

# Spin-Transition Behaviour of Transition Metal Complexes with 2,6-bis-(Benzimidazol-2'-yl)-pyridine Induced by Deprotonation of the Complex

M. Enamullah<sup>1,†</sup>, W. Linert<sup>1,\*</sup>, V. Gutmann<sup>1</sup>, and R. F. Jameson<sup>2</sup>

<sup>1</sup> Institute of Inorganic Chemistry, Technical University of Vienna, A-1060 Vienna, Austria

<sup>2</sup> Department of Chemistry, The University, Dundee DD14HN, Scotland, United Kingdom

**Summary.** 2,6-bis-(Benzimidazol-2'-yl)-pyridine (*bzimpy* = H<sub>2</sub>L) acts as a bidentate ligand when combining with transition metal ions. The complexes [M(*bzimpy*)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (M = Fe<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup>) were obtained as solids. The protonation constants (log *K*) for the ligand and the complexes were evaluated in 30:70 (v/v) H<sub>2</sub>O:EtOH at 293 K and at constant ionic strength of 0.12 M KCl. Coordination of the ligand to the metal ions leads to an increase of acidity of the imino-hydrogen of the benzimidazole group of the ligand as a function of the complex stability. Deprotonation leads to a spin-state transition (intermediate spin-state → low-spin) of the iron(II)-complex, followed by a shift of the metal-to-ligand *charge transfer* band (*MLCT*) to lower energies ( $\lambda_{\text{max}}$  = 563 to 580 nm). The d-d absorption bands are found to shift to higher energies and the low-spin isomer is favoured at room temperature. An opposite shift of the *MLCT* band ( $\lambda_{\text{max}}$  = 563 to 557 nm) is observed when HClO<sub>4</sub> is added to the complex solution, rendering the high-spin state of the complex more favourable.

**Keywords.** 2,6-bis-(Benzimidazol-2'-yl)-pyridine; Spin-Crossover behaviour; Deprotonation; Transition metal complexes.

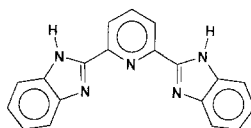
## Durch Deprotonierung induziertes *spin-transition*-Verhalten von Übergangsmetallkomplexen von 2,6-bis-(Benzimidazol-2'-yl)-pyridin

**Zusammenfassung.** 2,6-bis-(Benzimidazol-2'-yl)-pyridin (*bzimpy* = H<sub>2</sub>L) fungiert bei der Reaktion mit Übergangsmetallionen als zweizähliger Ligand. Die Komplexverbindungen [M(*bzimpy*)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (M = Fe<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup> und Ni<sup>2+</sup>) wurden als Feststoffe gewonnen. Die Protonierungskonstanten (log *K*) für den freien Liganden wie auch für die Komplexverbindungen wurden in H<sub>2</sub>O:EtOH (30:70 v/v) bei 293 K und konstanter Ionenstärke (0, 12 M KCl) bestimmt. Die Koordination des Liganden an ein Metallion bewirkt eine Erhöhung der Azidität des Imino-Wasserstoffs am Benzimidazolring in Abhängigkeit von der Komplexstabilität. Deprotonierung führt zu einem Spinübergang (Zwischenzustand → low-spin) des Eisen(II)-Komplexes, verknüpft mit einer bathochromen Verschiebung der Metall-Ligand *charge-transfer*-Bande (*MLCT*) zu niedrigeren Energien ( $\lambda_{\text{max}}$  = 563 nach 580 nm). Die d-d Absorptionsbanden verschieben sich zu höheren Energien, die low-spin-Verbindung wird bei Raumtemperatur bevorzugt. Zugabe von HClO<sub>4</sub> zur Komplexlösung bewirkt eine Verschiebung der *MLCT*-Bande zu höheren Energien ( $\lambda_{\text{max}}$  = 563 nach 557 nm), d.h. die high-spin-Komplexverbindung liegt bevorzugt vor.

<sup>†</sup> On leave from the Chemistry Department, Jahangirnagar University, Dhaka, Bangladesh

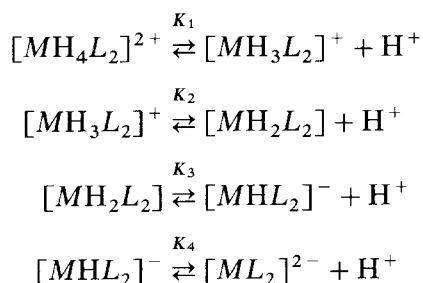
## Introduction

Coordination of 2-(2'-pyridyl)-imidazole, 4-(2'-pyridyl)-imidazole, 2-(2'-pyridyl)-imidazoline, and 2-(2'-pyridyl)-benzimidazole with bivalent first-row transition metal ions ( $M = \text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$ ) causes an increase of the acidity of the imino hydrogen of the imidazole and benzimidazole groups of the ligands [1–5]. Titration of these cationic complexes with bases leads to a deprotonation reaction and yields stable neutral complexes or salts with less positively charged cations [3, 6, 7, 13]. Recently, some complexes of 2,6-*bis*-(benzimidazol-2'-yl)-pyridine (*bzimpy* =  $\text{H}_2\text{L}$ ) with first-row transition metal ions,  $[\text{M}(\text{bzimpy})_2](\text{ClO}_4)_2$ , have been isolated as perchlorates [8–14].



[2,6-*bis*-(benzimidazol-2'-yl)-pyridine = *bzimpy* =  $\text{H}_2\text{L}$ ]

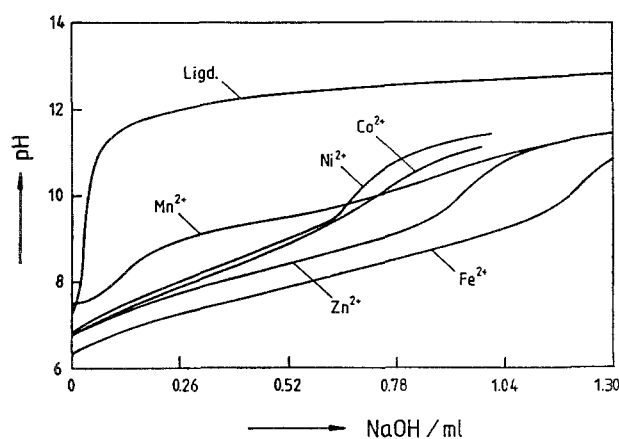
The complex  $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$  is found to exhibit a pronounced spin-crossover behaviour in solution [8–13]. However, solvolysis [8–11], ligand- and anion-exchange reactions [13–14], ligand substitution [8–9, 13–14], hydrogen bonding interactions [7–8], and complex deprotonation [11] are found to play an important role. Titration of  $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$  with  $\text{HClO}_4$ ,  $\text{Et}_3\text{N}$ , and  $\text{NaOH}$ , followed by potentiometry, UV-Vis spectroscopy, and  $^1\text{H NMR}$  spectroscopy suggests that the spin-state equilibria are accompanied by the deprotonation of the complex, as summarized in the general reaction schemes. The present paper deals with investigations concerning these relations.



## Results and Discussion

### Potentiometric titrations

The potentiometric titrations of 2,6-*bis*-(benzimidazol-2'-yl)-pyridine and of  $[\text{M}(\text{H}_2\text{L})_2](\text{ClO}_4)_2$  ( $M = \text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Zn}^{2+}$ ) with  $\text{NaOH}$  (0.025 *M*) were carried out in 30:70 (v/v)  $\text{H}_2\text{O}:\text{EtOH}$  at an ionic strength of 0.12 *M* in  $\text{KCl}$  at 293 K. The titration curves are shown in Fig. 1. To avoid ligand dissociation, hydrolysis or ligand exchange with hydroxo groups, the titrations were performed in presence of excess ligand ( $[\text{L}]_{\text{T}}/[\text{FeL}_2]_{\text{T}} \geq 8.0$ ). All curves indicate the deprotonation of the imidazole ring at  $p\text{H} > 6.0$  [1–7, 31, 32]. The values of the



**Fig. 1.** Titration curves of  $[\text{M}(\text{bzimpy})_2](\text{ClO}_4)_2$  in presence of excess ligand with NaOH (0.025 M) in 30:70 (v/v)  $\text{H}_2\text{O}:\text{EtOH}$   $I = 0.12 \text{ M}$ ,  $T = 20^\circ\text{C}$ ;  $[\text{bzimpy}] = 1.9193 \cdot 10^{-3} \text{ M}$ ;  $[\text{Fe}(\text{bzimpy})_2]^{2+} = 1.3334 \cdot 10^{-4} \text{ M}$ ,  $[\text{L}]/[\text{FeL}_2]^{2+} = 7.58$ ;  $[\text{Zn}(\text{bzimpy})_2]^{2+} = 1.6821 \cdot 10^{-4} \text{ M}$ ,  $[\text{L}]/[\text{ZnL}_2]^{2+} = 6.00$ ;  $[\text{Ni}(\text{bzimpy})_2]^{2+} = 1.1314 \cdot 10^{-4} \text{ M}$ ,  $[\text{L}]/[\text{NiL}_2]^{2+} = 8.92$ ;  $[\text{Co}(\text{bzimpy})_2]^{2+} = 1.2038 \cdot 10^{-4} \text{ M}$ ,  $[\text{L}]/[\text{CoL}_2]^{2+} = 8.39$ ;  $[\text{Mn}(\text{bzimpy})_2]^{2+} = 1.4945 \cdot 10^{-4} \text{ M}$ ,  $[\text{L}]/[\text{MnL}_2]^{2+} = 6.75$

**Table 1.** Protonation constants of  $[\text{MH}_4\text{L}_2](\text{ClO}_4)_2$  ( $\text{H}_2\text{L} = \text{bzimpy}$ ) in presence of excess ligand in 30:70 (v/v)  $\text{H}_2\text{O}:\text{EtOH}$ ; titrant = NaOH (0.025 M);  $I = 0.12 \text{ M}$ ;  $T = 20^\circ\text{C}$

Complex	$[\text{L}]/[\text{MH}_4\text{L}_2]^{2+}$	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$
$[\text{H}_2\text{LH}_2]^{2+}$ <sup>a</sup>	–	–	3.73	5.55	–
$[\text{H}_2\text{L}]$	–	16.33	12.31	–	–
$[\text{MnH}_4\text{L}_2]^{2+}$	6.8	11.18	9.76	9.54	8.45
$[\text{FeH}_4\text{L}_2]^{2+}$	7.6	8.65	8.45	7.45	7.18
$[\text{CoH}_4\text{L}_2]^{2+}$	8.4	10.75	9.15	8.21	7.47
$[\text{NiH}_4\text{L}_2]^{2+}$	8.9	11.01	8.98	8.20	7.79
$[\text{ZnH}_4\text{L}_2]^{2+}$	6.0	11.57	9.27	8.29	7.64

<sup>a</sup> Protonation of  $[\text{H}_2\text{L}]$  to  $[\text{H}_2\text{LH}_2]^{2+}$

All values are  $\pm 0.1$

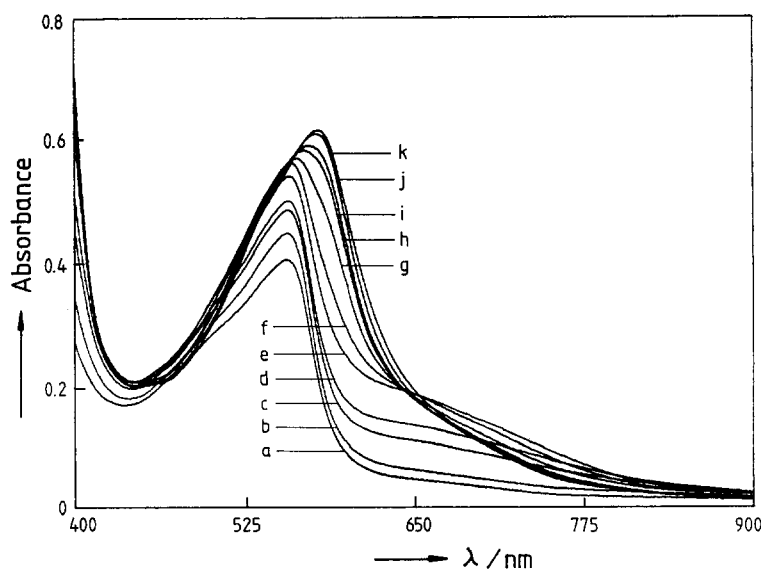
protonation constants (see Table 1) were calculated using the computational method described by *A. E. Martell* and *R. J. Motekaitis* [20]. Coordination of metal ions to the nitrogen atoms of the ligand tends to decrease the electron availability at the imino-nitrogen, thereby facilitating the dissociation and increasing the acidity of the ligands [1–7, 31, 32]. For the bivalent first-row transition metal complexes with 2-(2'-pyridyl)-imidazole and 4-(2'-pyridyl)-imidazole, the stability decreases in the order of  $\text{Cu} > \text{Ni} > \text{Co} > \text{Zn} > \text{Fe}$  [1, 4] and  $\text{Ni} > \text{Co} > \text{Zn} > \text{Mn}$  [5], respectively. The first and second deprotonation constants of  $[\text{M}(\text{II})\text{-}2\text{-(}2'\text{-pyridyl)-imidazole}]$  are found to decrease in the order  $\text{Cu} > \text{Co} > \text{Fe} > \text{Zn} > \text{Ni}$ . Including the third deprotonation step, the sequence  $\text{Fe} > \text{Cu} \approx \text{Co} > \text{Zn} > \text{Ni}$  is found [2]. The acidities of  $[\text{M}(\text{bzimpy})_2](\text{ClO}_4)_2$  follow the order  $\text{Fe} > \text{Co} \approx \text{Ni} > \text{Zn} > \text{Mn}$  (see Table 1) which is in good agreement with the reported acidity and stability constants [1, 2, 4–5]. The relatively high acidity of the iron-complex might be

considered as a result of the high stability of the Fe-ligand bond which in turn leads to a stabilization of the low-spin state of the iron(II) complex [8–14]. Compared with complexes where the 4-position of the ligand is substituted by Cl and OH groups (where the high-spin ground state is observed [8–9]), a pronounced spin-crossover behaviour can be found with temperatures.

### Spectrophotometric titrations

Figure 2 shows the UV-Vis spectra of  $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$  in presence of excess ligands in 30:70 (v/v)  $\text{H}_2\text{O}:\text{EtOH}$  at room temperature when being titrated with  $\text{NaOH}$  (0.025 M) and  $\text{HClO}_4$  (0.175 M). The absorbance depends strongly on the  $\text{pH}$  of the solution. With increasing  $\text{pH}$ , the colour changes from pink-red to wine-red and further to red-violet and bluish-violet, until finally a blue colour is reached. The spectra of  $[\text{Fe}(\text{bzimpy})_2]^{2+}$  exhibit (i) a very strong absorption band in the region of 400–450 nm, associated with the  $\pi \rightarrow \pi^*$  transition of the ligand, (ii) a strong absorption band (450–600 nm,  $\epsilon_{\text{max}} \approx 6000\text{--}7000 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ), associated with the metal-to-ligand charge transfer band ( $T_{2g} \rightarrow \pi^*$ ), and (iii) a broad weak absorption band at 600–800 nm ( $\epsilon_{670} \approx 2000 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) which is attributed to an d-d transition [8–14, 16, 21–26]. 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 degenerated level ( $b_2 + e$ ). The transitions ( $d_\pi(b_2) \rightarrow \pi_1^*$ ) and ( $d_\pi(e) \rightarrow \pi_1^*$ ) yield the strongest absorption band (MLCT), including a shoulder at higher energy [8, 9, 13, 21].

The MLCT band shifts to shorter wavelength by about 6 nm with continuous decreasing of intensity during the titration with  $\text{HClO}_4$  (Table 2). Increasing proton concentration leads to a hindrance of the imino-hydrogen atom so that the bond



**Fig. 2.** UV-Vis spectra of  $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$  ( $2.3933 \cdot 10^{-4} \text{ M}$ ) with excess ligands ( $[\text{L}]/[\text{FeL}_2]^{2+} = 8.5$ ) in 30:70 (v/v)  $\text{H}_2\text{O}:\text{EtOH}$  (293 K);  $\text{pH}$ : (a) 3.35, (b) 4.25, (c) 4.95, (d) 5.11, (e) 5.91, (f) 6.48, (g) 6.92, (h) 7.28, (i) 7.42, (j) 7.6, and (k) 8.03

between metal and ligand weakens because of hyperconjugation. This effect is further facilitated by the solvation of the lone pair of the imino nitrogen atom with addition of acid [23]. As a result, the high-spin state complex is favoured [15]. The d-d absorption band shifts to lower energy (weak field) and is separated from the *MLCT* band (see Fig. 2) in the high-spin state complex [27]. The low absorptivity of the high-spin complex ( $\epsilon_{\text{hs}} = 4300$ ;  $\epsilon_{\text{ls}} = 6600 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  at 563 nm) is due to a weak overlap between the metal  $t_{2g}$  and the ligand  $\pi^*$  orbitals [8–16, 23]. These results are in good agreement with the effect of raising temperature on the spin-state equilibria ( ${}^1\text{A}_1 \rightarrow {}^5\text{T}_{2g}$ ), favour the high-spin state [8–13]. The values of  $\lambda_{\text{max}}$  are not affected (557 nm) within the *pH* region of 4.3 to 3.2 where the pure high-spin state of complexes are present.

Titration of the complex with base (NaOH, 0.025 M) causes a stepwise deprotonation of the imino hydrogen [1–7, 31–32] as suggested in the reaction schemes. The *MLCT* bands are found to shift to longer wavelength ( $\lambda_{\text{max}} = 563$  to 580 nm) with addition of base (Table 2). The deprotonation of the imino hydrogen increases the electron density on the imidazole ring of the complex as well as the ligand to metal ( $L \rightarrow M$ )  $\sigma$ -donation, which probably is accompanied by an increase in back donation ( $t_{2g} \rightarrow \pi^*$ ) assisting the formation of the methine chromophore characteristic of the low-spin state. Simple charge and inductive effects expected from deprotonation, methylation, and oxidation of the complex cannot account for the observed red shift at constant spin-state, since the direct or inductive increase of electronic charge at the ligand should raise the energies of ligand  $\pi$ -orbitals [13]. However, this effect was explained by considering the ligand-to-metal *charge transfer* band at  $[\text{Fe}(\text{phen})_3]^{3+}$  instead of *MLCT* [13, 24]. Deprotonation increases

**Table 2.** Change of spin-equilibrium constants and absorption maxima of  $(\text{Fe}(\text{bzimpy})_2)(\text{ClO}_4)_2^{\text{a}}$  with variation of *pH* in 30:70 (v/v)  $\text{H}_2\text{O}:\text{EtOH}$ ;  $I = 0.12 \text{ M}$ ;  $T = 20^\circ \text{C}$

<i>pH</i>	$\lambda_{\text{max}}$ (nm)	$\epsilon$ (563 nm) ( $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ )	$K_{\text{sc}}^{\text{b}}$
3.20	556.5	4380	0.97
3.49	557.0	4752	0.82
3.70	557.0	4892	0.76
4.25	557.0	5075	0.68
4.64	557.5	5373	0.56
5.11	558.0	5709	0.42
5.91	558.5	6222	0.21
6.48	560.0	6513	0.10
6.92	563.5	6600	0.05
7.10	565.5	6665	0.03
7.28	569.5	6716	0.01
7.42	572.5	6730	0.008
7.76	578.0	6725	0.01
8.03	580.0	6709	0.02

<sup>a</sup> With excess ligand  $[\text{L}]/[\text{Fe}(\text{bzimpy})_2]^{2+} = 6.5$ ; <sup>b</sup> at 563 nm

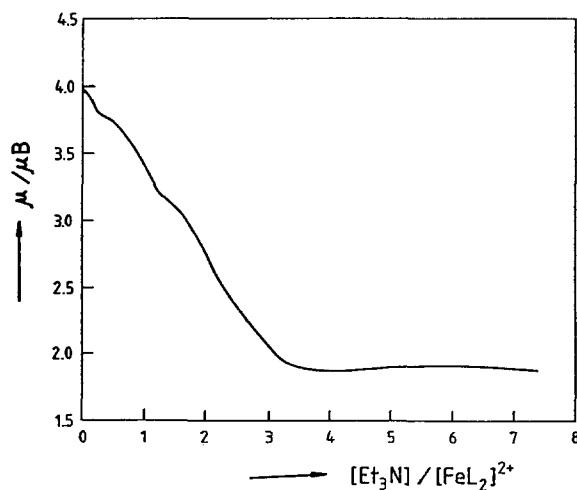
the stability of the complex and leads to increasing ligand field splitting energy (10 Dq). This favours the low-spin state of the complex [11, 13–14]. The d-d absorption band shifts to shorter wavelength in the low-spin complex (see Fig. 2). The existence of the solid deprotonated complex  $[\text{Fe}(\text{bzimpy}-\text{H})_2] \cdot \text{H}_2\text{O}$  ( $\lambda_{\text{max}} = 580 \text{ nm}$ ) and of the iron(III) complex  $[\text{Fe}(\text{bzimpy}-\text{H})_2][\text{NHEt}_3] \cdot 4\text{H}_2\text{O}$  in the low-spin state has been demonstrated [13–14]. The broad absorption spectra observed for the deprotonated complex (Fig. 2) result from the overlap between the strong *MLCT* and the weak d-d band. The position of the absorption maxima is not affected ( $\lambda_{\text{max}} = 580 \text{ nm}$ ) when further base is added ( $\text{pH} \approx 8.0$ ). An isosbestic point at about 645 nm refers to the spin-crossover equilibria of the complex in the *pH* region of about 5.5–8.0. Outside this range, two pure spin-isomers, either the low-spin or the high-spin species, are predominant which is indicated by constant  $\lambda_{\text{max}}$  values (557 nm and 580 nm, respectively). The existence of different isosbestic points near 600 nm, 660 nm, and 725 nm (Fig. 2) is presumably a result of spin-equilibria for the different deprotonated species.

Since the molar absorptivity at given wavelength and temperature results from a combination of contributions from the high-spin and low-spin isomer [8, 9, 11, 13], the values of spin-equilibrium constants ( $K_{\text{sc}}$ ) (Table 2) can be calculated using Eq. 1. The values of  $\epsilon_{\text{ls}}$  ( $6700 \pm 501 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) and  $\epsilon_{\text{hs}}$  ( $4300 \pm 501 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) were estimated at 563 nm for both spin states of the complex at *pH* of 3.2 and 8.0, respectively.

$$K_{\text{sc}} = c_{\text{hs}}/c_{\text{ls}} = (\epsilon_{\text{obs}} - \epsilon_{\text{ls}})/(\epsilon_{\text{hs}} - \epsilon_{\text{ls}}) \quad 1$$

#### <sup>1</sup>H NMR spectroscopic titrations

The values of the magnetic moment for titration of  $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$  with  $\text{NEt}_3$  in methanol at 298 K, evaluated by *Evan's* method based on <sup>1</sup>H NMR shifts [18], are listed in Table 3. The variation of the magnetic moment (Table 3 and Fig. 3) indicates that the spin-state of the complex is changed with the formation of different deprotonated species of low-spin state. Magnetic moments are not affected at about  $[\text{Et}_3\text{N}]/[\text{FeL}_2]^{2+} \approx 4.0$  due to complete deprotonation. The magnetic moments vary between  $1.5 \mu_{\text{B}}$  and  $4.0 \mu_{\text{B}}$  and refer to the range between low-spin ( $S = 0$ ,



**Fig. 3.** Variation of magnetic moments as a function of  $[\text{NEt}_3]/[\text{FeL}_2]^{2+}$  for  $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$  in methanol at 298 K;  $[\text{FeL}_2]_{\text{T}} = 3.359 \cdot 10^{-4} \text{ M}$

**Table 3.** Variation of spin-equilibrium constants, magnetic moments and absorption maxima with the deprotonation of [Fe(*bzimpy*)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>

[Et <sub>3</sub> N]/[FeL <sub>2</sub> ] <sup>2+</sup>	λ <sub>max</sub> (nm)	μ/μ <sub>B</sub>	K <sub>sc</sub>
0	557.0	3.94	0.90
0.25	557.5	3.63	0.65
0.49	558.5	3.57	0.60
0.74	559.5	3.43	0.51
0.98	560.5	3.21	0.41
1.23	563.5	3.01	0.32
1.48	568.0	2.91	0.28
1.72	578.5	2.76	0.24
2.22	581.0	2.27	0.12
2.71	582.0	1.89	0.05
3.20	581.5	1.56	0.006
3.69	582.0	1.47	0.004
4.18	581.5	1.46	0.004

0–0.5 μ<sub>B</sub>) and high-spin (*S* = 2, 5.0–5.5 μ<sub>B</sub>) state, respectively [8, 12, 13, 15, 16, 26–30]. From the observed magnetic moments, the values of the spin-equilibrium constant (*K*<sub>sc</sub>) were evaluated using the Eq. 2. (Table 3).

$$K_{sc} = x_{hs}/x_{ls} = (\mu_{\text{expt}}^2 - \mu_{ls}^2)/(\mu_{hs}^2 - \mu_{\text{expt}}^2) \quad 2$$

In Eq. 2, *x* is the mole fraction of the spin-isomer and μ<sub>hs</sub> and μ<sub>ls</sub> are the effective magnetic moments for high-spin and low-spin forms, respectively. For the low-spin isomer, the value of μ<sub>ls</sub> (1.5 μ<sub>B</sub>) was estimated from the deprotonated species. This agrees well with low temperature measurements (μ = 1.6 μ<sub>B</sub> at 223 K) [8–9]. The value of μ<sub>hs</sub> (5.5 μ<sub>B</sub>) for the high-spin isomer was taken from the literature [8, 9, 13]. The *K*<sub>sc</sub> values decrease with deprotonation of the complex whereas the low-spin isomer is increasingly populated. This result is consistent with the preservation of intramolecular <sup>1</sup>A<sub>1g</sub> (*S* = 0) ⇌ <sup>5</sup>T<sub>2g</sub> (*S* = 2) spin-equilibrium processes in solution. Studies of solvent polarity effects on spin-equilibria of complexes *via* hydrogen bonding interactions between the –NH<sub>2</sub> group of the ligand and the solvent yield the same results [16].

In conclusion, it can be said that the deprotonation of the coordinated, ligand is closely related to the observed spin-transition of the complexes. Generally, the acidity of the ligand is increased by coordination. This mutual interrelation seems to be of importance for the occurrence of spin-transition of the complexes in solution and explains the solvent influence.

## Experimental

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

*Preparation of Ligands and Complexes.* The ligand was prepared by the method of A. W. Addison and P. J. Burke [17]. The complexes were prepared according to the literature [8–14] and recrystallized three times from methanol. For details, see Refs. [8, 9, 11, 12].

*Potentiometric Titrations.* Potentiometric titrations were performed using a WTW GmbH D 8120 Weilheim pH 521 potentiometer at  $20 \pm 0.5^\circ\text{C}$  and 0.12 M KCl. Homogeneity with respect to temperature and concentration was ensured by the use of a magnetic stirrer. A continuous nitrogen stream was passed through the titration cell during the experiments. Before all titrations, the pH meter was standardized with buffer solutions of pH 2.0 and 9.0 (Riedel-de Haen). Potentiometric titrations of  $[M(\text{bzimpy})_2](\text{ClO}_4)_2$  in presence of an excess of ligand with NaOH (0.025 M) and HClO<sub>4</sub> (0.17457 M) were carried out at complex concentrations between  $1.0 \cdot 10^{-4}$  M and  $2.0 \cdot 10^{-4}$  M in 30:70 (v/v) H<sub>2</sub>O:EtOH at room temperature.  $1.0$  to  $3.0 \cdot 10^{-3}$  M solutions in the ligand were titrated with NaOH and HClO<sub>4</sub> in 30:70 (v/v) H<sub>2</sub>O:EtOH.

*Spectrophotometric Measurements.* UV-Vis spectra were obtained with a Hitachi U-2000 spectrophotometer equipped with an electronically thermostated cell holder (Hitachi) for the range of 0–100 °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 the use of a magnetic stirrer. Spectrophotometric titrations of  $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$  with NaOH (0.025 M) and HClO<sub>4</sub> (0.17457 M) were performed over a complex concentration range of 1.0 to  $2.0 \cdot 10^{-4}$  M in 30:70 (v/v) H<sub>2</sub>O:EtOH at room temperature. Titrations of  $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$  with N,N-triethylamine were performed at complex concentrations of 1.0 to  $2.0 \cdot 10^{-4}$  M with and without excess of ligand in MeOH at room temperature.

*Magnetic Measurements.* <sup>1</sup>H NMR spectra were recorded on a Bruker AC 250 FT NMR spectrometer in high precision NMR sample tubes of type 528-PP (Wilma Glass Co., New Jersey) with sealed Wilma coaxial inserts (WGS-5BL) containing 5% TMS as external standard in acetone-d<sub>6</sub>. Magnetic susceptibilities in solution were measured by the Evans <sup>1</sup>H NMR method [18] using methanol for temperature calibration [19]. 1% (v/v) cyclohexane was used as internal reference compound. Titrations of  $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$  with N,N-triethylamine were performed at a complex concentration of  $4.0 \cdot 10^{-4}$  M in MeOH at 298 K.

## Acknowledgements

Financial supports by the “Österreichischer Akademischer Austauschdienst” (ÖAD) and the “Fonds zur Förderung der wissenschaftlichen Forschung” (Project 8795) are acknowledged.

## References

- [1] Eilbeck W. J., Holmes F. (1967) *J. Chem. Soc. A*: 1777
- [2] Boggess R. K., Martin R. B. (1974) *Inorg. Chem.* **13**: 1525
- [3] Chiswell B., Lions F., Morris B. S. (1964) *Inorg. Chem.* **3**: 110
- [4] Eilbeck W. J., Holmes F., Phillips G. G., Underhill A. E. (1967) *J. Chem. Soc. A*: 1161
- [5] Harkins T. R., Freiser H. (1956) *J. Am. Chem. Soc.* **78**: 1143
- [6] Geldbard J. F., Lions F. (1962) *J. Am. Chem. Soc.* **84**: 2262
- [7] Geldbard J. F., Lions F. (1963) *Inorg. Chem.* **2**: 270
- [8] Enamullah M., Linert W., Gutmann V., Jameson R. F. (1994) *Monatsh. Chem.* (in press)
- [9] Enamullah M., Linert W., Konecny M. (submitted to *J. Chem. Soc. Dalton Trans.*)
- [10] Strauß B., Gutmann V., Linert W. (1993) *Monatsh. Chem.* **123**: 391
- [11] Strauß B., Gutmann V., Linert W., Jameson R. F. (1992) *Monatsh. Chem.* **123**: 537
- [12] Strauß B., Gutmann V., Linert W. (1993) *Monatsh. Chem.* **124**: 515
- [13] Addison A. W., Burman S., Wahlgren, C. G., Rajan O. A., Rowe T. M., Sinn E. (1987) *J. Chem. Soc. Dalton Trans.* 2621



- [14] Rüttimann S., Moreau C. M., Williams A. F., Bernardinelli G., Addison A. W. (1992) *Polyhedron* **11**: 635
- [15] Sams J. R., Tsin T. B. J. (1976) *Chem. Soc. Dalton Trans.* 488
- [16] Chum H. Li., Vanin J. A., Holland M. I. D. (1982) *Inorg. Chem.* **21**: 1146
- [17] Addison A. W., Burke P. J. (1983) *J. Heterocycl. Chem.* 1481
- [18] Evans D. F. (1959) *J. Chem. Soc.* 2003
- [19] Raiford D. S., Fisk C. L., Becker E. D. (1979) *Anal. Chem.* **51**: 2050
- [20] Martell A. E., Motekaitis R. J. (1992) *Determination and use of stability constants*. VCH Publishers, New York
- [21] Krumholz P. (1965) *Inorg. Chem.* **4**: 612
- [22] Krumholz P. (1971) *Struct. Bond* **9**: 150
- [23] Sone K., Fukuda Y. (1987) *Inorganic thermochromism*. Springer, Berlin Heidelberg New York Tokyo, p 95
- [24] Williams R. J. P. (1955) *J. Chem. Soc.* 137
- [25] Jorgensen C. K. (1957) *Acta Chem. Scand.* **11**: 166
- [26] König E., Madeja K. (1967) *Inorg. Chem.* **6**: 48
- [27] Jesson J. P., Trofimenko S., Eaton D. R. (1967) *J. Am. Chem. Soc.* **89**: 3158
- [28] Reeder K. A., Dose E. V., Wilson L. (1978) *Inorg. Chem.* **17**: 1071
- [29] Goodgame D. M. L., Machado A. A. S. C. (1969) *Inorg. Chem.* **8**: 2031
- [30] Dosser R. J., Eilbeck W. J., Underhill A. E., Edwards P. R., Johnson C. E. (1969) *J. Chem. Soc. A*: 810
- [31] Coryell C. D., Pauling L. (1940) *J. Biol. Chem.* **132**: 769
- [32] Holmes F., Jones K. M., Torrible E. G. (1961) *J. Chem. Soc.* 4790

*Received March 30, 1994. Accepted April 3, 1994*