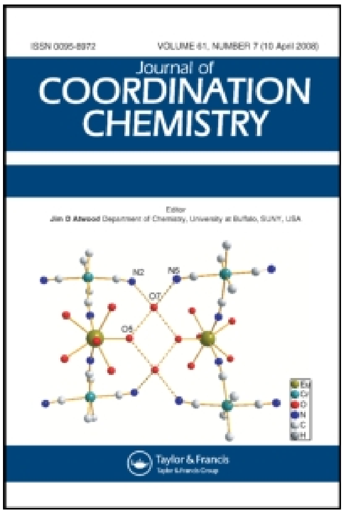

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# SPIN-CROSSOVER OF [Fe(Cl-BZIMPY)$_2$](ClO$_4$)$_2$ INDUCED BY DEPROTONATION

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# SPIN-CROSSOVER OF $[Fe(Cl\text{-}BZIMPY)_2](ClO_4)_2$ INDUCED BY DEPROTONATION

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The ligand 4-Cl-2,6-*bis*-(benzimidazol-2'-yl)-pyridine(Cl-bzimpy;$H_2L$) acts as a bidentate when coordinated with transition metal ions and the complex $[Fe(Cl\text{-}bzimpy)_2](ClO_4)_2$ was isolated as a solid. The protonation constants (logK). The free ligand and the complex were evaluated in 30:70 (v/v) $H_2O$:EtOH at room temperature and ionic strength of 0.13M (KCl). Coordination of the ligand to the metal ion leads to an increase of the acidity of the imino-hydrogen of the benzimidazole group. Deprotonation leads to a change in the spin-state (to the low-spin state; HS → LS transition) of the complex associated with a decrease in the spin-crossover equilibrium constant ($K_{SC}$). An opposite shift of spin-state is observed when $HClO_4$ is added to the complex solution, thus showing the reversibility of the process.

KEYWORDS: iron(II), spin-crossover, 4-Cl-2,6-bis-(benzimidazol-2'-yl)-pyridine, $[Fe(Cl\text{-}bzimpy)_2](ClO_4)_2$, protonation

## INTRODUCTION

Temperature induced spin-state equilibria between the low-spin (LS) and the high-spin (HS) states of transition metal complexes with $d^4$ to $d^7$ electronic configuration are observed when the ligand field splitting energy ($\Delta_o$ = 10Dq) is approximately outweighed by the spin-pairing energy (P).[1-6] Recently, a series of M(II)-imine complexes (M = $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$ and $Zn^{2+}$) with 4-X-2,6-*bis*-(benzimidazol-2'-yl)-pyridine (**1**) has been prepared and investigated by means of electronic spectroscopy, FT-IR, $^1H$ NMR and potentiometry.[7-11] Substituents in the pyridine ring of the ligand were used for fine-tuning the ligand field energy which in turn leads to a change in the spin-state of the complexes.[8,10,11] Coordination of the ligand with the metal ions causes an increase of acidity of the imino hydrogen atom of benzimidazole group of the ligand as a function of complex stability.[14-18] Titration of these cationic complexes with base leads to deprotonation of the imino hydrogen and results in a transition in the spin-state to the

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LS-state ($^5T_{2g}\rightarrow{}^1A_{1g}$) yielding stable, neutral complexes or salts with less positively charged cations.[12,14–18]

Titration of $[Fe(Cl\text{-}bzimpy)_2](ClO_4)_2$ with $HClO_4$ (0.17M) and NaOH (0.05M) solutions followed by potentiometry, electronic and $^1$H-NMR spectroscopy suggests that spin-state changes are accompanied by deprotonation of the complex, as summarized below. The present paper is concerned with investigations along these lines.

$$[FeH_4L_2)^{2+} \overset{K_1}{\rightleftharpoons} [FeH_3L_2)^{+} + H^{+}$$

$$[FeH_3L_2]^{+} \overset{K_1}{\rightleftharpoons} K2[FeH_2L_2] + H^{+}$$

$$[FeH_2L_2] \overset{K_1}{\rightleftharpoons} [FeHL_2] + H^{+}$$

$$[FeHL_2]^{-} \overset{K_1}{\rightleftharpoons} K_4[FeL_2]^{2-} + H^{+}$$

$$\underset{[HS]}{[FeH_4L_2]^{2+}} \overset{K_1}{\rightleftharpoons} K_{SC}\underset{[LS]}{[FeH_nL_2]^{(2-n)+}} + nH^{+}$$

## EXPERIMENTAL

### *Chemicals*

Chemicals were obtained from Riedel, Fluka, Loba and Merck. Commercial grade methanol (MeOH) was refluxed over CaO for 24 hours and fractionally distilled. Absolute ethanol (EtOH) was used as received from Riedel-de Haen. *N,N*-triethylamine ($Et_3N$) (Loba) was used after fractional distillation from NaOH (24 hours).

### *Preparation of Ligands and Complexes*

The ligands, 4-Cl-2,6-*bis*-(benzimidazol-2′-yl)-pyridine (Cl-bzimpy) and the complex, $[Fe(Cl\text{-}bzimpy)_2](ClO_4)_2$, were synthesized according to the literature.[10,12,13,19] The obtained complex was recrystalized three times from methanol. Details can be found in several previous papers.[7–10]

### *Potentiometric Titrations*

Potentiometric titrations were performed using a WTW Gmbh D 8120 Weilheim pH 521 Potentiometer. Uniform titrations and homogeneous temperature distribution within cells was ensured by using a magnetic stirrer. A continuous nitrogen stream was passed through the titration cell during the experiment. In all titrations, the pH meter was initially standardized with buffer solutions at pH 2.0 and 9.0, supplied from Riedel-de Haen. Titrations of $[Fe(Cl\text{-}bzimpy)_2](ClO_4)_2$ solution with NaOH (0.05M) were carried out at complex concentrations between 1.0 x 10 - 4 M and $6.0 \times 10^{-5}$ M in 30:70 (v/v) $H_2O$:EtOH. All determinations were followed at 20 ± 1 °C and 0.13M in KCl. The ligand solution ($7.7 \times 10^{-4}$ M) was titrated with NaOH (0.05 M) in 30:70 (v/v) $H_2O$:EtOH at 20°C.

### *Spectrophotometric Measurements*

Electronic spectra were obtained with a Hitachi U-2000 Spectrophotometer, equipped with an electronically thermostatted cell holder (Hitachi) for the range 0–100 (±0.5)°C; the quartz cell had a path length of 1.0 cm. The temperature was recorded by a Copper-Constantan thermocouple mounted within the cell. Homogeneous temperature distribution within the cell was provided by use of a magnetic stirrer. Spectrophotometric titrations of the complex with NaOH (0.05 M) and $HClO_4$ (0.17M) were performed at a concentration of $1.4091 \times 10^{-4}$ M in 30:70 (v/v) $H_2O$:EtOH and at ionic strength of 0.13(KCl) at 293 K.

### *Magnetic Measurement*

$^1$H NMR spectra were run on a Bruker AC 250 FT spectrometer operating at 250 MHz. High precision NMR sample tubes of type 528-PP (Wilmad Glass Co., New Jersey) with sealed Wilmad coaxial inserts (WGS-5BL) containing 5% TMS in acetone-$d^6$ were used as external standard and instrument lock. Magnetic susceptibilities in solution were measured by the Evans $^1$H NMR method[20] using the methanol for temperature calibration;[21] 1%(v/v) cyclohexane was used as an internal reference compound. Titrations of $[Fe(Cl\text{-}bzimpy)_2](ClO_4)_2$ ($1.1061 \times 10^{-4}$ M) with *N,N*-triethylamine ($NEt_3$) were performed in MeOH at 295 K.

## RESULTS AND DISCUSSION

### *Potentiometric Titrations*

Titration curves (pH *vs* NaOH/ml, Fig. 1) of the free ligand ($H_2L$ = Cl-bzimpy = 4-Cl-2,6-*bis*-(benzimidazol-2′-yl)-pyridine and the complex, $[Fe(H_2L)_2](ClO_4)_2$, indicates the deprotonation of the imino-hydrogen from the imidazole ring ($>N\text{-}H \rightleftarrows\, > N^- + H^+$) of the complex.[14–18,30] Two values of protonation constants ($\log K_1$ and $\log K_2$) for the free ligand and four values for the complex ($\log K_1$, $\log K_2$, $\log K_3$ and $\log K_4$) (see Table 1) were evaluated using the computational method described by Martell and Motekaitis.[22] Coordination of the ligand to the metal ion decreases the electron availability on the imino nitrogen atom through hyperconjugation and thereby increases the acidity of the imino hydrogen atom of the ligand as a function of complex stability.[14–18] As a result, low values of protonation constants (logK) were found for the complex as compared to the free ligand

**Table 1** Protonation constants of $[Fe(H_2L)_2](ClO_4)_2$($H_2L$ = Cl-bzimpy) in 30:70 (v/v) $H_2O$:EtOH; titrant = NaOH (0.05M) at I = 0.13M and 20°C.

| Complex | $\log K_1$ | $\log K_2$ | $\log K_3$ | $\log K_4$ |
|---|---|---|---|---|
| $[H_2L]$ | 12.24 | 8.21 | | |
| $[H_2L]$* | 16.33 | 12.31 | | |
| $[Fe(H_2L)_2]^{2+}$ | 17.4 | 10.08 | 6.66 | 4.61 |
| $[Fe(H_2L)_2]^{2+}$ | 8.65 | 8.45 | 7.45 | 7.18 |

*$H_2L$ = H-bzimpy, from Ref. 14. All values are ±0.1.

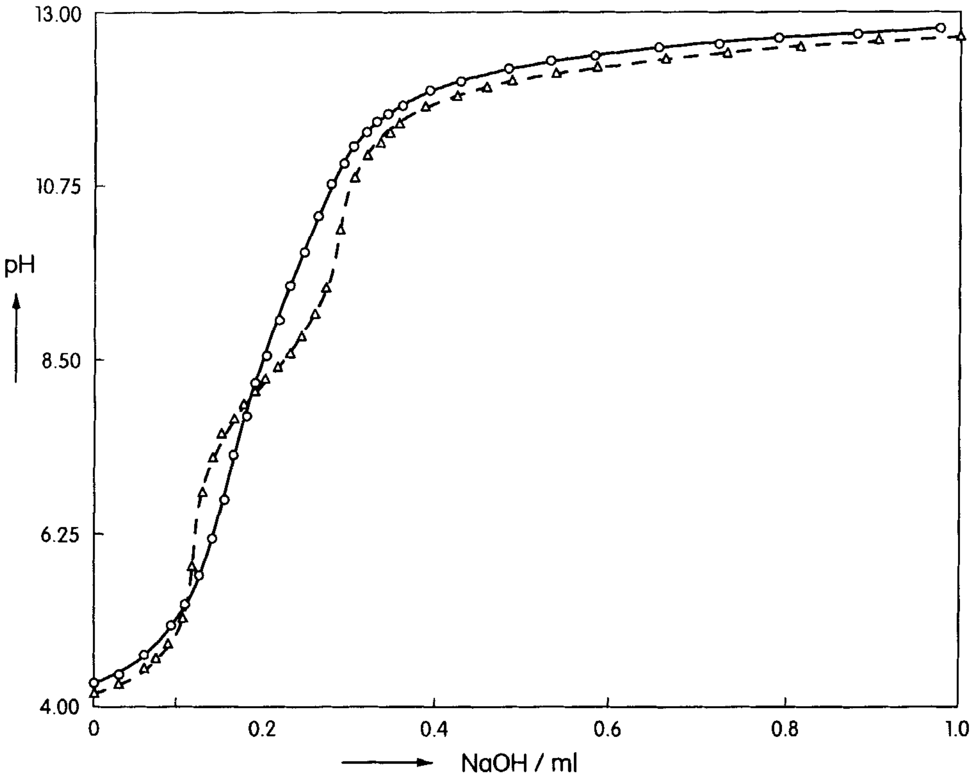

**Figure 1** Titration curves of the free ligand ($H_2L$ = Cl-bzimpy) and the complex, $[Fe(H_2L)_2]^{2+}$, in 30:70 (v/v) $H_2O$:Et OH at I = 0.13M and 293K; titrated with NaOH (0.05M): (a) [Cl-bzimpy] = $2.8811 \times 10^{-4}$M, (b) $[Fe(Cl\text{-}bzimpy)_2]^{2+}$ = $9.9163 \times 10^{-5}$M.

(see Table 1). These results are in good agreement with reported values for the unsubstituted analogue.[14]

### *Spectrophotometric Titrations*

Electronic absorbtion spectra of $[Fe(Cl\text{-}bzimpy)_2](ClO_4)_2$ are shown in Figure 2 over the pH region of 2.7 to 11.7 in 30:70 (v/v) $H_2O$:EtOH at room temperature. Colour changes from light-rose to rose, pink-red and finally, to wine-red with increasing pH in solution. The absorbtion maxima ($\lambda_{max}$) and the molar extinction ($\varepsilon$/l mol$^{-1}$ cm$^{-1}$) are strongly dependent on the pH of the solution (see Fig. 2 and Table 2). The spectra in Figure 2 are assigned as follows: (i) very strong absorbtion bands <410 mm are associated with the internal ligand transitions $\pi \rightarrow \pi^*$, (ii) strong broad absorbtion bands at 420–700 nm ($\varepsilon_{max}$ ≈660–3700 mol$^{-1}$ cm$^{-1}$) are attributed to the usual metal-to-ligand charge transfer band ($T_{2g} \rightarrow \pi^*$, MLCT) and finally, (iii) broad, but weak bands > 700 nm ($\varepsilon$700 nm ≈150–500 l mol$^{-1}$ cm$^{-1}$) are attributed to the *d-d* absorbtion of the metal ion.[10–13,23–27] The MLCT band of the solution at an initial pH of 4.2 (*i.e.*, without adding acid or base solution) consists of a main

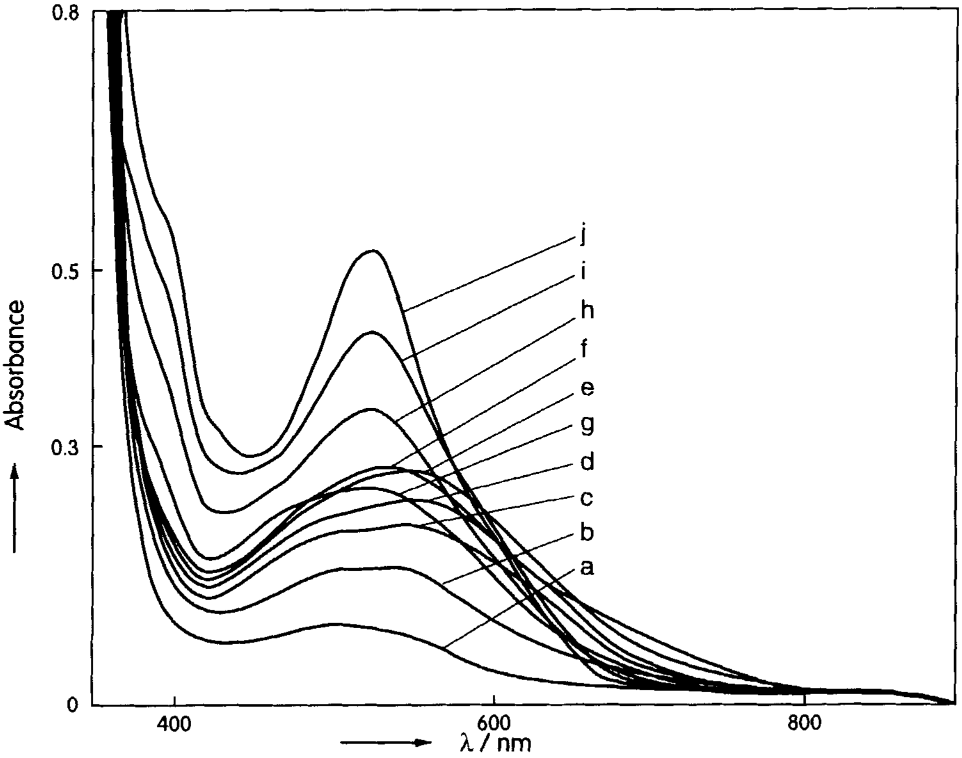

**Figure 2** Electronic spectra of $[Fe(Cl\text{-}bzimpy)_2]^{2+}$ ($1.4091 \times 10^{-4}$M) in 30:70 (v/v) $H_2O$:EtOH at 293K and at different pH: (a) 2.73; (b) 3.38; (c) 3.86; (d) 4.22; (e) 5.00; (f) 5.74; (g) 8.92; (h) 9.97 (i) 10.44; (j) 11.70.

absorbtion maximum at 552 nm (ε552 nm = 1690 l $mol^{-1}$ $cm^{-1}$) and a shoulder at higher energy (502 nm; ε502 nm ≈360 l $mol^{-1}$ $cm^{-1}$) (see Fig. 2d), associated with the LS and HS-isomers of the complex, respectively.[10,14,28] The lowest unfilled ligand π* orbitals are assumed to occur at relatively higher energies in the high-spin isomer than in the low-spin one, leading to a higher energy MLCT transition. The intense band at 552 nm results from the increasingly populated LS state in solution. However, an alternative explanation could be the strong and weak overlap between the metal $t_{2g}$- and ligand π* orbitals leading to an intense and a weak band for the LS and HS-isomer, respectively.[8,10–14] In previous communications, it was shown that the complex is predominantly HS (*i.e.*, $X_{hs} \approx 85\%$ and $\varepsilon_{hs}$/max = 650 l $mol^{-1}$ $cm^{-1}$, μHS = 4.6μB) with an absorbtion maximum at about 500nm (HS isomer band) and a shoulder at lower energy (LS isomer band) in MeOH at room temperature.[8,10] Accordingly, the complex shows an absorbtion maximum at 578 nm and a shoulder at 520–480 nm associated with the MLCT band for the LS and HS isomer in the solid state at room temperature.[10,11]

The lowering of symmetry from $O_h$ to $D_{2d}$ causes a splitting of the degenerate $t_{2g}$ level ($d_\pi$-orbitals) into a single and a double degenerate level ($b_2 + e$). The

**Table 2** Change of absorption maxima, molar extinction and spin-equilibria of $[Fe(Cl\text{-}bzimpy)_2](ClO_4)_2$ ($1.4091.10^{-4}$M) with variation of pH of solution in 30:70 (v/v) $H_2O$:Et OH at I = 0.13M and 20°C.

| pH | $\lambda_{max}$ [nm] | ε/552nm [$l\ mol^{-1}\ cm^{-1}$] | Ksc$^+$ |
|---|---|---|---|
| 2.73 | 502 | 560 | 0.99 |
| 2.98 | 505 | 759 | 0.91 |
| 3.38 | 515 | 1085 | 0.77 |
| 3.86 | 549 | 1440 | 0.62 |
| 4.22* | 552 | 1689 | 0.52 |
| 4.41 | 551 | 1774 | 0.48 |
| 5.00 | 545 | 1916 | 0.42 |
| 5.74 | 534 | 1887 | 0.43 |
| 6.67 | 519 | 1696 | 0.51 |
| 7.66 | 512 | 1604 | 0.55 |
| 8.23 | 510 | 1604 | 0.55 |
| 8.92 | 522 | 1653 | 0.53 |
| 9.45 | 525 | 1788 | 0.47 |
| 9.97 | 524 | 2121 | 0.33 |
| 10.44 | 525 | 2590 | 0.13 |
| 10.97 | 524 | 2870 | 0.02 |
| 11.70 | 524 | 2890 | 0.004 |

*pH of solution without adding acid or base solution. $^+K_{SC}$ at 552nm. All values are ±0.05.

observed broad MLCT band for both spin isomers might result from the overlap of the two nearby transitions $(d_\pi(b_2) \rightarrow \pi_1^*)$ and $(d_\pi(e) \rightarrow \pi_1^*)$.[8,10–12,29]

Figure 2 shows that the intense LS isomer band ($\lambda_{max}$ = 552 nm; Fig. 2d) gradually disappears and the shoulder (HS isomer band, at 502 nm) becomes strong as the pH of solution decreases. Finally, at low pH (<3) the HS isomer band appears as the main absorbtion band ($\lambda_{max}$ = 502 nm; $\varepsilon_{hs}$/max = 670 $mol^{-1}$ $cm^{-1}$ at pH = 2.73) and the LS isomer band appears a shoulder ($\varepsilon_S$/552 nm = 560 $mol^{-1}$ $cm^{-1}$ at pH = 2.73) (see Fig. 2a to 2d). Decreasing pH of solution leads to hindrance of the imino hydrogen dissociation from the ligand so that the interaction between the metal ion and the ligand becomes weak (*i.e.*, weak ligand field) and favours the HS isomer of the complex.[11,23]

Titration of the complex with base indicates a stepwise deprotonation of the imino hydrogens of the benzimidazole groups of the complex. Deprotonation enhances σ donation from ligand to metal ion through hyperconjugation, accompanied by an increase in back donation $(t_{2g} \rightarrow \pi^*)$ assisting the formation of the methine chromophore characteristic for the low-spin state of the complex.[10–12] With increasing pH (pH = 4.2) the absorbtion maximum of the MLCT band is found to shift to shorter wavelength ($\lambda_{max}$ from 552 nm to 510 nm with pH = 4.2 to 8.2) and then to longer wavelength ($\lambda_{max}$ from 510 nm to 524 nm with pH = 8.2 to 9.2) and finally, remains unchanged ($\lambda_{max}$ ≈524nm at pH up to 11.7) (see Table 2 and Fig. 3). According to the reaction scheme, the deprotonated species are LS isomers with different absorbtion maxima. Moreover, at high pH (<8.5) the HS isomer bands completely disappear and only the most intense LS bands of the complex anion ($[FeL_2]^{2-}$) are found. In this pH region the absorbtion maxima of the MLCT bands are found to be constant ($\lambda_{max}$ ≈524 nm; see Fig. 3). However, the MLCT band shifts to longer wavelength with a transition to the

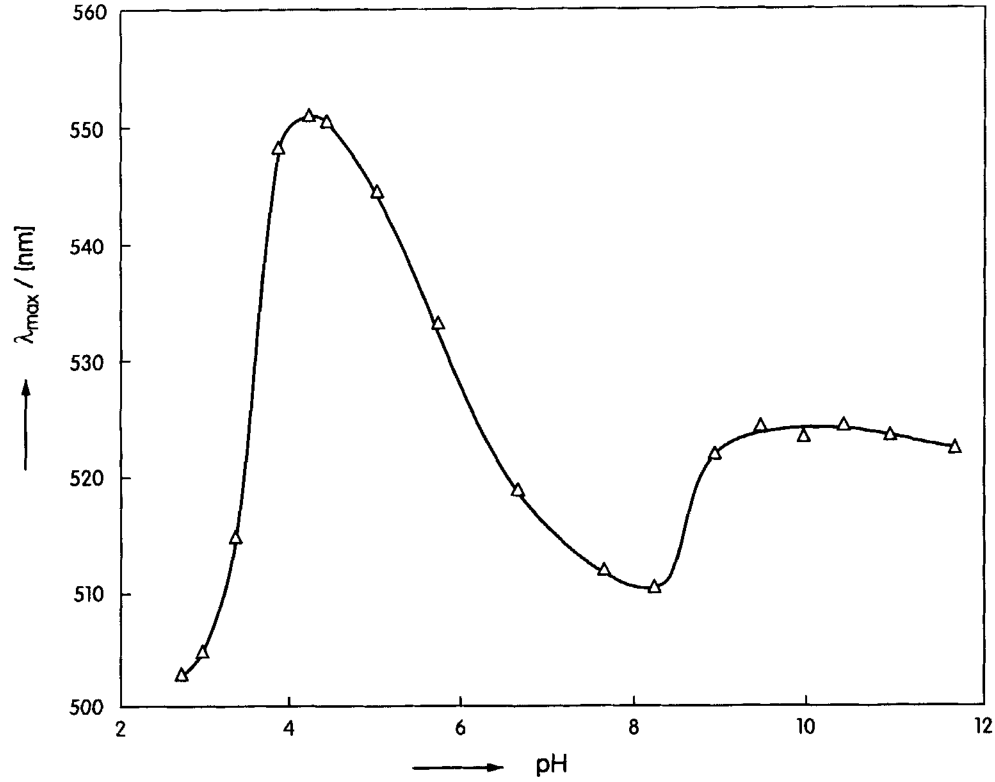

Figure 3 Change of absorbtion maxima with pH of $[Fe(Cl\text{-}bzimpy)_2]^{2+}$ (1.4091 x $10^{-4}$M) solution in 30:70 (v/v) $H_2O$:EtOH at 293K.

LS-state for the unsubstituted analogue[10,14] and as well as for other iron(II)-2-(2'-pyridyl)imidazole complexes.[16]

The *d-d* absorbtion bands (700–800 nm) are shift to shorter wavelength (strong ligand field) with increasing pH as the LS isomer is favoured and finally, at high pH (>8), the band is overlapped with the nearby strong MLCT band (see Figs. 2–4). On the other hand, at low pH (<3) where the HS isomer is favoured, the *d-d* bands (weak ligand field) are quite separate from the MLCT band.[10,11,14] Further, two shoulders at about 400 nm and 420 nm becomes important at high pH (>9); these might be due to internal ligand bands.

Since the molar absorptions at a given wavelength and pH of the solution result from a combination of contributions from the HS and LS isomer,[7,8,10–14] values of spin-equilibria constants ($K_{SC}$) can be calculated using (*1*) (Table 2900 ± 50 l mol$^{-1}$ cm$^{-1}$) were estimated at 552 nm for the HS and LS isomer of the complex at the limits of pH (2.7 and 11.7), respectively, at 20°C.

$$K_{SC} = \varepsilon_{hs}/\varepsilon|_S = (\varepsilon_{obs} - \varepsilon|_S)/(\varepsilon_{hs} = \varepsilon|_S) \qquad (1)$$

These results (see Table 2 and Fig. 5) indicate that the spin-equilibrium constant

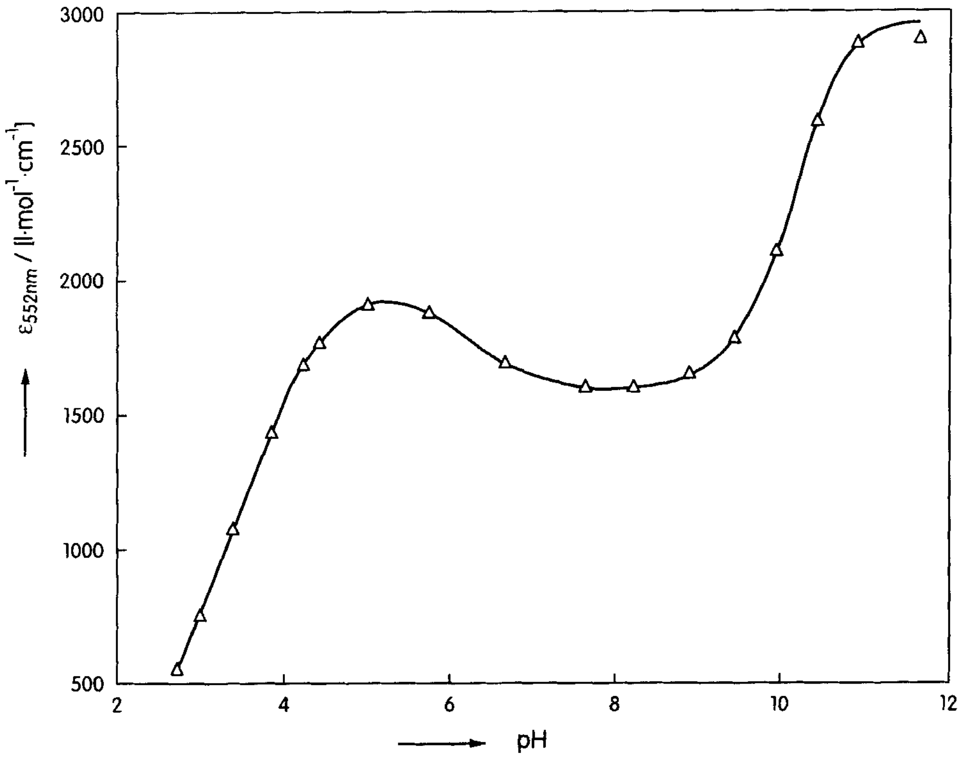

**Figure 4** Change of molar absorption with pH of $[Fe(Cl\text{-}bzimpy)_2]^{2+}$ (1.4091 x $10^4$M) solution in 30:70 (v/v) $H_2O$:EtOH at 293K.

decreases with increasing pH due to increasingly populated LS isomer *via* the deprotonation of the complex and *vice versa.*

### *H-NMR Spectroscopic Titrations*

Magnetic moments ($\mu/\mu B$) obtained for titration of $[Fe(Cl\text{-}bzimpy)_2](ClO_4)_2$ with $NEt_3$ in methanol at 295K are listed in Table 3 and shown in Figure 6. The magnetic moment decreases with the formation of different deprotonated species of the LS state (see Fig. 6). At high ratios of $[Et_3N]/[FeL_2]^{2+}$ ($\geq$4.0), the magnetic moment seems to be constant due to complete deprotonation of the complex. The magnetic moments vary between $3.0\mu_B$ and $4.5\mu_B$ and refer to the range between the LS state ($S = 0$, $0\text{–}0.5\mu_B$) and the HS state ($S = 2.0$, $5.0\text{–}5.5\mu_B$), respectively.[5–8,12,10,27–31] The values of spin-equilibrium constant ($K_{SC}$) were evaluated from the observed magnetic moment data using (*2*) and are listed in Table 3,

$$K_{SC} = x_{hs}/x|_S = (\mu_{expt}^2 - \mu|_S^2)/(\mu_{hs}^2\ \mu_{expt}^2) \qquad (2)$$

where, x is the mole fraction of the spin isomer and $\mu_{hs}$ and $\mu_{ls}$ are the effective magnetic moments for high-spin and low-spin forms, respectively. The value of

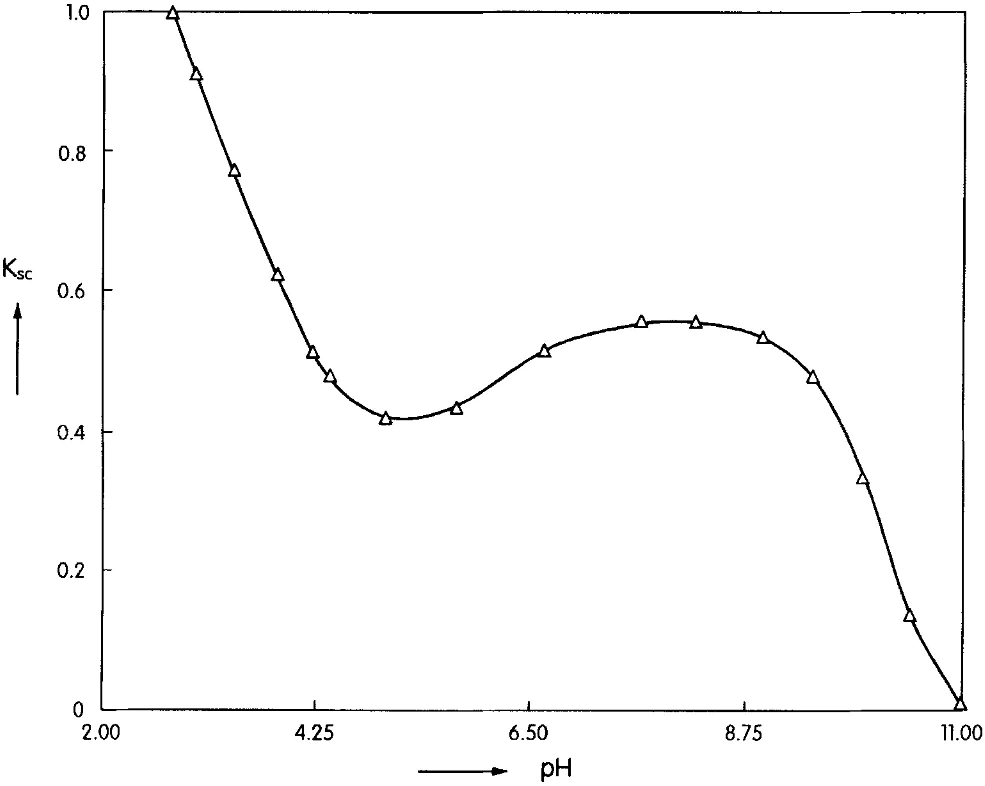

**Figure 5** Change of spin-crossover equilibrium constants ($K_{SC}$) with pH of $[Fe(Cl\text{-}bzimpy)_2]^{2+}$ ($1.4091 \times 10^{-4}$M) solution in 30:70 (v/v) $H_2O$:EtOH at 293K.

**Table 3** Variation of magnetic moments and spin-equilibrium constant accompanying the titration of $[Fe(Cl\text{-}bzimpy)_2](ClO_4)_2$ ($1.1061 \times 10^{-4}$M) with $NEt_3$ at 22°C in MeOH.

| $[Et_3N]/[FeL_2]^{2+}$ | $\mu/\mu B$ | $K_{SC}$* |
|---|---|---|
| 0 | 4.32 | 1.42 |
| 0.42 | 4.14 | 1.14 |
| 0.75 | 4.07 | 1.05 |
| 0.98 | 3.88 | 0.84 |
| 1.48 | 3.72 | 0.77 |
| 1.92 | 3.70 | 0.69 |
| 2.42 | 3.59 | 0.61 |
| 3.20 | 3.52 | 0.57 |
| 3.69 | 3.40 | 0.50 |
| 4.38 | 3.37 | 0.48 |
| 5.12 | 3.30 | 0.45 |

* All values are ±0.05.

$\mu_{hs}$ = 5.5μB was taken from the literature[8,28,31] and $\mu_{ls}$ = 1.5μB was used for the deprotonated unsubstituted analogue.[14]

The results in Tables 2 and 3 show that the value of $K_{SC}$ decreases with

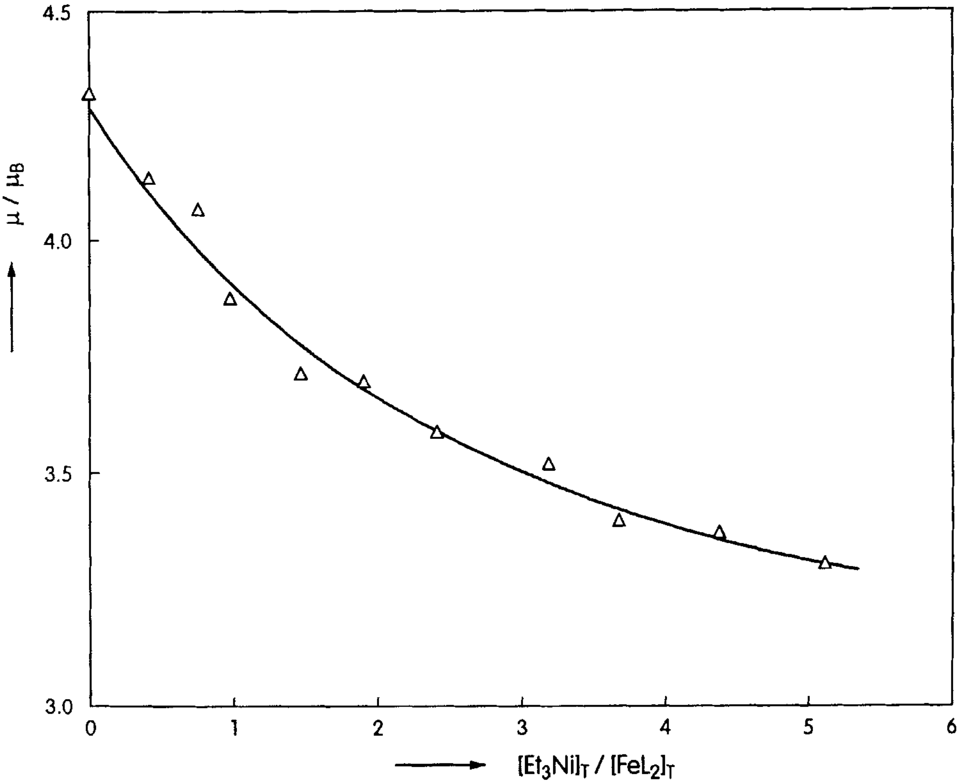

**Figure 6** Variation of magnetic moments as a function of $[NEt_3]/FeL_2]^{2+}$ for $[Fe(Cl\text{-}bzimpy)_2]^{2+}$ ($1.1061 \times 10^{-4}$M) in MeOH at 293K.

deprotonation of the complex. However, studies of solvent donicity/polarity effects on the spin-equilibria of the complex *via* hydrogen-bonding interactions between the $-NH_2$ group (ligand) and solvent show the same results.[6,8,28,31]

In conclusion, it can be said that deprotonation of the coordinated ligand is closely related with the observed spin-state transition of the complex. Generally, the acidity of the ligand is increased by coordination with metal ions. This mutual interrelation seems to be of importance for the occurrence of the spin-transition in solution and can explain solvent influences.

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