

## Spin-Crossover Complexes in Solution, I. Substitutional Lability of $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$ \*\*

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**Summary.** The iron(II) complexes of the nitrogen donor ligand 2,6-bis(benzimidazol-2'-yl)pyridine (*bzimpy*) have been investigated in nonaqueous solvents using various spectrophotometric methods. Measurements in methanol at 20°C revealed that *bzimpy* can act as a bi- or tridentate ligand towards iron(II) in this solvent, forming  $[\text{Fe}(\text{bzimpy})]^{2+}$  (tridentate,  $\log K = 5.54$ ),  $[\text{Fe}(\text{bzimpy})_2]^{2+}$  (bis-tridentate,  $\log K = 4.12$ ) and  $[\text{Fe}(\text{bzimpy})_3]^{2+}$  (tris-bidentate,  $\log K = 3.85$ ). The pronounced thermochromism of the compound is shown to be the result of both spin-crossover and dissociation equilibria. Furthermore, in solvents of higher donor numbers ( $\geq 30$ ), partial or complete deprotonation of the complex  $[\text{Fe}(\text{bzimpy})_3]^{2+}$  is observed. Triethylamine added stepwise to methanolic solutions causes successive deprotonation.

**Keywords.** 2,6-Bis(benzimidazol-2'-yl)pyridine; Complex formation; Deprotonation; Spin-crossover; Substitutional lability; Thermochromism.

### Spin-crossover-Komplexe in Lösung, 1. Mitt.: Substitutionslabilität von $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$

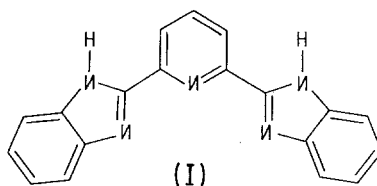
**Zusammenfassung.** Es wurden Eisen(II) komplexe des Stickstoffdonorliganden 2,6-bis(benzimidazol-2'-yl)pyridin (*bzimpy*) in nichtwässrigen Lösungsmitteln mit Hilfe verschiedener spektrophotometrischer Methoden untersucht. Messungen in Methanol bei 20°C zeigten, daß *bzimpy* gegenüber Eisen(II) sowohl als zwei- als auch als dreizähliger Ligand auftreten kann. Es werden dabei die Verbindungen  $[\text{Fe}(\text{bzimpy})]^{2+}$  (tridentat,  $\log K = 5.54$ ),  $[\text{Fe}(\text{bzimpy})_2]^{2+}$  (bis-tridentat,  $\log K = 4.12$ ) und  $[\text{Fe}(\text{bzimpy})_3]^{2+}$  (tris-bidentat,  $\log K = 3.85$ ) gebildet. Das ausgeprägte Thermochromieverhalten der Titelverbindung setzt sich aus einem dissoziativen und einem Spin-crossoveranteil zusammen. Weiters wurde in Lösungsmitteln höherer Donorzahl ( $\geq 30$ ) eine teilweise oder auch vollständige Deprotonierung des Komplexes  $[\text{Fe}(\text{bzimpy})_3]^{2+}$  beobachtet. Die schrittweise Zugabe von Triethylamin zu methanolischen Lösungen bewirkt eine fortschreitende Deprotonierung.

### Introduction

Since the investigations of Cambi et al. [1], transition-metal complexes with four to seven d-electrons are known which show unusual magnetic moments that can not be described by either high-spin (HS) or low-spin (LS) electronic ground states.

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\*\* This paper is dedicated to Professor Dr. Wolfgang Beck on the occasion of his 60th birthday with warmest personal wishes



The origin of this behaviour has been found to be in a thermal equilibrium between both spin states. In the solid state the spin transition may be gradual, abrupt or a twosteps process showing more or less pronounced hysteresis effects associated with residual para-and/or diamagnetism. These effects in part depend upon anions, preparation, mechanical treatment, metal-dilution, ageing, kind of solvates, isotopic effects, etc. In solution, one might expect a more simple situation, since there exist no "lattice-effects" as in the solid state. Indeed, only crossover of the gradual type has been observed so far. However, one has to consider solution-specific problems such as ligand substitution, ion-pairing or *pH*-influences as will be shown in some detail in the following paper. So far, spin-crossover compounds have been the topic of numerous investigations, mainly done in the solid state. In solution, the interest has focused on the dynamics of the spin transition. The results of previous investigations have been reviewed in several articles [2–5]. Only little attention has been paid to the investigation of further equilibria in solution which are related to the change of spin state, although the role of this state is known to play an important role in chemical reactivity [6], not least in biological processes of hemoproteins [7]. In the present work we chose the iron(II)complex of 2,6-bis(benzimidazol-2'-yl)pyridine (*bzimpy*, in the following also denoted as "ligand" or "*L*") to study the different kinds of solution equilibria of a compound that exhibits spin-crossover behaviour in the solid state [8].

## Experimental Part

### Materials

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (Riedel) and  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  (Fluka) were both analytical grade and used as received. Triethylamine ( $\text{NEt}_3$ ) was distilled off NaOH. 2,6-Bis(benzimidazol-2'-yl)pyridine was prepared by the method of Addison and Burke [9] and recrystallized three times from *MeOH*.  $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$  was prepared according to literature [8] (found: C 51.94, H 2.96, N 15.93, Cl 8.13; calc. for  $\text{C}_{38}\text{H}_{26}\text{Cl}_2\text{FeN}_{10}\text{O}_8$ : C 52.02, H 2.99, N 15.96, Cl 8.08%).

### Solvents

For all distillations performed, the first 10% of the distillate was discarded. Starting materials were reagent grade unless otherwise noted. The water content of all solvents except acetone was analysed by Karl Fischer titration and was found to be below  $100\text{ mg l}^{-1}$  throughout all measurements. Commercial grade acetone (*Ac*) was distilled twice off  $\text{CaSO}_4$  and once off  $\text{B}_2\text{O}_3$ . Acetonitril (*An*) was refluxed once off NaOH and twice off  $\text{P}_2\text{O}_5$ . Chloroform ( $\text{CHCl}_3$ ) was distilled off  $\text{P}_2\text{O}_5$ . Dimethylsulfoxide (*DMSO*) was dynamically dried with molecular sieve  $4\text{ \AA}$  and subsequently distilled under reduced pressure. Hexamethylphosphoric acid triamide (*HMPA*) was fractionally distilled under reduced pressure. Commercial grade methanol (*MeOH*) was refluxed for 24 hours over CaO and fractionally distilled. Nitromethane (*NM*) was used as received. Propanediolcarbonate (*PDC*) was refluxed for 24 hours under reduced pressure and was subsequently fractionally distilled. Pyridine (*P*) was distilled off NaOH.

*Physical Methods*

UV-Vis absorption spectra were obtained on a Hitachi U-2000 spectrophotometer. A Hitachi electronic thermostatted cell holder in the range of 0–100°C provided temperature control ( $\pm 0.5^\circ\text{C}$ ) and temperatures were recorded using a CC thermocouple. A homogenous temperature distribution within the cells was ensured by using a magnetic stirrer. Due to the pronounced thermochromism of the system under study, temperature-constancy could be easily followed on an absorbance vs. time plot; a constant value was reached after 6 minutes.

*Calculation of Thermodynamic Data*

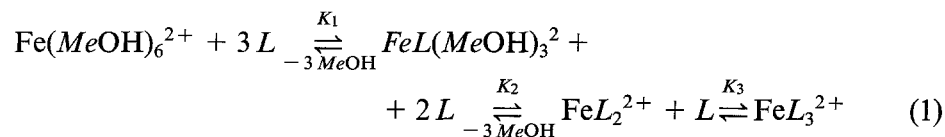
Experimental data were corrected with respect to temperature induced density changes. Due to the limited experimental temperature range, minimizing the sum of squares of errors in a curve fitting procedure was found to be not sufficient to obtain a reliable set of thermodynamic parameters. Thus, the molar extinction coefficients of comparable iron(II) complexes of defined spin states were used to obtain additional boundary conditions. The values used are  $\epsilon_{LS} = 11\,000 - 12\,000 \text{ l mol}^{-1} \text{ cm}^{-1}$  [10] and  $\epsilon_{HS} \geq 1\,100 \text{ l mol}^{-1} \text{ cm}^{-1}$  [4]. The resulting thermodynamic parameters are given in Table 3, the corresponding molar extinction coefficients are  $\epsilon_{LS}(\text{FeL}_3^{2+}) = 12\,450 \pm 500 \text{ l mol}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{HS}(\text{FeL}_3^{2+}) = 1\,200 \pm 400 \text{ l mol}^{-1} \text{ cm}^{-1}$ .

*Spectrophotometric Titrations*

All solutions were prepared in a nitrogen atmosphere using deoxygenated solvents to avoid oxidation of  $\text{Fe}^{2+}$ . To investigate the influence of the ionic strength, titration series with  $(\text{Fe}^{2+}) = 1.425 \cdot 10^{-4} \text{ M}$  were performed successively in pure *MeOH* and in the solvent containing  $0.1 \text{ M NaClO}_4 \cdot \text{H}_2\text{O}$ . The addition of ligand to a  $\text{Fe}^{2+}$ -solution containing  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  caused precipitation of  $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$  at ligand-to-metal ratios higher than three. Up to this precipitation-reaction the formation-curves are identical to those without  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ , thus indicating that there is no significant influence of the ionic strength and the presence of  $\text{H}_2\text{O}$  in concentrations up to  $0.1 \text{ M}$ .

**Results and Discussion***Complex Formation Equilibria*

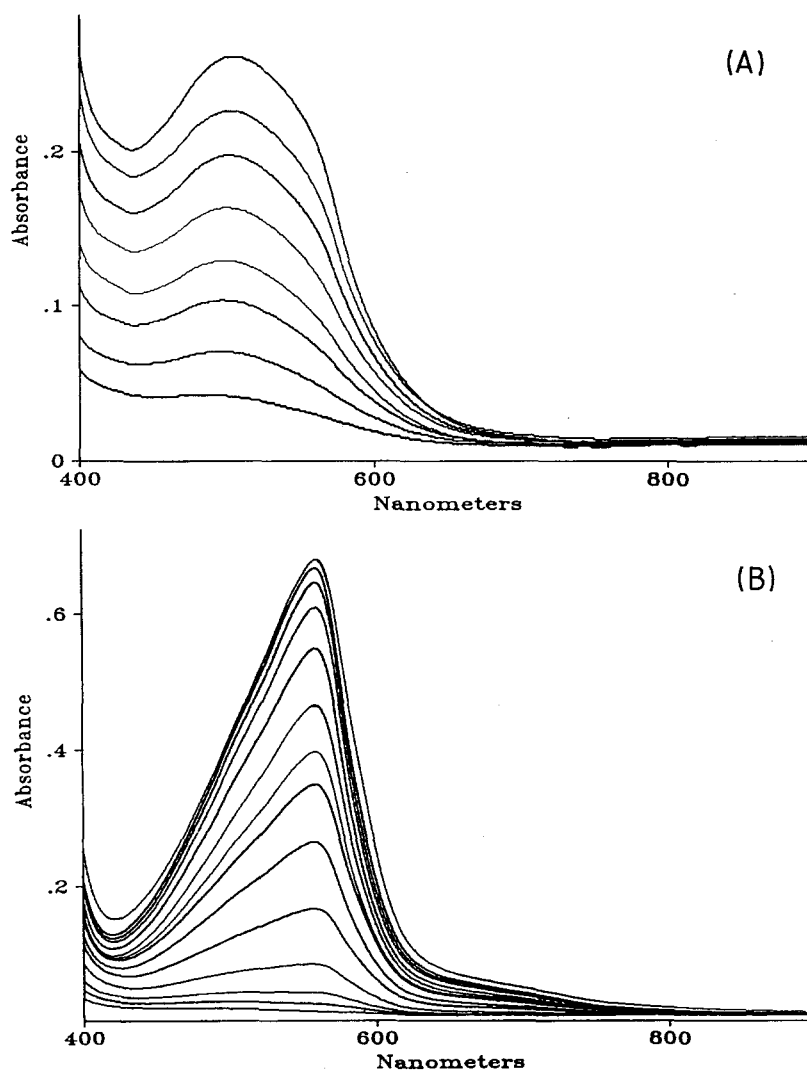
By means of spectrophotometric titrations of  $\text{Fe}^{2+}$  in *MeOH* with ligand solutions, the following equilibria have been established:



Formation curves only can be fitted satisfactorily by a model involving at least three ligated species. The UV-visible spectra of the 1:1 and 1:3 complexes have been identified since they are separately obtainable at low and high ligand to iron(II) ratios respectively (Fig. 1, Table 1). The spectrum of  $\text{FeL}_2^{2+}$ , however, does not differ significantly from that of  $\text{FeL}_3^{2+}$ , preventing its accurate characterisation. By varying the  $\text{Fe}^{2+}$ -concentration in a range of  $1.3953 \cdot 10^{-3} \text{ M} - 9.91 \cdot 10^{-5} \text{ M}$  and the ratio of  $(L_T)/(\text{Fe}_T)$  from 0–48, we have obtained formation constants  $K_{1-3}$  and molar absorptancies at 557 nm by curve fitting,  $\lambda_{\text{max}}$  and  $\epsilon_{\text{max}}$  of  $\text{FeL}^{2+}$  and  $\text{FeL}_3^{2+}$  have also been obtained (Table 1). The agreement between calculated and observed values is satisfactory (Fig. 2 A).

**Table 1.** Formation constants and UV-Vis spectrometric data of  $[\text{Fe}(\text{bzimpy})_n]^{2+}$  complexes in *MeOH* at 20°C

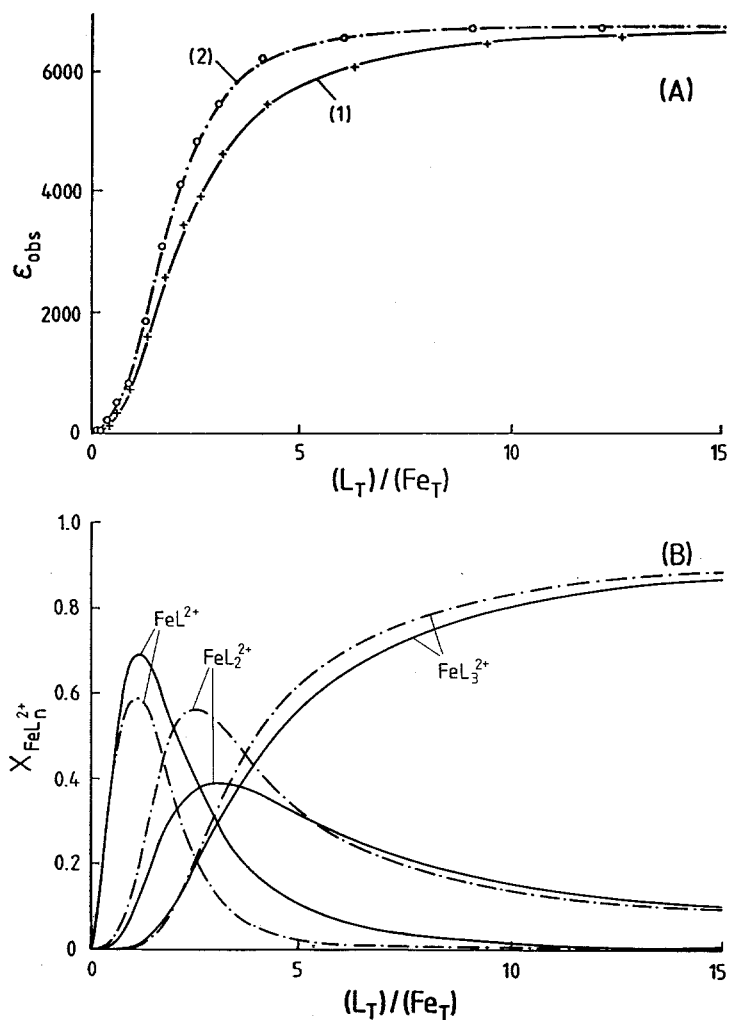
Complex	$\lambda_{\text{max}}$ [nm]	$\epsilon_{\text{max}}$ [ $\text{l mol}^{-1} \text{cm}^{-1}$ ]	$\log K$	$\epsilon_{557\text{nm}}$ [ $\text{l mol}^{-1} \text{cm}^{-1}$ ]
$\text{FeL}^{2+}$	504	$390 \pm 30$	$5.54 \pm 0.06$	$270 \pm 20$
$\text{FeL}_2^{2+}$	$\sim 550$	-	$4.12 \pm 0.06$	$5900 \pm 300$
$\text{FeL}_3^{2+}$	557	$6770 \pm 50$	$3.85 \pm 0.03$	$6770 \pm 50$



**Fig. 1.** a) Formation of  $[\text{Fe}(\text{bzimpy})]^{2+}$  in *MeOH* at 20°C and  $d=1.000$  cm. Spectra are obtained by increasing the ligand to metal ratio at a total iron concentration of  $1.3953 \cdot 10^{-3} \text{ M}$  in steps of 0.051 up to 0.408; b) Vis-spectra of  $\text{Fe}^{2+}$ -*bzimpy*-mixtures in *MeOH* at 20°C and  $d=1.000$  cm. The iron concentration is  $9.909 \cdot 10^{-5} \text{ M}$  and ligand to metal ratios in the order of increasing absorbances are 0.21/0.42/0.62/0.94/1.35/1.77/2.18/2.60/3.12/4.16/6.24/9.35/20.79/41.57

**Table 2.** Effect of  $\text{CHCl}_3$  addition on the formation equilibria of  $[\text{Fe}(\text{bzimpy})_n]^{2+}$  complexes in *MeOH* at  $20^\circ\text{C}$ 

$\text{CHCl}_3$ in <i>MeOH</i>	$\log K_1$	$\log K_2$	$\log K_3$
0	$5.54 \pm 0.06$	$4.12 \pm 0.06$	$3.85 \pm 0.03$
3	$5.65 \pm 0.06$	$4.55 \pm 0.06$	$3.85 \pm 0.03$
10	$5.78 \pm 0.06$	$4.79 \pm 0.06$	$3.90 \pm 0.03$



**Fig. 2.** a) Calculated and observed absorbance coefficients of the system  $\text{Fe}^{2+}/\text{bzimpy}$  at  $557\text{ nm}$  and  $20^\circ\text{C}$ . (1):  $(\text{Fe}^{2+}) = 9.909 \cdot 10^{-5}\text{ M}$  in pure *MeOH* (obs.: + + + calc.: —); (2):  $(\text{Fe}^{2+}) = 1.10018 \cdot 10^{-4}\text{ M}$  in *MeOH* with 10% v/v  $\text{CHCl}_3$  (obs.: °°° calc.: - - - -) b) Corresponding distribution of ligated species for (1) (—) and (2) (- - - -)

Formation constants were also obtained in the solvent containing 3 and 10% v/v  $\text{CHCl}_3$ . The latter is frequently used as a so-called “inert reference compound” for determining solution magnetic moments with NMR via the Evans technique

[11]. As can be seen from Fig. 2 and Table 2, an increasing addition of  $\text{CHCl}_3$  to the solvent causes an increasing shift of the equilibria towards the higher ligated species  $\text{FeL}_2^{2+}$  and  $\text{FeL}_3^{2+}$ . This can be explained by a competitive reaction between solvent and ligand towards the  $\text{Fe}^{2+}$ -ion. In the case of  $\text{CHCl}_3$ -addition the ligand is favoured because of the reduction of the effective concentration as well as the bulk donicity of *MeOH*.

In Table 3 the formation constants for *bzimpy* with iron(II) are compared with those of some other ligands with an  $\alpha$ -diimine structure.

The values of  $\log K_1$  and  $\log K_2$  are all of a similar magnitude and a decrease is observed on going from  $\text{FeL}^{2+}$  to  $\text{FeL}_2^{2+}$ . In  $\log K_3$  the influence of changes in spin state on the complex formation process is reflected: for *phen* and *bipy* a drastic thermodynamic stabilisation due to an abrupt change to the *LS*-state on formation of the  $\text{FeL}_3^{2+}$  species is observed [12]. For the spin crossover compounds of *pyim* and *bzimpy*, the energetic differences of the two spin states are too small (which is a prerequisite for spin-crossover systems) to be reflected in the formation constants. Because of the significantly increased  $K_1$  value in relation to  $K_1$  of the bidentate *pyim* (Table 3) we expect tris-coordination for  $\text{FeL}^{2+}$ . For  $\text{FeL}_3^{2+}$ , bis-coordination of the ligands appears to be most likely. In the case of  $\text{FeL}_2^{2+}$ , the similarity of the electronic spectrum to that one of  $\text{FeL}_3^{2+}$  suggests a similar electronic environment of the  $\text{Fe}^{2+}$ -ion and hence it seems highly likely that no solvent molecule is present in the inner coordination sphere. This assumption is confirmed by the observation that the addition of  $\text{CHCl}_3$  to *MeOH* has no significant effect on  $K_3$  (implying that no solvent molecule is involved in the step  $\text{FeL}_2^{2+} \rightarrow \text{FeL}_3^{2+}$ ).

### Deprotonation of the Complex

#### Characterization of Products

Deprotonation was performed by titration of methanolic solutions of  $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$ , with and without excess ligand, with  $\text{NEt}_3$ . Due to the large number of absorbing species ( $\geq 5$ ), the calculation of deprotonation constants from spectrophotometric data is not possible [14]. The change in the Vis-spectrum during titration is illustrated in Fig. 3. The molar-ratio-method indicates three

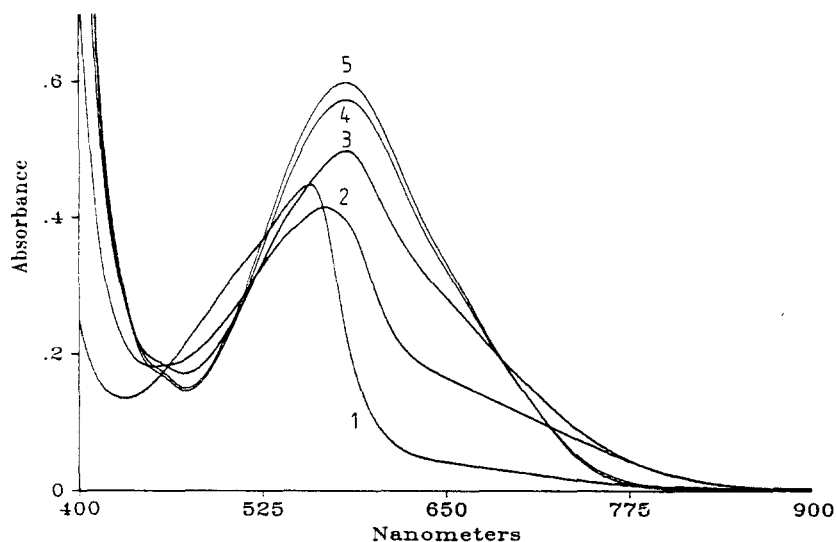
**Table 3.** Formation constants of iron(II) imine complexes

Ligand	$t$ [°C]	$\log K_1$	$\log K_2$	$\log K_3$	Ref.
<i>phen</i> <sup>a</sup>	25.0	5.8	5.2	10.0	[12]
<i>bipy</i> <sup>b</sup>	25.0	4.3	3.7	9.5	[12]
<i>pyim</i> <sup>c</sup>	25.0	4.10	3.80	3.70	[13]
<i>bzimpy</i>	20.0	5.54	4.12	3.85	this work

<sup>a</sup> 1,10-phenantroline

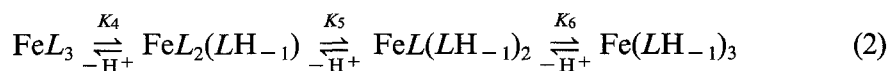
<sup>b</sup> 2,2'-bipyridyl

<sup>c</sup> 2,2'-pyridylimidazole



**Fig. 3.** Vis-spectra of solutions of  $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$  ( $1.231 \cdot 10^{-4} \text{ M}$ ) in *MeOH* at  $20^\circ\text{C}$  and  $d = 1.000 \text{ cm}$  with  $\text{NEt}_3/\text{Fe}$ -ratios of 0.00 (1), 1.05 (2), 2.10 (3), 3.15 (4), 49.03 (5)

distinct species at ratios of  $(\text{NEt}_3)/(\text{Fe}) = 1, 2$  and  $3$  at a wavelength of  $745 \text{ nm}$ . This result is in accordance with the following deprotonation equilibria:



In [15] similar subsequent deprotonation equilibria of a  $\text{FeL}_3$ -complex with 2-(2'-pyridyl)imidazol as a ligand are reported. The existence of the solid state deprotonation products  $[\text{Fe}(\text{H}_{-1}\text{bzimpy})_2] \cdot \text{H}_2\text{O}$  and of the iron(III) compound  $[\text{NHEt}_3][\text{Fe}(\text{H}_{-2}\text{bzimpy})_2] \cdot 4\text{H}_2\text{O}$  has been demonstrated [8].

### The Role of the Solvent

Solutions of  $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$  in *DMSO* ( $DN = 29.8$ ) show partial deprotonation. The degree of deprotonation increases with decreasing complex-concentration as well as decreasing ligand to metal ratio, addition of excess ligand suppresses deprotonation. Titration of methanolic solutions with *DMSO* leads to a considerable bleaching which increases with the *DMSO*-content. This is due to increasing ligand dissociation of the complex, caused by more favourable solvation of the free  $\text{Fe}^{2+}$ -cation by the strong donating solvent *DMSO*. Deprotonation – indicated by a slight shift of the visible absorbance maximum towards higher wavelength – is observed at *DMSO* concentrations above 30%.

The successive addition of *Py* ( $DN = 33.1$ ) to a methanolic complex solution leads to the same spectral changes which are observed in titration with  $\text{NEt}_3$ . At *Py* concentrations of 8% the deprotonation is complete (*Py* is a stronger Brønsted base than *DMSO*). Complex solutions in pure *Py* are dark green and although no detailed studies have been made, partial substitution of the ligand by solvent is likely.





**Table 4.** Thermodynamic parameters for iron(II) imine spin equilibria systems in solution

Complex	Solvent	$\Delta H^\circ$ [kJ·mol <sup>-1</sup> ]	$\Delta S^\circ$ [kJ·mol <sup>-1</sup> ·K <sup>-1</sup> ]	Ref.
[Fe(2-pic) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	MeOH/H <sub>2</sub> O	18.0	58.6	[18]
"	An/H <sub>2</sub> O	21.3	71.1	"
[Fe(pyim) <sub>3</sub> ](BPh <sub>4</sub> ) <sub>2</sub>	Ac	15.9	48.5	[16]
"	An/MeOH	15.5	52.7	"
[Fe(pybzim) <sub>3</sub> ](BPh <sub>4</sub> ) <sub>2</sub>	Ac	19.7	77.8	"
"	An/MeOH	21.3	92	"
[Fe(6-Mepy) <sub>2</sub> (Py)tren](PF <sub>6</sub> ) <sub>2</sub>	Ac; DMSO	11.9	36	[19]
[Fe(bzimpy) <sub>3</sub> ] <sup>2+</sup>	MeOH	17.7 ± 1.5	59 ± 5	this work

In general, the HS-form is expected to undergo ligand dissociation reaction in spin-crossover compounds [17]. The thermochromic behaviour of complex solutions with a sufficient excess of ligand allows us to observe the spin only equilibrium,  $\text{FeL}_3^{2+}(\text{LS}) \leftrightarrow \text{FeL}_3^{2+}(\text{HS})$ . By fitting the experimental data to equations (4) and (5), we obtained a set of parameters describing this spin equilibrium (Table 4):

$$\text{i) } \Delta H - T\Delta S = -RT \ln K \quad (4)$$

$$\text{ii) } K = \frac{x_{\text{HS}}}{x_{\text{LS}}} = \frac{(\varepsilon_{\text{obs}} - \varepsilon_{\text{LS}})}{(\varepsilon_{\text{HS}} - \varepsilon_{\text{LS}})} \quad (5)$$

The values of  $\Delta H$  and  $\Delta S$  confirm the values of similar spin equilibria systems. This supports the reaction scheme suggested in (3). Out of these parameters we achieve an equilibrium constant  $K_{\text{SC}2} = 0.95$  at 298 K. In contrast, the solid state product  $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$  is more on the low spin side at room temperature [8]. These observations confirm a general trend that dissolution of spin equilibria systems results in a shift of the spin equilibrium towards the high spin side [4].

Measurements in further solvents were carried out under the presence of a sufficient excess of ligand to avoid dissociation and a different behaviour for each system was revealed. The different thermochromic behaviour in the solvents *An*, *NM*, *PDC* and *Ac* is less pronounced than the influence of ligand excess in *MeOH* (Fig. 4) and yet it is reproducible. In conclusion, two complementary mechanisms of solvent influence can be proposed: i) Preferential formation of the  $\text{FeL}_2^{2+}$ -species as well as a crossover behaviour which is governed by  $K_{\text{SC}1}$  and ii) Influence of the spin equilibrium via a coordinative bond between the donor-solvent and the amine proton, at the backbone of the ligand. The importance of this proton-solvent interaction can be seen from the deprotonating effect of strong donor solvents on  $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$ . A similar mechanism has been found for the hexadentate crossover compound  $[\text{Fe}(\text{Sal})_2\text{trien}](\text{PF}_6)$  [20]. Contemporary work is in progress to extend our results for solution magnetic data.

### Acknowledgements

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