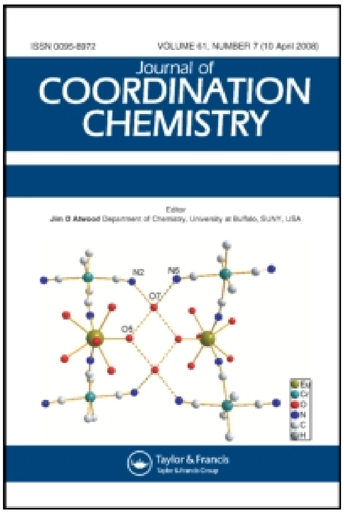

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SPIN-TRANSITION IN $[Fe(OH\text{-}BZIMPY)_2](ClO_4)_2 \cdot 3H_2O$ INDUCED BY DEPROTONATION

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Coordination of 4-OH-2,6-*bis*-(benzimidazol-2′-yl)pyridine (OH-bzimpy = H_3L) with ironI(II) increases the acidity of the iminohydrogen atoms of the benzimidazole groups. The first three protonation constants ($logK_n$) both for the free ligand, (OH-bzimpy) and the complex, $[Fe(OH\text{-}bzimpy)_2](ClO_4)_2 \cdot 3H_2O$, were evaluated in 30:70 (v/v) H_2O:EtOH. Deprotonation of $[Fe(OH\text{-}bzimpy)_2](ClO_4)_2 \cdot 3H_2O$ leads a change in spin-state to the low-spin (LS) state associated with a decrease of the spin-crossover equilibrium constant (K_{SC}) and a shift of absorbtion maxima. An opposite shift of spin-state to the high-spin (HS) state is observed with addition of acid to the complex solution. Values of spin-equilibra constants (K_{SC}) are given for different pH values. The magnetic moment ($\mu/\mu B$), as well as the spin-equilibrium constant (K_{SC}) decreases during titration of the complex of *N,N*-triethylamine (Et_3N) in MeOH, resulting in a change in the spin-state to the low-spin (LS) state.

KEYWORDS: Spin transition; 4-OH-2,6-*bis*-(benzimidazol-2′-yl)pyridine iron, deprotonation, solvation.

INTRODUCTION

Spin-transition behaviour between the low-spin (LH) and high-spin (HS) states of transition metals complexes with d^4 to d^7 electronic configuration is observed both in solid and in solution.[1–7] Cationic complexes, $[M(X\text{-}bzimpy)_2]^{2+}$ ($M = Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}; 4-Xbzimpy = 4-X-2,6-*bis*-(benzimidazol-2′-yl)-pyridine, X = H, OH, Cl and CH_3) were isolated in the solid state and investigated using electronic far-FT-IR, ^{1}H-NMR and Mössbauer spectroscopy and potentiometry.[8–13] Ligand substitution,[2–3,5,8–9,11] variation of the solvent donor-acceptor properties,[5–7,10–11] ligand- and anion-exchange reactions[4,8–9] crystal water,[4,15–16] complex deprotonation[8,10,15–17] and hydrogen bonding[4,6–7,13–15] are found to play an important role in determining the spin-state of the complexes. Coordination of the unsubtituted and the 4-Cl-substituted bzimpy ligand with metal ions is associated an increase of the acidity of the imino hydrogen atoms of the benzimidazole group of the respective ligand as a function of complex

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stability.[13,18–21] Titration of these complexes with alkali solution leads to a deprotonation of the imino hydrogen and results in a transition in the spin-state to the LS-state ($^5T_{2g} \rightarrow {}^1A_{1g}$) and with acid ($HClO_4$) solution demonstrates a change in the spin-state to the high-spin state.[10,13,15–17]

The above findings suggest that $[Fe(OH\text{-}bzimpy)_2](ClO_4)_2 \cdot 3H_2O$ is an excellent candidate to exhibit spin-state transition accompanied by deprotonation of the ligand according to reaction. Titration with acid ($HClO_4$) solution should result in a shift of the spin-state to the high-spin state, and titation with bases should lead to a shift towards the low spin state. The present paper is concerned with investigations along these lines.

$$[FeH_6L_2]^{2+} \overset{K_n}{\rightleftharpoons} [FeH_{6\text{-}n}L_2]^{(2\text{-}n)-} + nH^+ \qquad (1)$$

EXPERIMENTAL

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

The ligand, 4-OH-2,6-*bis*-(benzimidazol-2′-yl)pyridine (OH-bzimpy = H_3L) and the complex, $[Fe(OH\text{-}bzimpy)_2](ClO_4)_2 \cdot 3H_2O$, were synthesized according to the literature[8–11,22] and recrystallized three times from methanol.

Potentiometric titrations were performed using a WTW Gmbh D8120 Weilheim pH 521 potentiometer. Uniform titrations and homogeneous temperature distribution within the cells was ensured by using a magnetic stirrer. A continuous nitrogen stream was passed through the titration cell during the experiment. Before all titrations, the pH meter was standardized with buffer solutions at pH 2.0 and 9.0, supplied from Riedel-de-Haen. Titrations of $[Fe(OH\text{-}bzimpy)_2](ClO_4)_2 \cdot 3H_2O$ solution with NaOH (0.09 M) were carried out at complex concentrations between 1.2×10^{-4} M and 3.2×10^{-5} M in 30:70 (v/v) H_2O:EtOH. All determinations were followed at $20 \pm 1\,^\circ C$ and 0.13 M in KCl solution. Ligand solution (1.0384×10^{-3} M) was titrated with NaOH (0.09 M) in 30:70 (v/v) H_2O:EtOH at $20 \pm 1\,^\circ C$.

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 and homogeneous temperature distribution within the cell was provided by use of a magnetic stirrer. Spectrophotometric titrations of $[Fe(OH\text{-}bzimpy)_2](ClO_4)_2 \cdot 3H_2O$ (1.8527×10^{-4} M) with NaOH (0.1385 M) and $HClO_4$ (0.12 M) solution were performed in 30:70 (v/v) H_2O:EtOH and at ionic strength of 0.125 M KCl at about 22°C.

^1H-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 ^1H-NMR method[23] using the solvent methanol for temperature calibration[24]; 1% (v/v) cyclohexane was used as an internal reference compound. Titrations of $[Fe(OH\text{-}bzimpy)_2](ClO_4)_2 \cdot 3H_2O$ (7.5147×10^{-5} M) with *N,N*-triethylamine were performed in MeOH at 20°C.

RESULTS AND DISCUSSION

Potentiometric Studies

Potentiometric titration curves of the free ligand (OH-bzimpy = H_3L) and the complex, $[Fe(OH\text{-}bzimpy)_2](ClO_4)_2 \cdot 3H_2O$, are shown in Figure 1. The colour of the solution changes from light-rose to wine-red, pink and finally, to redish-violet with increasing pH. Figure 1 indicates the deprotonation of the iminohydrogen from the coordinated ligand of complex, as summarized in reaction (*1*).[13,15,18–21] Titrations were performed with and without excess ligand. No considerable ligand dissociation, hydrolysis or ligand exchange with the hydroxo groups seems to occur. Three values of protonation constants ($\log K_1$, $\log K_2$ and $\log K_3$) both for the free ligand and the complex (see Table 1) were evaluated using the method of Martell and Motekaitis.[25] Coordination of the ligand to the metal ion decreases the electron availability on the imino nitrogen of the ligand through hyperconjugation and thereby increases the acidity of the imino hydrogen (*i.e.*, facilitating the dissociation) of the ligand as a function of complex stability.[13,15–17,18–21] As a result, low values of protonation constants ($\log\beta$) were found for the complex in comparison to the free ligand (see Table 1). These results are in good agreement with values reported for the unsubstituted[13] and 4-Cl-substituted[15] analogues (see Table 1).

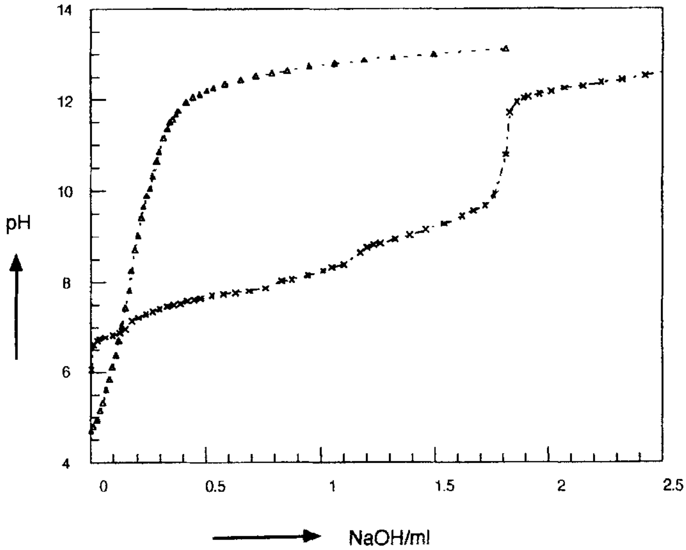

Figure 1 Titration curves of the free ligand and the complex, in 30:70 (v/v) H_2O:EtOH at I = 0.13 M and 20°C; titrant NaOH (0.09 M); (x) [OH-bzimpy] = 1.0384×10^{-3} M; (Δ)$[Fe(OH\text{-}bzimpy)_2]^{2+}$ = 1.1209×10^{-4} M.

Table I Values of protonation constants of OH-bzimpy (1.0384×10^{-3}M) and $[Fe(H_3L)_2](ClO_4)_2 \cdot 3H_2O$ 1×1209.10^{-4} M) in 30:70 (v/v) (H_2O:EtOH; I = 0.13 M and 20°C; titrant = NaOH (0.09 M)

Complex	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$
$[H_3L]^*$	9.38	7.90	7.58	
$[Fe(H_3L)_2]^{2+}$	8.17	6.02	5.13	
$[Fe(H_2L')_2]^{2+a}$	8.65	8.45	7.45	7.18
$[Fe(H_2L'')_2]^{2+b}$	17.4	10.08	6.66	4.61

$^*H_3L$ = OH-bzimpy; $^aH_2L'$ = H-bzimpy from Ref. 13 and ^{b} H_2L'' = Cl-bzimpy from Ref. 15. All values are ±0.1.

Spectrophotometric Studies

Electronic absorbtion spectra of $[Fe(OH\text{-}bzimpy)_2](ClO_4)_2 \cdot 3H_2O$ at different pH values in 30:70 (v/v) H_2O:EtOH are shown Figure 2. Absorption maxima (λ_{max}) and molar extinctions (ε/l mol^{-1} cm^{-1}) are strongly dependent on the pH in solution (see Fig. 2 and Table 2). Spectra in Figure 2 are assigned as follows: (i) very strong absorbtion bands at <420 nm, associated with internal ligand transitions (π–π^*), (ii) strong broad absorbiton bands at 420–600 nm ($\varepsilon_{max} \approx 1100\text{–}5900$ l mol^{-1} cm^{-1}) attributed to metal-to-ligand charge transfer ($T_{2g} \rightarrow \pi^*$, MLCT) and finally, (iii) broad-weak bands at 600–720 nm ($\varepsilon_{600nm} \approx 420\text{–}2150$ l mol^{-1} cm^{-1}) attributed to the d-d absorbtion of the metal ion.[8–11, 13–15, 26–29] The MLCT band of a complex solution at a pH of 4.63 (*i.e.*, without adding acid or base solution) consists of a main absorbtion maximum at 532 nm (ε532 nm = 1943 l mol^{-1} cm^{-1}) and a shoulder at higher energy (at about 510 nm and ε508 nm ≈ 1830 l mol^{-1} cm^{-1}) (see Figure 2, Spectrum f), associated with the LS- and HS-isomer bands of the complex, respectively.[7,11,13–15] 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 of MLCT transition.[2,7,9,13–16] The intense band centred at 532 nm results from the increasingly populated LS isomer in solution. An alternative explanation could be a strong and a weak overlap between the metal T_{2g} and ligand π^* orbitals, leading to intense and weak bands for the LS and HS isomers, respectively.[8–9,13–15] However, the complex was found to be in the HS state ($X_{HS} \approx 75\%$ and ε_{HS}/max = 1440 l mol^{-1} cm^{-1}, ε_{LS} = 4.2µB) with an absorbtion maximum at 503 nm (HS-isomer band) and a shoulder at longer wavelength (LS isomer band) in MeOH at room temperature.[11] Accordingly, the complex shows an absorbtion maximum at 580 nm and a shoulder at 530–460 nm attributed to the MLCT bands for the LS and HS isomers in the solid state at room temperature.[14]

Figure 2 (Spectra g-p) shows spectra following the titration of the complex with base (NaOH) solution and indicates the stepwise deprotonation of the imino hydrogens of the coordinated ligands.[10,13,15–21] Deprotonation enhances σ-donation from ligand to metalion through hyperconjugation, accompanied by an increase in back donation ($t_{2g} \rightarrow \pi^*$), assisting the formation of the methine chromophore characteristic of the LS state of complex.[9,13,15,19] With deprotonation (pH > 4.6) the MLCT bands both for the LS nd HS species are found to overlap with each other; the HS isomer bands disappear and finally, at pH > 9.0, only the most intense LS isomer bands of anionic complexes and/or neutral complexes are found (see Figure 2 (Spectra g-p)). Different deprotonated species refer to different MLCT bands for the LS species in solution[10,13,15–18] so that it becomes difficult to label the absorbtion maxima for these deprotonated species individually. With increasing pH the absorbtion maxima shift to higher energy (*i.e.*, λ_{max} from 532 nm to 500 nm with pH = 4.6 to 8.5) and then to lower energy (*i.e.*, λ_{max} from 500 nm to 522 nm with pH = 8.5 to 10.0) and finally, remain unchanged ($\lambda_{max} \approx 523$ nm ast pH up to 12.0; see Table II and Figure 3a). At high pH (> 9.0) the LS isomer bands of anionic complexes and/or neutral complexes are indicated by the constant absorbtion maxima at about 523 nm (see Figure 2l-p). Molar absorbtion change with pH and indicate the existence of spin-equilibria (Table II and Figure 3b). However, transition to the LS state induced by the deprotonation of the unsubstituted[10,13] and 4-Cl-substituted[15–16] analogues, as well as for iron(II)-2-(2′-Pyridyl)imidazole complexes[18] are reported.

Figure 2 (a–e) shows that the intense LS isomer band centred at 532 nm (ε_{LS}/532 nm = 1943 l mol^{-1} cm^{-1} at pH = 4.65) gradually disappears and the HS isomer band (shoulder at about 507 nm) becomes strong with decreasing pH in solution. Finally, at low pH (<3.5) the HS isomer band is the main absorbtion band (λ_{max} = 507nm; ε_{HS}/max = 1193 l mol^{-1} cm^{-1} at pH = 2.85) and the LS isomer band appears as a shoulder (ε_{LS}/532 nm = 1139 l mol^{-1} cm^{-1} at pH = 2.85; see Table 2). These results strongly indicate a transition in the spin-state to the HS state of the complex in solution[11,13,15] and can be explained by protonation of the lone-pair electrons on the imino nitrogen of the benzimidazole group (ligand) with addition of acid. This diminishes the σ-donation from ligand to metal ion through hyperconjugation accompanies a decrease in back donation, and results in weak interaction between the ligands and metal ions (*i.e.*, weak ligand field) favouring the HS state.[4,13,15–17,30] However, an alternative explanation could be the hindrance of hydrogen-bonding ability between the imino hydrogen and the solvent with addition of acid, favouring the HS isomer of complex *via* weak interaction between the metalion and ligand[4,7,13,15–17]

The d-d absorption bands (600–720 nm) shift to shorter wavelength (*i.e.*, strong ligand field) with deprotonation and indicate transition to the low-spin state and finally, at high pH (>9.5) the band overlaps with the nearby strong MLCT band[13,15–17] (see Figure 2 h–p). On the other hand, at low pH (<3.5) the d-d bands (*i.e.*, weak ligand field) are quite separate from the MLCT bands (see Figure 2 a–e) and indicate transition to the high-spin state[2,13,15–17] Further, two shoulders at about 398 nm and 417 nm become important at high pH (>9.2); these might be due to internal ligand bands as observed in the Cl-substituted analogue.[15–17]

Since the molar absorbtions at a given wavelength and pH in solution result from a combination of contributions from the HS and LS isomers of the complex,[8,10,13,15] values of spin-equilibria constants (K_{SC}) were calculated using the (*2*); see Table II). Values of molar absorbtions (εHS = 550±50 l mol^{-1} cm^{-1} and εLS = 5750±100 l mol^{-1} cm^{-1}) were estimated at 532 m at limiting ends of the pH region (2.3 and11.7) for the HS and LS isomers of the complex, respectively.[13,15–16]

$$K_{SC} = \varepsilon_{HS}/\varepsilon_{LS} = (\varepsilon_{obs} - \varepsilon_{LS})/(\varepsilon_{HS} - \varepsilon_{obs}) \qquad (2)$$

Results (Table II Figure 4) show that K_{SC} changes with pH. K_{SC} decreases with increase of pH as LS isomers are increasingly populated and *vice versa*. These results

Table II Change of absorbtion maxima, molar absobtivities and spin-equilibria of $[Fe(OH\text{-}bzimpy)_2](ClO_4)_2 \cdot 3H_2O$ (1.8527×10^{-4} M) with changing pH in 30:70 (v/v) H_2O:EtOH solution at 20°C

pH	λ_{max} [nm]	ε/532 m [l mol^{-1} cm^{-1}]	$K_{SC}{}^{+}$
2.85	507.0	1139	7.21
3.15	509.5	1366	5.06
3.46	513.0	1582	3.85
3.82	517.5	1749	3.20
4.21	534.0	1862	2.85
4.63*	532.5	1943	2.63
4.92	529.0	2078	2.32
6.55	506.5	2040	2.12
7.40	499.0	2181	2.40
8.57	500.0	2094	2.29
9.20	513.0	2343	1.84
9.83	521.5	2967	1.26
10.35	523.0	3714	0.63
10.80	522.5	4464	0.32
11.22	523.5	5538	0.042
11.56	522.5	5749	0.004

* The pH of solution without adding acid or base solution. $^{+}$ K_{SC} at 532 nm and all values are ±0.10.

are in good agreement with those reported for unsubstituted and Cl-substituted analogues.[13,15–17] However, studies of solvent donicity/polarity effects on the spin-equilibria of complexes *via* hydrogen bonding between the imino hydrogen (ligand) and the solvent show the same results.[4–7,9,15]

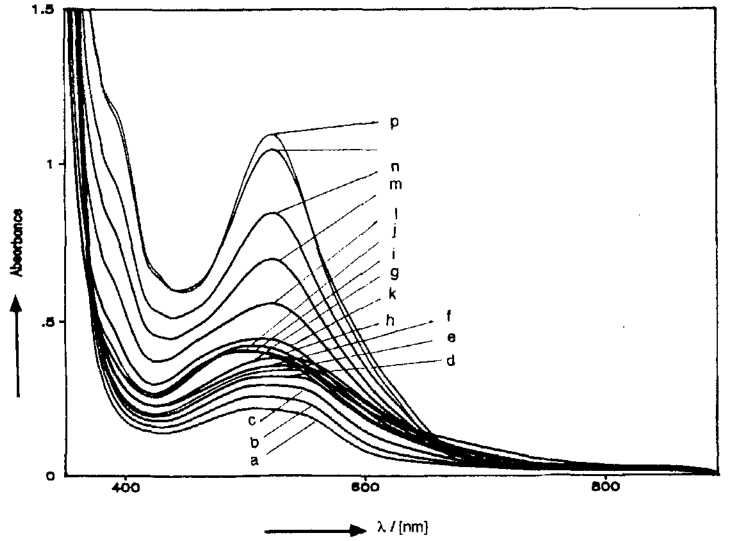

Figure 2 Electronic absorbtion spectra of $[Fe(OH\text{-}bzimpy)_2]^{2+}$ (1.8527×10^{-4} M) in 30:70 (v/v) H_2O:EtOH at different pH values at 20°C: (a) 2.85; (b) 3.15; (c) 3.46; (d) 3.82; (e) 4.21; (f) 4.63; (g) 4.92; (h) 6.55; (i) 7.40; (j) 8.57; (k) 9.20; (l) 9.83; (m) 10.35; (n) 10.80; (o) 11.22; and (p) 11.56.

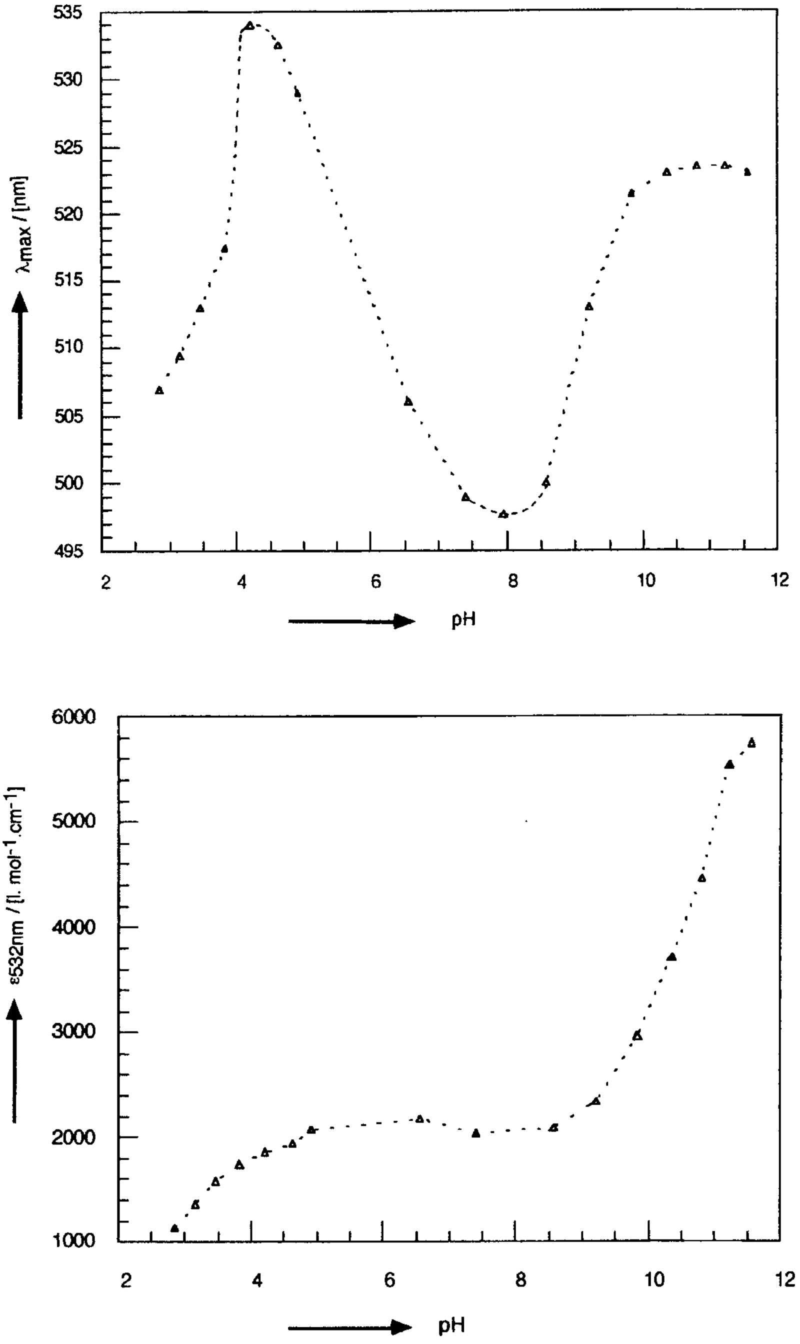

Figure 3 Changes of absorbtion maxima (a) and molar absorbtions (b) with changing pH for $[Fe(OH\text{-}bzimpy)_2]^{2+}$ (1.8527×10^{-4} M) solution in 30:70 (v/v) H_2O:EtOH at 20°C.

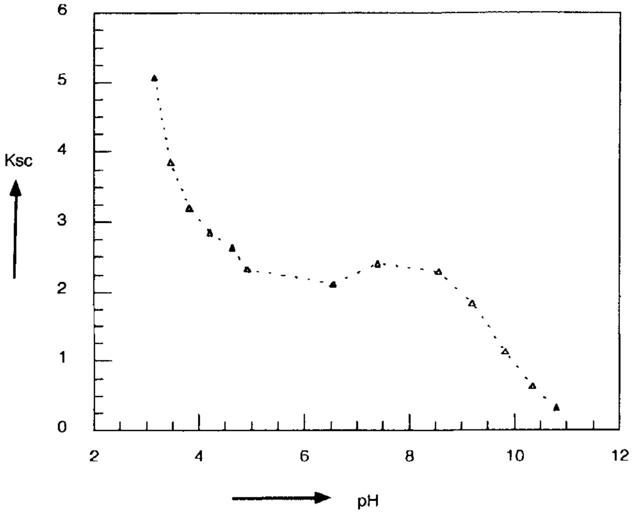

Figure 4 Change of spin-equilibria constant (K_{SC}) values with changing pH for $[Fe(OH\text{-}bzimpy)_2]^{2+}$ ($1 \times 1.8527.10^{-4}$ M) solution in 30:70 (v/v) H_2O:EtOH at 20°C.

H NMR Spectroscopic Studies

Values of magnetic moments ($\mu/\mu B$) for titration of $[Fe(OH\text{-}bzimpy)_2](ClO_4)_2 \cdot 3H_2O$ with *N,N*-triethylamine (NEt_3) were calculated in methanol at 20°C and are listed in Table III. In *N,N*-triethylamine solution the imino hydrogen atom of the coordinated ligand dissociates and this leads to a change in the spin-state of the complex. Magnetic moments are found to decrease as a function of $[Et_3N]/[Fe(H_3L)_2]^{2+}$ with the formation of different deprotonated species of LS state (see Figure 5). At high ratios of $[Et_3N]/[Fe(H_3L)_2]^{2+}$ (≥ 5.0), the magnetic moment seems to be unchanged due to the completion of deprotonation. Magnetic moments vary between 3.3 μB and 5.0 μB and refer to the range between the LS state (S = 0, 0–0.5 μB) and the HS-state (S = 2.0, 5.0–5.5μB), respectively.[2–4,6–8,11,13,15] Values of K_{SC} were evaluated from the observed magnetic moment data using (*3*)[2–4,6–8,11,13,15] and listed in Table III. The value of μHS = 5.5 μB was taken from the literature[6–7,11,13,15] and μLS = 1.5 μB was used for the deprotonated, unsubstituted analogue.[13] K_{SC} decreases for titration of the complex with Et_3N, and thus indicates a change to the LS state (see Table III).

$$K_{SC} = x_{HS}/x_{LS} = (\mu_{expt}^2 - \mu_{LS}^2)/(\mu_{HS}^2 - \mu_{expt}^2) \qquad (3)$$

Here, x is the mole fraction of the spin isomer and μHS and μLS are the effective magnetic moments for high spin and low spin isomers, respectively. In conclusion, it can be said that the acidity of the ligand is increased by coordination with metal ions. Deprotonation of the coordinated ligand is closely related with the observed spin state transition of the complex and favours LS isomers in solution. Protonation of the lone-pair electrons of the imino-nitrogen of the benzimidazole group (ligand) with addition of acid solution leads to a change to the HS-state. The magnetic moment (μ/μB) decreases accompanied with a change to the low-spin (LS) state.

Table III Magnetic moments (μ/μB) and spin-equilibrium constants (K_{SC}) for the titration of $[Fe(OH\text{-}bzimpy)_2](ClO_4)_2 \cdot 3H_2O$ (7.514×10^{-5} M) with Et_3N (1.436×10^{-3} M) in MeOH at 20°C

$[Et_3N]/[Fe(H_3L)_2]^{2+}$	μ/μB	K_{SC} +
0	4.97	4.11
0.38	4.90	3.49
0.76	4.83	3.06
1.52	4.70	2.45
1.91	4.57	1.99
2.48	4.42	1.62
3.06	4.22	1.26
3.82	4.20	1.22
4.78	4.07	1.05
5.74	3.78	0.75
7.07	3.73	0.71
8.60	3.57	0.60
10.52	3.47	0.53
13.38	3.36	0.45

+ All values are ± 0.05.

These results seem to be of importance for the occurrence of spin transitions of the complexes in solution and explain solvent influence.

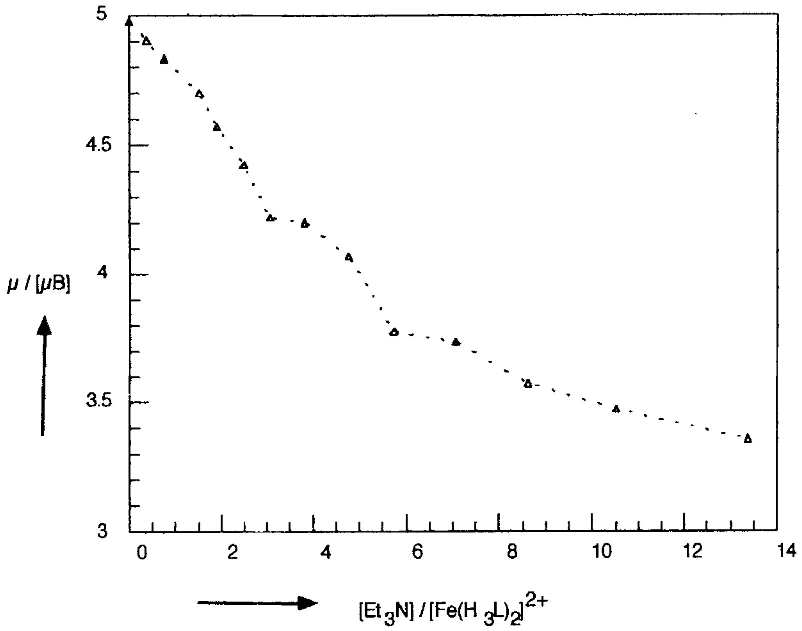

Figure 5 Variation of magnetic moments (μ/μB) as a function of $[Et_3N]/[Fe(H_3L)_2]^{2+}$ for titration of $[Fe(OH\text{-}bzimpy)_2]^{2+}$ (7.5147×10^{-5} M) with Et_3N in MeOH at 20°C.

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