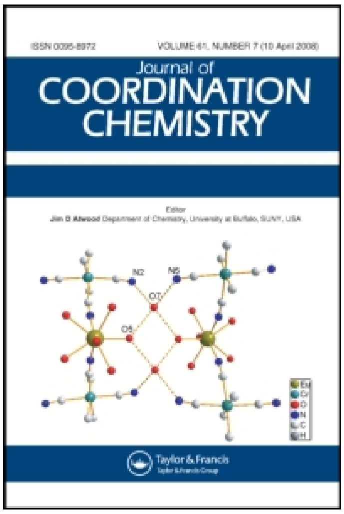

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Studies of the spin crossover complex iron(ii)-2,6-*bis* (benzimidazol-2'-yl)pyridine in propanediol-l,2-carbonate

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STUDIES OF THE SPIN CROSSOVER COMPLEX IRON(II)-2,6-*BIS*-(BENZIMIDAZOL-2′-YL)PYRIDINE IN PROPANEDIOL-1,2-CARBONATE

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Variable temperature studies on iron(II)-2,6-*bis*-(benzimidazol-2′-yl)pyridine complex with and without excess ligand show that spin equilibria are influenced by complexation equilibria in propanediol-1,2-carbonate (PDC). In the presence of excess ligand the complex shows only spin crossover behaviour. The complex exhibits strong thermochromic behaviour and increasing of temperature leads to a change to the high-spin (HS) state and *vice versa*. Values of spin equilibria constants (K_{SC}) and associated thermodynamic parameters (ΔH_{SC} and ΔS_{SC}) were evaluated and found to be influenced by complexation equilibria. In accordance with solvent polarity effects on spin equilibria, the complex is more stable in the LS case in PDC than in MeOH. This is reflected by the high values of enthalpic and entropic terms in PDC (4.2 kcal mol^{-1} and 14.8 cal mol^{-1} K^{-1})* than in MeOH (3.9 kcal mol^{-1} and 12.9 cal mol^{-1} K^{-1}).

Keywords: spin crossover; complexation; iron(II); 2,6-*bis*-(benzimidazol-2′-yl)pyridine

INTRODUCTION

Spin crossover behaviour of transition metal ions (d^4 to d^7) between the low-spin (LS) and high-spin (HS) states is observed when the ligand field splitting energy (10Dq) becomes comparable with the electron pairing energy (P) as a function of temperature.[1–3] The ligand 2,6-*bis*-(benzimidazol-2′-yl)pyridine (bzimpy) coordinates with iron(II) as a terdentate and forms both *mono*- and *bis*-species, $[Fe(bzimpy)S_3]^{2+}$ (S = solvent) and $[Fe(bzimpy)_2]^{2+}$, in 50% (v/v) PDC/MeOH and in MeOH solutions.[3–4] Complexation equilibria are complicated by partial dissociation of the complex even in the presence of excess ligand in MeOH.[3–4,6]

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* 1 Cal = 4.184J.

Indeed, complete complexation at stoichiometric amounts of bzimpy to iron(II) (*i.e.*, [L]/[Fe(II)] = 2.0) is only found in 50% (v/v) PDC/MeOH.[3–4] However, $[Fe(bzimpy)_2]^{2+}$ was isolated as a salt, investigated in detail and found to exhibit pronounced spin crossover behaviour both in solution and the solid state.[3–11] Here, ligand substitution, solvent donor-acceptor properties, lattice water, complex deprotonation and hydrogen bonding strongly influence the spin crossover of the complex as reported before.[3–11] Further, the spin crossover might influence complexation equilibria as shown for complexes of phen and bipy with iron(II).[12]

In view of the above, it was planned to investigate spin crossover behaviour of $[Fe(bzimpy)_2]^{2+}$ with and without excess ligand, both with heating and cooling, in propanediol-1,2-carbonate (PDC) and to observe the relationship of complexation equilibria with spin equilibria. In addition, values of spin equilibria constant (k_{SC}) and the associated thermodynamic parameters (ΔH_{SC} and ΔS_{SC}), excluding any influence of complexation equilibria, have been evaluated.

EXPERIMENTAL

The ligand, 2,6-*bis*-(benzimidazol-2′-yl)pyridine (bzimpy) and the complex, $[Fe(bzimpy)_2](ClO_4)_2$, were prepared according to the literature.[3–7,13] Propanediol-1,2-carbonate (PDC) (Loba) was refluxed for 24 hours under reduced pressure and fractionally distilled.

Spectrophotometric Measurements

Electronic spectra were obtained with a Hitachi U-2000 spectrophotometer, equipped with an electronically thermostatted cell (Hitachi) in the range 0–100 (± 0.5)°C; the quartz cell had a path length of 1.0 cm. Temperature was recorded by a copper-constantan thermocouple mounted within the cell and homogeneous temperature distribution was provided by use of a magnetic stirrer. Observed molar absorbtivities ($\varepsilon/M^{-1}\ cm^{-1}$) were corrected for changes in the solvent density, changing concentration of solute and temperature variation.[14–15] The concentration of complex with (*i.e.*, $[L]/[FeL_2]^{2+} = 20$) and without excess ligand was 1.7710×10^{-4}M and 2.0417×10^{-4}M, respectively.

Magnetic Measurements

^1H NMR spectra were run on a Bruker AC 250 FT spectrometer operating at 250 MHz. High precision NMR sample tubes (type 528-PP, Wilmad Glass Co.) with sealed Wilmad coaxial inserts (WGS-5BL) containing 5% TMS in acetone-d^6

were used as external standard and instrument lock. Magnetic moments [μ/μB] of the complex (5.2572 × 10^{-4}M) with excess ligand ([L]/$[FeL_2]^{2+}$ = 8.05) were measured in PDC by the Evans ^{1}H NMR method[16] using methanol for temperature calibration.[17] Observed magnetic moments (μ/μB) were corrected for changes in the solvent density, changing concentration of solute and temperature variation.[14–15] Dioxane (0.5% v/v) was used as internal reference.

RESULTS AND DISCUSSION

Variable temperature electronic spectra of $[Fe(bzimpy)_2](ClO_4)_2$ were obtained in the range 276 to 342K in PDC. The spectra are shown in Figure 1 and data are summarized in Table I. The metal-to-ligand charge transfer band ($T_{2g} \rightarrow \pi^*$, mlct) found at 420–620nm consists of a main absorbtion band at 554.5nm (at 294K) and a shoulder at shorter wavelength (see Figure 1), associated with the low-spin (LS)- and high-spin (HS)-isomers of the complex, respectively.[5–10] The lowest unfilled ligand π* orbitals are assumed to occur at relatively higher energies in the HS isomer than in the LS one, resulting in a higher energy mlct transition.[3,5,8–9,18-19] The intense band centred about 554nm results from the increasingly populated LS isomer in PDC. However, the strong and weak overlap between metal T_{2g} and ligand π* orbitals result in intense and weak bands for the LS and HS isomers, respectively.[3–5,8–9] Weak and broad bands at 620–730nm (see Figure 1) are attributed to the *d-d* transition of the metal ion.[3–8]

TABLE I Variable temperature spectroscopic data for $[Fe(bzimpy)_2]^{2+}$ with and without excess ligand for both heating and cooling in PDC

T^a [K]	λ_{max} [nm]	ε557nm [$M^{-1}cm^{-1}$]	T^b [K]	λ_{max} [nm]	ε557nm [$M^{-1}cm^{-1}$]
277.1$^+$	555.0	6399	276.9$^+$	555.0	7266
280.5	555.0	6075	280.5	555.0	6920
284.7	555.0	5771	285.0	555.0	6572
289.1	554.5	5466	289.5	555.0	6236
293.5	554.5	5159	293.9	554.5	5905
298.1	554.5	4865	298.6	554.5	5577
302.7	554.5	4574	303.3	554.5	5265
307.5	554.0	4296	308.0	554.0	4961
313.2	554.0	3979	314.6	554.0	4582
317.1	553.5	3774	318.4	554.0	4368
321.6	553.0	3554	322.5	553.5	4159
326.4	552.5	3292	327.4	554.0	3933
331.3	552.0	3044	332.3	553.5	3712
335.9	552.0	2839	337.3	553.0	3507
340.3*	551.5	2657	341.6$^+$	552.5	3333

TABLE I (*Continued*)

T^a [K]	λ_{max} [nm]	ε557nm [$M^{-1}cm^{-1}$]	T^b [K]	λ_{max} [nm]	ε557nm [$M^{-1}cm^{-1}$]
336.6	551.5	2754	337.4	553.0	3507
332.0	551.5	2914	332.6	553.5	3719
327.2	552.5	3093	328.1	553.5	3907
322.7	553.0	3276	323.3	553.5	4133
317.6	553.0	3510	319.0	554.0	4359
313.8	553.0	3702	314.4	554.0	4593
309.2	553.5	3930	309.9	554.0	4855
305.2	554.0	4148	305.4	554.5	5149
301.1	554.0	4380	300.9	554.5	5452
296.1	554.0	4684	296.5	554.5	5765
291.8	554.5	4946	291.8	555.0	6096
287.2	554.5	5247	287.5	555.0	6416
282.8	554.5	5529	282.3	555.0	6796
277.9	554.5	5864	277.7	555.0	7127

^{a}Complex solution without and ^{b}with excess ligand ($[L]/[FeL_2]^{2+}$ = 20).
$^+$Heating and *cooling start.

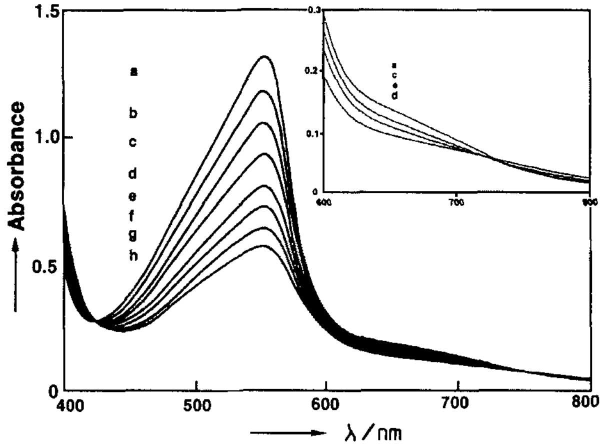

FIGURE 1 Electronic absorbtion spectra of $[Fe(bzimpy)_2](ClO_4)_2$ (1.771×10^{-4} M) with excess ligand ($[L]/[FeL_2]^{2+}$ = 20) in propanediol-1,2-carbonate at different temperatures: (a) 276.9K, (b) 285.0K, (c) 293.9K, (d) 303.3K, (e) 314.6K, (f) 322.5K, (g) 332.3K and (h) 341.6K.

Complexation Equilibria

Both heating and cooling spectra of the complex, $[Fe(bzimpy)_2]^{2+}$ were obtained in the temperature range 276 to 341K in PDC. Changes of molar absorbtivities with temperatures for both sets of spectra are shown in Figure 2a and the data are listed in Table I. Deviation of the heating from the cooling curve (see Figure 2a and Table I) suggests dissociation of the complex and favours the

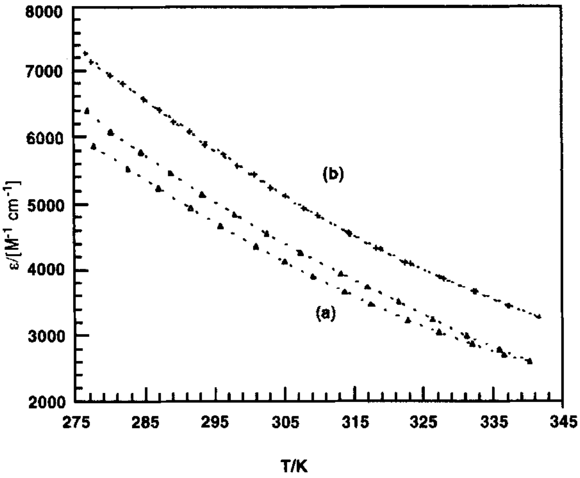

FIGURE 2 Changes in molar absorbtivities at 557nm (ε557nm/M^{-1} cm^{-1}) with temperature for both heating and cooling spectra of [Fe(bzimpy)$_2$]$^{2+}$: (a) without and (b) with excess ligand in PDC.

low absorbing *mono* complex [Fe(bzimpy)S$_3$]$^{2+}$ with heating. To avoid such an undesirable situation, both heating and cooling spectra of the complex with excess ligand were obtained. Changes of molar absorbtivities with temperature are shown in Figure 2b and data are listed in Table I. Here, the heating and the cooling curves coincide and this strongly indicates the absence of any involvement of complexation equilibria in spin equilibria. Indeed, the complex is more stable in the LS state and the high stability of [Fe(bzimpy)$_2$]$^{2+}$ in PDC diminishes dissociation of the complex in the high temperature range (>300K). On the other hand, spin eqilibria as well as complexation equilibria are affected by partial dissociation of [Fe(bzimpy)$_2$]$^{2+}$ even in the presence of excess ligand in MeOH.[3-4,6] Dissociation of the complex leads to a change to the HS state.[6,8]

Thermochromism

The visible colour (red-violet) of the complex solution gradually changes and becomes blue-violet with increasing temperature from 277 to 341K. The mlct bands become less intense and the absorbtion maxima (λ_{max}) of the bands shift to shorter wavelength (see Figure 1 and Table I). These results illustrate the strong thermochromic behaviour of the complex in solution. However, spin equilibria are known to be reflected in pronounced thermochromic behaviour of the complex in solution.[3-10] The molar absorbtivity of the complex with and without excess ligand decreases to 54% and 58%, respectively, with rising temperature to 341K as the low absorbing HS isomer is increasingly populated.

These results are in good agreement with the change in spin-state of the complex to the HS state ($^1A_{1g} \rightleftarrows {}^5T_{2g}$) with increasing temperature and *vice versa*.[3–10,18–21] Further, the decrease of molar absorbtivity in the case without excess ligand indicates the involvement of complexation equilibria.

The *d-d* bands in the range 620–730nm are well separated from strong, broad mlct bands as shown in Figure 1.[3–4,7–8,19] These bands shift to longer wavelength with rising temperature as the ligand field parameter (10Dq) decreases for the HS isomer.[3–8] On the other hand, the *d-d* bands shift to shorter wave length (high energy) upon lowering the temperature and overlap the mlct bands.

Since the molar absorbtivities at a given wavelength and temperature result from a combination of contributions from the HS and LS isomers of the complex in solution,[3,5,7–8] values of spin equilibria constants (K_{SC}) were calculated using (*1*) and listed in Table II. The molar absorbtivity of the HS species (εHS = 750 ± 50 M^{-1} cm^{-1}) can be estimated from high temperature spectra of the 4-Cl-substituted analogue ($[Fe(Cl\text{-}bzimpy)_2]^{2+}$) in MeOH.[8] Due to the experimentally limited temperature range (277–341K), the value εLS is not accessible directly and was evaluated (13000 ± 500 M^{-1} cm^{-1}) by means of least-squares fitting of (*2*).[3,5,7–8] The K_{SC} value increases with increasing temperature as the HS isomer is increasingly populated. Further, the parameters ΔH_{SC} and ΔS_{SC} associated with the spin equilibria were evaluated from (*2*)[3,5,7–8] and are also listed in Table II. The complex without excess ligand shows higher values of thermodynamic parameters which might include small contributions from complexation equilibria to the thermochromism. However, these values are high (ΔH_{SC} = 4.2 kcal mol^{-1} and ΔS_{SC} = 14.8 cal mol^{-1} K^{-1}) in comparison to those found in MeOH (3.9 kcal mol^{-1} and 12.9 cal mol^{-1} K^{-1}).[3,8]

$$K_{SC} = X_{HS}/X_{LS} = (\varepsilon - \varepsilon_{LS})/(\varepsilon_{HS} - \varepsilon) \qquad (1)$$

$$\begin{gathered} \ln K_{SC} = \ln(\varepsilon - \varepsilon_{LS})/(\varepsilon_{HS} - \varepsilon) = -\Delta H/RT + \Delta S/R \\ \varepsilon = (\varepsilon_{LS} + \varepsilon_{HS} \cdot \exp(\Delta S/R - \Delta H/RT))/(1 + \exp(\Delta S/R - \Delta H/RT)) \end{gathered} \qquad (2)$$

TABLE II Spin equilibrium constants (K_{SC}) and thermodynamic parameters (ΔH_{SC} and ΔS_{SC}) for $[Fe(bzimpy)_2]^{2+}$ with and without excess ligand in PDC

T/K [a]	K_{SC} [+]	T/K [b]	K_{SC} [+]
277.1	1.153	276.9	0.886
280.5	1.268	280.5	0.976
284.7	1.423	285.0	1.103
289.1	1.599	289.5	1.232
293.5	1.794	293.9	1.374
298.1	2.013	298.6	1.536
302.7	2.253	303.3	1.714
307.5	2.523	308.0	1.906

TABLE II (*Continued*)

T/K [a]	K_{SC} [+]	*T/K* [b]	K_{SC} [+]
313.2	2.873	314.6	2.198
317.1	3.128	318.4	2.379
321.6	3.446	322.5	2.588
326.4	3.808	327.4	2.852
331.3	4.207	332.3	3.135
335.9	4.611	337.3	3.441
340.3	5.018	341.6	3.727
ΔH_{SC}/[kcal mol^{-1}]	= 4.4	4.2	
ΔS_{SC}/[cal mol^{-1}K^{-1}]	= 16.0	14.8	

[a] Complex solution without and b with excess ligand ([L]/[FeL$_2$]$^{2+}$ = 20).
[+] K_{SC} values were evaluated at 557nm.

Magnetic moments (μ/μB) of the complex with excess ligand (*i.e.*, [L]/[FeL$_2$]$^{2+}$ = 8.05) from 232 to 350K in PDC are listed in Table III. Spin equilibria constants and thermodynamic parameters were evaluated according to the literature.[3,10,18,20] K_{SC} increases with increasing temperature as discussed in the above section. However, the values of ΔH_{SC} (5.7 kcal mol^{-1}) and ΔS_{SC} (17.7 cal mol^{-1} K^{-1}) are different to those from spectroscopic measurements. This might be due to the restricted temperature range available in the latter case and errors in molar absorbtivities εHS and εLS.

A correlation between the magnetic moments and molar absorbtivities with temperature (with excess ligand) was attempted as shown in Figure 3. Increasing

TABLE III Changes of magnetic moment with increasing temperature and thermodynamic parameters for [Fe(bzimpy)$_2$]$^{2+}$ (5.2572 × 10^{-4}M) with excess ligand ([L]/[FeL$_2$]$^{2+}$ = 8.05) in PDC

T/K	*μ/[μB]*	K_{SC} [+]
232.05	0.691	0.016
242.35	1.011	0.035
252.15	1.505	0.081
263.99	1.895	0.135
273.76	2.231	0.197
284.59	2.673	0.309
295.41	3.063	0.449
307.25	3.435	0.640
318.07	3.718	0.842
329.42	3.859	0.970
340.21	3.983	1.102
350.51	4.107	1.260
ΔH_{SC}/[kcal mol ^{1}]	= 5.7	
ΔS_{SC}/[cal mol ^{1}K ^{1}]	= 17.7	

[+] $K_{SC} = X_{HS}/X_{LS} = (\mu^2 - \mu_{LS}^2)/(\mu_{HS}^2 - \mu^2)$; μHS = 5.5μB and μLS = 0 were used.[3,8,10, 18-20]

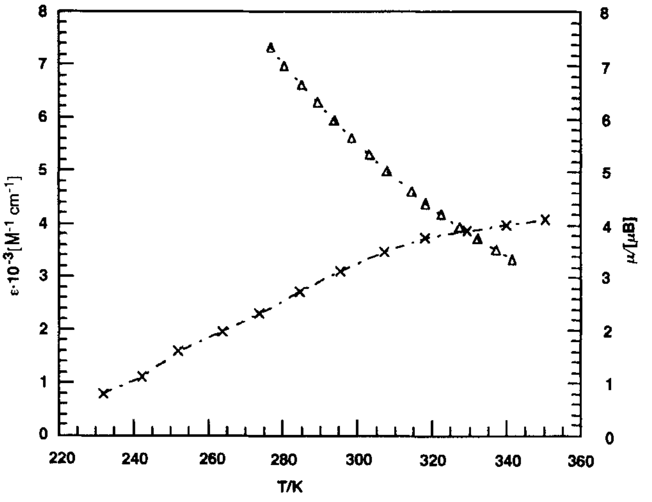

FIGURE 3 Changes in magnetic moments (μ/μB) and molar absorbtivities (ε557nm/M^{-1} cm^{-1}) with temperature of a [Fe(bzimpy)$_2$]$^{2+}$ solution with excess ligand in PDC.

magnetic moments and decreasing molar absorbtivities are observed with rising temperature as the HS isomer is increasingly populated. These results are in good agreement with the observed thermochromic behaviour of iron(II)-imine complexes.[3-8,18-21]

Solvent Influence

Comparisons of the present results with those reported for MeOH[3,8] reflect the fact that the spin crossover is influenced by the polarity of the solvent. The polar solvent, *via* hydrogen bonding between the imino hydrogen (ligand) and the solvent molecule, leads to a change to the LS state.[3,8,10,18-22] Hence, the LS complex is more stable in PDC ($\varepsilon = 65.0$ and $\mu = 4.98$) than in MeOH ($\varepsilon = 32.6$ and $\mu = 1.70$). This is further reflected in the high values of enthalpic and entropic terms in PDC. However, the more stable LS form causes a thermodynamic stabilization of [Fe(bzimpy)$_2$]$^{2+}$ in PDC as compared with MeOH.[3,12] This is shown by the high stability constant of [Fe(bzimpy)$_2$]$^{2+}$ in 50% (v/v) PDC/MeOH ($\log_{10}\beta_2 = 11.45$) *versus MeOH* ($\log_{10}\beta_2 = 10.7$).[4]

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