the chemical literature of correlations between the optical energies of charge-transfer transitions and electrochemical potentials of transition metal complexes.[1-23] The main goal of these correlations is to provide information on the differences of solvation energies of the ground and excited states and the contributions due to the reorganization energies involved in the electronic transitions. Although most authors sought only qualitative relationships in the combined analysis of their optical and electrochemical data, the work developed by Lever *et al.*[1,6,14-17,23] and Meyer *et al.*[12,18,20,21] provides a significant evidence of the amount of quantitative information which can be obtained through an appropriate treatment of the experimental data.

In a simple view the problem is reduced to the analysis of the thermodynamic cycle shown in (1). It is quite clear that the

$$\begin{tikzcd}
M^{(+)}-L \arrow[rrd, shift left, "CT"] & & \\
M-L \arrow[u, "-e"] \arrow[rr, "-e"'] & & M-L^{(+)} \arrow[llu, shift left]
\end{tikzcd} \qquad (1)$$

energy associated with a charge-transfer (CT) transition involving the $M^{(+)}$–L and the M–$L^{(+)}$ species can be considered as the difference between the energies involved in the one electron redox processes $M^{(+)}$–L/M–L and M–$L^{(+)}$/M–L. It is obvious that it is impossible to experimentally observe both of the redox processes, since only the one requiring lower energy can be detected. Nevertheless, by choosing an appropriate system, it is possible to reasonably estimate the redox potential associated with the undetectable process. Under this hypothesis it is possible to calculate the free energy difference between the two electronic isomers $M^{(+)}$–L and M–$L^{(+)}$. This quantity corresponds to the free energy associated with the transition from the electronic ground state to the first charge-transfer excited state. It must be recalled that both states are in vibrational and solvent environmental equilibrium. An optical transition on the other hand involves an excitation from a ground donor level in vibrational equilibrium to a nonequilibrium acceptor level, according to the Franck–Condon principle. The difference between the optical free energy and that calculated from electrochemical potentials, therefore, is due to the difference in solvation energy of the ground and excited states and to the reorganization energy of the excited state and provides useful information on these processes.

There is one point in this approach deserving consideration. From the Franck–Condon principle, the free energy change of a molecular system undergoing an optical transition corresponds in practice to an enthalpy change of the system,[24] and therefore the optical energy should be better correlated with the enthalpy changes associated with the redox couples appearing in (1). These

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quantities can be determined with reasonable accuracy by measuring the temperature dependence of the redox potentials.[25,26] In all the correlations established so far only free energy changes, i.e. the electrochemical potentials of the redox couples, were used, and all of the reported conclusions are based on the assumption that the entropy changes are small and then negligible.

The goal of the present study is to show how, by determining all the thermodynamic quantities associated with the equilibria appearing in (1), a different analysis of the electrochemical and optical data can be made. The system considered here concerns the iron(III)–catecholato complexes Fe(CTH)(DTBCat)$^+$ and Fe(CTH)(TCCat)$^+$, $M^{(+)}$–L in (1), (CTH = *d,l*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; DTBCat = 3,5-di-*tert*-butyl-catecholate, TCCat = tetrachlorocatecholate), which can be prepared by one-electron oxidation of the corresponding iron(II) complex (M–L).[27] The electronic spectrum of this compound is dominated by strong LMCT transitions, having solvatochromic character. In previous papers it was shown that the one-electron oxidation of complexes of general formula M^{II}(CTH)(Cat) (M = Ni, Zn; Cat = DTBCat, TCCat), which in the thermodynamic cycle in (1) can be related to the M–L species, involves the dioxolene ligand, yielding the semiquinonato derivative M^{II}(CTH)(SQ)$^+$, *i.e.* the M–L$^+$ species in (1).[28,29] All these complexes are six-coordinate, the macrocyclic ligand being ligated in a folded configuration and the dioxolene acting as a bidentate ligand. The fact that the ligand-centered oxidation processes for the different metal derivatives occur at very similar potential values suggested to us to attempt for this system a combined analysis of the electrochemical and optical data.

Experimental Section

Materials. M(CTH)(DTBSQ)PF$_6$, M(CTH)(TCCat) (M = Ni, Zn), Fe(CTH)(DTBCat)PF$_6$, and Fe(CTH)(TCCat)PF$_6$ were prepared as previously described.[27-29] Tetrabutylammonium hexafluorophosphate (Fluka) was recrystallized from ethanol and dried *in vacuo.* 1,2-Dichloroethane (DCE), acetonitrile (AN), propylene carbonate (PC), and dimethylformamide (DMF) were dried on molecular sieves and then distilled under vacuum.

Physical Methods. The electrochemical analysis by cyclic voltammetry was carried out by using an electrochemical unit (Amel Model 553 potentiostat equipped with Amel 863, 560/A, and 568 elements and an Amel 731 integrator) and a classical three-electrode thermostated cell equipped with a thermometer. The working electrode was a platinum microsphere, the auxiliary electrode was a platinum disk, and the reference electrode was a calomel electrode in aqueous saturated KCl (SCE). The salt bridge between the working cell and the calomel electrode was constituted by a 0.1 M NBu$_4$PF$_6$ salt bridge in the appropriate solvent and aqueous 1 M KCl. The liquid junctions between the four compartments were formed using glass frits (average porosity 1 μm) which prevented significant mixing of the solutions on the time scale of the experiments (3–4 h). The working compartment, i.e. the cell and partially the liquid junction, were thermostated by a jacket through which liquid was circulated. The temperature of this compartment was controlled to within 0.1 °C. The calomel electrode was thermostated at 25 °C by a separate jacket. The temperature of the cell solution was varied from 260 to 323 K. The temperature dependence of the potential was approximated to that of the Galvani metal–solution potential difference at the working electrode.[25,26] All potentials were measured against the ferrocenium/ferrocene couple (Fc$^+$/Fc), which was used as the internal standard. Cyclic voltammograms were obtained with sweep rates of 0.05 V s^{-1}. Before each experiment the solutions were carefully deareated with a nitrogen flow. Electronic spectra were recorded using a Perkin-Elmer Lambda 9 spectrophotometer.

Table I. Absorption Maxima (kJ mol^{-1}) of the LMCT Transition $\pi^*(\mathrm{Cat}) \rightarrow 3d_\pi$ of the Fe(CTH)(Cat)$^+$ Chromophores in Various Solvents Containing 0.1 M NBu$_4$PF$_6$ at 25 °C[a]

solvent	DTBCat	TCCat
DCE	136.3	160.3
AN	144.1	167.4
PC	143.5	170.4
DMF	148.3	173.9

[a] Estimated error: ±0.3 kJ mol^{-1}.

Results and Discussion

The Fe(CTH)(Cat)$^+$ complexes are characterized by two intense absorption bands in the visible region, whose energies are solvent dependent.[27] The two bands have been assigned as LMCT, *i.e.* Fe(III)-Cat → Fe(II)SQ, and this means that the electric dipole moments of the transitions lie in the opposite direction with respect to the permanent dipole moment of the chromophores. In the following, for the sake of simplicity, we shall limit our discussion only to the CT band occurring at lowest energy, *i.e.* that assigned as $3b_1(\pi^*) \rightarrow 3d(\pi)$. In order to relate the optical energies associated to this transition to the electrochemical data, the electronic spectra were recorded in solutions containing 0.1 M NBu$_4$PF$_6$. The presence of the electrolyte markedly affects the spectral properties of the TCCat chromophore, the absorption maxima being red shifted by 600–800 cm^{-1} with respect to the pure solvents. The spectra of the DTBCat chromophore are not significantly affected by the addition of the electrolyte. As shown in Table I, the chromophores exhibit a negative solvatochromism on increasing the donor power of the solvent. The optical energies fall in the range 136–148 and 160–174 kJ mol^{-1} for the DTBCat derivative and the TCCat one, respectively.

For the present system the thermochemical cycle in (1) can be written as

$$\begin{tikzcd}
\mathrm{Fe(III)Cat} \arrow[dr, "\mathrm{CT}"] & \\
\mathrm{Fe(II)Cat} \arrow[u, "-e"] \arrow[r, "-e"'] & \mathrm{Fe(II)SQ}
\end{tikzcd} \qquad (2)$$

In order to evaluate the thermodynamic quantities associated with the CT equilibria, the free energy changes associated with the equilibria

$$\mathrm{M(CTH)(Cat)} + \mathrm{Fc}^+ \rightleftarrows \mathrm{M(CTH)(SQ)}^+ + \mathrm{Fc} \qquad (3)$$
$$\mathrm{M} = \mathrm{Ni, Zn}$$

and

$$\mathrm{Fe^{II}(CTH)(Cat)} + \mathrm{Fc}^+ \rightleftarrows \mathrm{Fe^{III}(CTH)(Cat)} + \mathrm{Fc} \qquad (4)$$

(Fc$^+$/Fc = ferrocenium/ferrocene) were determined by cyclic voltammetry experiments in the temperature range 260–323 K in four different solvents, *i.e.* 1,2-dichloroethane (DCE), propylene carbonate (PC), acetonitrile (AN), and dimethylformamide (DMF). The supporting electrolyte was always 0.1 M NBu$_4$PF$_6$. All the above couples are reversible in these solvents, with the exception of the zinc–TCCat derivative in DCE solution and the nickel analogue in the high temperature range. The observed electrochemical potentials at 298 K are shown in Table II. It is apparent that the ΔG values associated with equilibrium 3 are very similar to each other. It was therefore assumed that the ΔG, calculated as the average of these values, characterizes also the equilibrium

$$\mathrm{Fe^{II}(CTH)(Cat)} + \mathrm{Fc}^+ \rightleftarrows \mathrm{Fe^{II}(CTH)(SQ)}^+ + \mathrm{Fc} \qquad (5)$$

which cannot be measured experimentally. The assumption holds within the approximation that the free energy characterizing the ligand-centered redox couple M^{II}(CTH)(SQ)$^+$/M^{II}(CTH)(Cat) depends only on the nature of the dioxolene ligand, and all the

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Table II. Electrochemical Potentials $E_{1/2}$ (mV vs Fc$^+$/Fc)[a] at 25 °C and Their Temperature Coefficients dE/dT (mV K^{-1})[b] for the M(CTH)(diox)$^{+/0}$ Couples (M = Fe, Ni, Zn; diox = dioxolene) in Various Solvents[c]

couple		DCE	AN	PC	DMF
Ni(CTH)(DTBSQ)$^{+/0}$	$E_{1/2}$	−1136	−971	−965	−997
	dE/dt	−1.43	−1.06	−0.50	−0.38
Zn(CTH)(DTBSQ)$^{+/0}$	$E_{1/2}$	−1120	−909	−906	−930
	dE/dT	−1.37	−1.04	−0.50	−0.36
Fe(CTH)(DTBSQ)$^{+/0}$	$E_{1/2}$[d]	*−1128*	*−940*	*−935*	*−963*
	dE/dT[d]	*−1.40*	*−1.05*	*−0.50*	*−0.37*
Fe(CTH)(DTBCat)$^{+/0}$	$E_{1/2}$	−1360	−1190	−1200	−1267
	dE/dT	−0.80	−0.55	0.05	0.21
Ni(CTH)(TCSQ)$^{+/0}$	$E_{1/2}$	−407[e]	−286	−262	−282
	dE/dT		−0.38	0.21	−0.08
Zn(CTH)(TCSQ)$^{+/0}$	$E_{1/2}$	i[f]	−254	−222	−238
	dE/dT		−0.44	0.19	−0.04
Fe(CTH)(TCSQ)$^{+/0}$	$E_{1/2}$[d]	*−407*	*−270*	*−242*	*−260*
	dE/dT[d]	–	*−0.42*	*0.20*	*−0.06*
Fe(CTH)(TCCat)$^{+/0}$	$E_{1/2}$	−900	−802	−818	−862
	dE/dT	0.75	0.08	0.76	0.46

[a] The potentials are the average anodic and cathodic peak potentials in cyclic voltammograms recorded at 50 mV s^{-1}. Estimated error: ±3 mV. [b] The temperature coefficients are determined in the temperature range 260–323 K. Estimated error: ±0.1 mV K^{-1}. [c] For solutions ca. 10^{-3} M. [d] These data are the average of those observed for the Ni and Zn analogues (see text). [e] Irreversible at $T \geq 300$ K. [f] i = irreversible.

differences in metal–ligand interactions—crystal field stabilization energies, spin coupling between the radical ligand and the paramagnetic metal ions, etc.—which in turn depend on the nature of the divalent metal ion, are negligible. It is reasonable to believe that the estimation of the free energy associated with (5) by following this procedure is affected by an absolute error not larger than 5 kJ mol^{-1}. Support to this statement is provided by the electrochemical data observed for the Mn^{II}(CTH)(DBSQ)$^+$ complex which undergoes a one-electron reduction at −947, −938, and −1020 mV vs Fc$^+$/Fc in AN, PC, and DMF, respectively, in good agreement with the values shown in Table II for the Ni and Zn analogues.[30] It is also reasonable to suggest that this uncertainty does not affect the main conclusions of this study, if one considers the regular pattern of the electrochemical data in the various solvents.

Thus by subtracting (5) from (4) the ΔG value for the LMCT process

$$\mathrm{Fe^{III}(CTH)(Cat)^+ \rightleftarrows Fe^{II}(CTH)(SQ)^+} \qquad (6)$$

can be calculated, and the obtained values are given in Table III.

A satisfactory linear dependence of the redox potentials vs $1/T$ was found in all of the investigated systems in the temperature range considered. The temperature coefficients of the observed potentials are shown in Table II. From the relationship

$$F\delta\Delta E/\delta T = -\delta\Delta G/\delta T = \Delta S$$

the enthalpy and entropy changes associated with the equilibria (3) and (4) were obtained and combined as outlined above for the free energy changes, yielding the enthalpy and entropy changes associated with equilibrium 6 in the four different solvents. The calculated values of these quantitites are shown in Table III.

As expected, the free energy changes associated to equilibrium (6) are positive and significantly larger for the TCCat derivative than for the DTBCat one, the difference being 25–30 kJ mol^{-1} in the various solvents. This result reflects the different substituent effects on the dioxolene ligands. It is worth mentioning, however, that for the free ligands a difference of 60–70 kJ mol^{-1} characterizes the redox couple SQ/Cat.[31] This indicates that coordination to iron(III) stabilizes the more basic DTBCat dianion better than the TCCat one.

Table III. Calculated Thermodynamic Parameters (**kJ** mol^{-1}) for the Equilibrium Fe^{III}(CTH)(Cat)/Fe^{II}(CTH)(SQ) in Various Solvents at 25 °C[a]

	DCE	AN	PC	DMF
	Cat = DTBCat			
ΔG	22.4	22.1	25.6	29.3
ΔH	39	39	41	46
$T\Delta S$	17	15	16	17
$\Delta(E_{op} - \Delta H)$	97	105	102	102
	Cat = TCCat			
ΔG	47.6	51.3	55.6	58.1
ΔH		66	72	75
$T\Delta S$		15	16	16.5
$\Delta(E_{op} - \Delta H)$		101	98	99

[a] Estimated errors: ΔG, 0.3 kJ mol^{-1}; ΔH, 3.5 kJ mol^{-1}; $T\Delta S$, 3.0 kJ mol^{-1}; $\Delta(E_{op} - \Delta H)$, 4 kJ mol^{-1}.

The endoergonic character of the processes is determined by the enthalpy contributions. It must be pointed out, however, that the entropy contributions are not negligible, even if associated with isoelectric equilibria. Their positive sign can be simply related to the fact the the orientation of the solvating molecules is reduced on passing from the iron(III)–catecholato species to the iron(II)–semiquinonato one. The entropy contributions, therefore, reduce the effect of the unfavorable enthalpy terms, shifting equilibrium (6) to the right as the temperature increases. The examples to date reported of equilibria involving valence tautomerism in dioxolene complexes , *i.e.* Mn^{IV}(py)$_2$(DTBCat)$_2$/Mn^{II}(py)$_2$(DTBSQ)$_2$[32] and Co^{III}L(DTBCat)(DTBSQ)/Co^{II}L(DTBSQ)$_2$ (L = diazine ligand)[33,34] support this view, since all these equilibria shift toward the semiquinonato species on increasing temperature.

The free energy changes associated with (6) increase on passing from DCE to AN, PC, and then DMF, thus indicating that the more polar iron(III)—catecholato species are stabilized with respect to the semiquinonato one on increasing the donor power of the solvent. A relevant aspect of the obtained results is the fact that the increase of the ΔG values is due to the increase of the enthalpy term, since the entropy contribution remains roughly constant. This means that the difference of the solvation entropies of the catecholato and semiquinonato species does not significantly depend on the nature of the solvent.

The increase of the enthalpy contribution on increasing the donor power of the solvent indicates that the stabilization of the iron(III)–catecholato species with respect to the iron(II)–semiquinonato species is due to a more favorable solvation enthalpy. This result does not follow the predictions of the continuous dielectric medium theory. According to this model, Born stated that the solvation enthalpy of an ionic species is given by the relationship

$$\Delta H_{\mathrm{solv}} = -Nz^2e^2[1 - (1 + T\delta(\ln D)/\delta T)/D]/2r$$

where z is the ionic charge, e the electronic charge, r the ionic radius and D the bulk dielelectric constant of the medium.[35] Since the charge-transfer process (6) is isoelectric and the ionic radius is expected to experience small variations on passing from a species to the other, the solvation enthalpies of both reactant and product

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(30) The electrochemical properties of Mn^{II}(CTH)(DTBSQ)$^+$ are similar to those of the Ni and Zn analogues in AN and PC (Dei, A. *Inorg. Chim. Acta*, in press). In DCE and, at low temperature, in DMF the Mn(CTH)(DTBSQ)$^+$/Mn(CTH)(DTBCat) system is not reversible and therefore this system was not considered for the present study.

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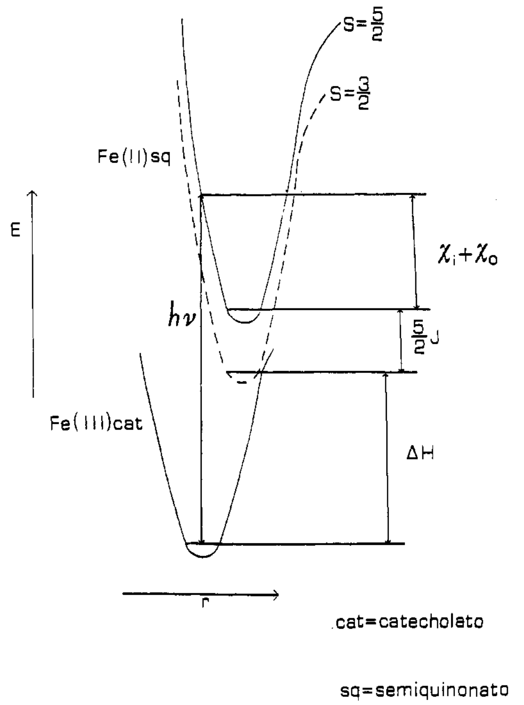

Figure 1. Energy-coordinate diagram of the LMCT transition for the Fe(CTH)(Cat)$^+$ chromophores.

in (6) are expected to be similar in a given solvent, and their differences are expected to not significantly vary in the different solvents. The observed experimental data, therefore, are not consistent with this model.

In the light of these results, we may return to consider the solvatochromic LMCT transition of the Fe(CTH)(Cat)$^+$ chromophores. The optical energies (Table I) associated with this transition are large compared to the enthalpy changes shown in Table III, but this result is not unexpected. In practice the optical energy corresponds to an enthalpy change of the system and can be considered the sum of three terms, *i.e.* the 0–0′ energy, the internal reorganization energy χ_i and the outer-sphere reorganization energy χ_o (Figure 1). The 0–0′ energy, even if the approximation we introduced in the procedure was fully correct, does not correspond to the enthalpy change associated with (6), since the complex contains high-spin iron(III) and then the LMCT transitions involve sextet states. It is reasonable to believe that the Fe^{II}(CTH)(SQ)$^+$ complexes should be characterized by a quartet ground state according to the fact that a strong antiferromagnetic coupling between the metal ion (S = 2) and the radical (S = $^1/_2$) is expected to be operative.[36] The energy difference between the quartet and sextet states is $5J/2$, where J is the exchange coupling constant,[37] but for metal–semiquinonato complexes this quantity is so large that it cannot be determined through magnetic measurements. If we arbitrarily assume that a J value of 500 cm^{-1} would characterize the exchange interaction, then the difference between the quartet ground state and the sextet excited state should be 1250 cm^{-1}, *i.e.* ca. 15 kJ. Under this hypothesis the energy differences between the vibrational 0–0′ levels of the sextet states are estimated to be something like 15 kJ mol^{-1} larger than those resulting from electrochemical data, which refer to species in their electronic ground states and in vibrational equilibrium.

Furthermore the term χ_i is expected to be large for these systems. Although no structural data are available for these Fe(CTH)(Cat)$^+$ complexes, the literature suggests that the difference between the metal–oxygen distances in the iron(III)–catecholato and iron(II)-semiquinonato species should be larger than at least 10 pm.[38,39] Also, the equilibrium geometries of the catecholato and semiquinonato moieties are known to be significantly different. As an example the C–O distances fall in the ranges 134–136 and 128–130 pm for catecholato and semiquinonato, respectively. Therefore, following the Franck–Condon principle, it is reasonable to expect that the excited states of the chromophores should be characterized by a large vibrational distortion.

It is interesting to stress that the differences between the optical energies and the enthalpy changes associated with (6) ($E_{op} - \Delta H$ in Table III) are very close to each other, the average value being 101 ± 4 kJ mol^{-1}. It is reasonable to assume that the contributions due to the exchange interactions and to the internal reorganization energies are roughly independent of the solvent. The fact that for these chromophores the difference $E_{op} - \Delta H$ is also roughly constant, means that the outer-sphere reorganization energy term χ_o does not experience significant variations in the different solvents. It does not seem inappropriate, therefore, to suggest that, in the light of the assumptions made and the uncertainties affecting the enthalpy and entropy changes, the solvatochromism of these chromophores is largely determined by the differences of the 0–0′ energies characterizing the sextet states, *i.e.* by the differences in their solvation enthalpies.

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