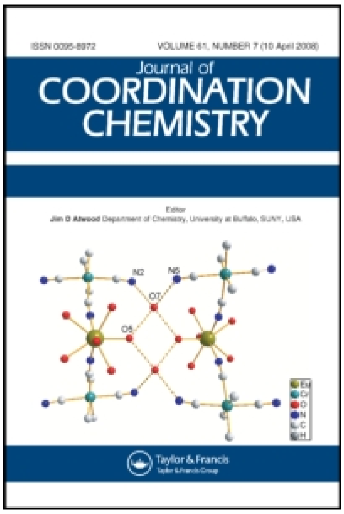

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SUBSTITUENT- AND SOLVENT-EFFECTS ON THE STABILITY OF IRON(II)-4-X-2,6-BIS-(BENZIMIDAZOL-2′-YL)PYRIDINE COMPLEXES SHOWING SPIN-CROSSOVER IN SOLUTION

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4-X-2,6-bis-(benzimidazol-2′-yl)pyridine (L = X-bzimpy; X = H, OH and Cl) acts as a tridentate when coordinated with iron(II) in solution. Both, mono- and bis-species, $[FeL]^{2+}$ and $[FeL_2]^{2+}$ are formed and the values of stability constants ($\log K_1$ and $\log K_2$) were calculated for these species in MeOH, 50% (v/v) PDC/MeOH and 10% (v/v) $CHCl_3$/MeOH at 20°C. The presence of electron-withdrawing substituents (Cl and OH) at 4-position on the pyridine ring of the ligand hardly influences the stability constants in contrast to a change in the spin-state to the high-spin (HS) state of the complexes. Studies of solvents influences on complexation equilibria reveal that the strong donor solvent causes the dissociation and thereby decreases the values of stability constants. The value of magnetic moments ($\mu/\mu B$) for free iron(II) ion decreases with the formation of complex species of low-spin (LS) state.

INTRODUCTION

Cationic complexes of transition metal-ions (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}) with 4-X-2,6-bis-(benzimidazol-2′-yl)pyridine (L = X-bzimpy; X = H, Cl, OH and CH_3) have been synthesized and investigated using the techniques of UV- Vis-, Far-FT-IR-, ^{1}H-NMR, Mössbauer-spectroscopy and potentiometry.[1–9] The ligand acts as a tridentat in complexation with the metal ions.[4, 6, 9] Two steps of complexation-equilibria are shown in a generalized reaction Scheme 1. The complexes exhibit strong spin-crossover behaviour both in solution and solid state.[1–2, 4, 7–11] Substitution on the pyridine ring of benzimidazol group of the ligand at 4-position leads to

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a change in the spin-state of the complexes.[4, 7, 10–11] Coordination of ligand with the metal-ions demonstrates an increase of the acidity of the imino-hydrogen of the ligand as a function of the complex stability.[6, 8, 12–13] Deprotonation of the complexes results a change in the spin-state towards the low-spin state (*i.e.*, HS ⇄ LS transition).[6, 8–11]

$$[FeS_6]^{2+} + L \underset{-3S}{\overset{K_1}{\rightleftharpoons}} [FeLS_3]^{2+} + L \underset{-3S}{\overset{K_2}{\rightleftharpoons}} [FeL_2]^{2+}$$

Scheme 1: S = Solvent, L = X-bzimpy

The complexation-equilibria might be influenced by substitution on the ligand. Obviously this should have some interrelations with the observed spin-state of the complexes. The present paper is concerned with investigations along these lines, mainly it was attempted to study the solvent's effects on the complexation-equilibria.

EXPERIMENTAL

Chemicals: $FeCl_2.4H_2O$ (Aldrich) was used in analytical grade as received. Commercial grade methanol (MeOH) was refluxed over CaO for 24 hours and fractionally distilled. Propanediolcarbonate (PDC) (Loba) was refluxed for 24 hours under reduced pressure and was fractionally distilled. Chloroform ($CHCl_3$) (Merck) was distilled off P_2O_5.

Preparation of Ligands: Ligands, 4-X-2,6-bis-(benzimidazol-2′-yl) pyridine (L = X-bzimpy; X = H, Cl and OH) were prepared according to the literature.[1–4, 9, 14]

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 (±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 $FeCl_2·4H_2O$ ($1·10^{-4}$ to $3·10^{-4}$M) with 4-X-2,6-bis-(benzimidazol-2′-yl)pyridine solutions were carried out at ligand-to-metal ration of $[L]T/[Fe^{2+}]$ T = 0 – 10 in MeOH, 50% (v/v) PDC/MeOH and 10% (v/v) $CHCl_3$/MeOH at 20°C. All measurements were carried out in nitrogen atmosphere with solvents deoxygenated by passing nitrogen gas to avoide any kind of oxidation effects.

Magnetic Measurements: ^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 an external standard and instrument lock. Magnetic susceptibilities in solution were measured by the Evans ^{1}H-NMR method[15] using the solvent methanol for temperature calibration.[16] 1% (v/v) cyclohexane was used as an internal reference compound. Titrations of $FeCl_2{\cdot}4H_2O$ ($1.04{\cdot}10^{-4}$ to $1.09 \cdot 10^{-4}$ M) with X-bzimpy solutions were followed by ^{1}H-NMR-spectroscopy at ligand-to-metal ratio of $[L]_T/[Fe^{2+}]_T = 0 - 10$ in MeOH at 20°C.

RESULTS AND DISCUSSIONS

Spectrophotometric Studies: The UV Vis titration spectra of $FeCl_2 \cdot 4H_2O$ with 4-X-2,6-bis-(benzimidazol-2′-yl)pyridine (L = X-bzimpy; X = H, OH and Cl) solutions are shown in Figure 1 with the spectral datas listed in Table I. The solution is intense red violet for X = H-bzimpy, deep pink for X = OH-bzimpy and light pink for X = Cl-bzimpy. With increasing ligand-to-metal ratio ($[L]_T/[Fe^{2+}]_T$), the mono- and *bis*-species are formed consecutively according to the reaction Scheme 1 increasing the absorbance of the spectra (see Figure 1). A peak at shorter wavelength, associated with $[FeL]^{2+}$ species, becomes important at very low ligand-to-metal ratio (*i.e.*, $[L]_T/[Fe^{2+}]_T < 0.5$) (see Figure 1A and Table I) in all solutions. At high ligand-to-metal ratio (*i.e.*, $[L]_T/[Fe^{2+}]_T > 2.0–10$), the peak for $[FeL_2]^{2+}$ species becomes increasingly populated (see Figure 1B

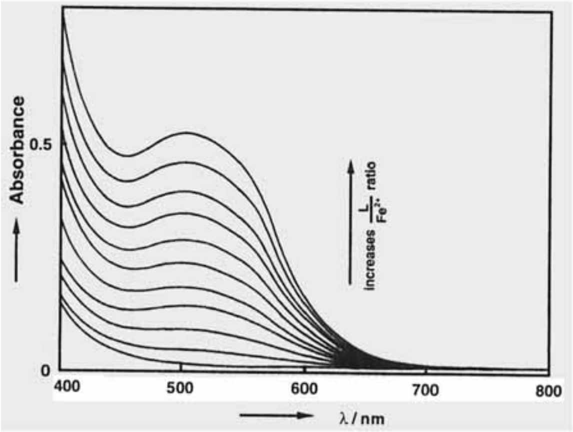

FIGURE 1A UV-Vis. titration spectra of $FeCl_2$, $4H_2O$ ($2.9861 \cdot 10^{-3}$M) with H-bzimpy solution in 50% (v/v) PDC/MeOH at 20°C: $[L]_T/[Fe^{2+}]_T$ = 0.0, 0.02, 0.05, 0.08, 0.12, 0.15, 0.18, 0.21, 0.24, 0.28, 0.31, and 0.34, respectively.

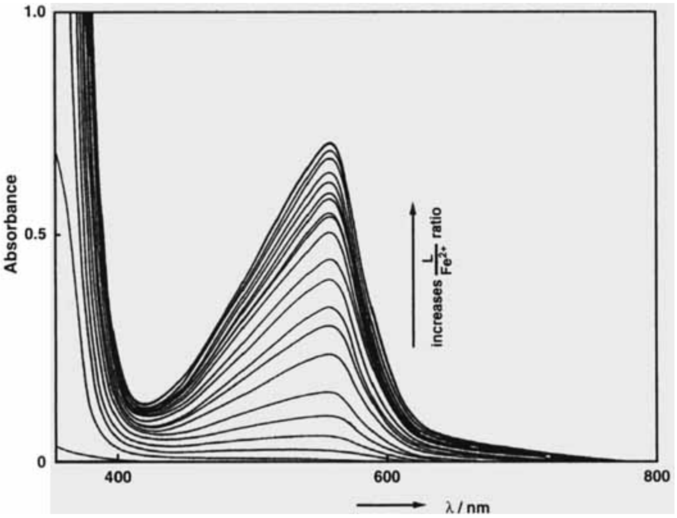

FIGURE 1B UV-Vis. titration spectra of FeCl$_2$, 4H$_2$O (6.2149 · 10^{-4}M) with H-bzimpy solution in 50% (v/v) PDC/MeOH at 20°C: [L]T/[Fe^{2+}]T = 0.0, 0.23, 0.46, 0.69, 0.92, 1.15, 1.38, 1.60, 1.82, 2.05, 2.29, 2.52, 2.75, 2.96, 3.21, 3.44, 4.58, 5.57, 8.59, 11.46, 17.193 and 22.92, respectively.

and Table I) at longer wavelength. The absorbtion maxima (λ_{max}) and the molar absorbtivities (ε) corresponding to the [FeL]$^{2+}$ and [FeL$_2$]$^{2+}$ species in different solvents are listed in Table I.

The spectra of [Fe(X-bzimpy)$_2$]$^{2+}$ (see Figure 1B) show three main features: (i) very strong absorption band in the region of < 450nm, associated with the $\pi \rightarrow \pi^\star$ transition of ligand, (ii) a strong absorption band at 450–600nm ($\varepsilon_{max} \approx$ 1500–6200 l.mol^{-1}.cm^{-1}), associated with metal-to-ligand charge transfer band ($T_{2g} \rightarrow \pi^\star$, MLCT) and (iii) a broad-weak absorption band at 600–750nm ($\varepsilon_{max} \approx$ 500–1000l.mol^{-1}.cm^{-1}), attributed to the d-d absorbtion band.[3–9, 17–19] The observed shift of MLCT band towards the shorter wavelength (see Table I) on going from substitution: X = H, OH and Cl might be due to the increased energy of the lowest unfilled ligand $\pi^\star$-orbitals, leading to relatively higher energies of the MLCT band (*i.e.*, a hyperconjugative effect arises due to the substituent).[4, 6-9]

The complexation equilibria are complicated by the partial dissociation of complexes even in the presence of excess ligand in MeOH as can be seen from the plots of molar absorptivities *vs.* [L]T/[Fe^{2+}]T (see Figure 2). The complexation is found to complete after the addition of the stoichiometric amount of H-bzimpy only in 50% (v/v) PDC/MeOH (see Figure 2).[3] The formation curves, obtained from the curve fitting of the respective spectrophotometric titration datas for H-bzimpy, OH-bzimpy and Cl-bzimpy (see Figure 3), confirms that only two species, (FeL^{2+} and FeL$_2$$^{2+}$) are formed according to reaction Scheme 1 at $[L]_T/[Fe^{2+}]_T$ = 1 and 2. The values of $\log K_1$ and $\log K_2$ (see Table II), evaluated from the curve fitting, show a decreasing tendency on going from $[FeL]^{2+}$ to $[FeL_2]^{2+}$ which might be due to steric effects. The large values of overall stability constants (X = H, Log β_2 = 11.45; X = OH, log β_2 = 12.04 and X = Cl, log β_2 = 11.95 in PDC/MeOH) in relation to the comparable ligands with an a-diimine structure, such as, 2-2′(pyridyl)imidazole (log β_2 = 7.9),[20] 4-2′(pyridyl)imidazile (log β_2 = 9.0)[21] and bipy (log β_2 = 8.0) [13] suggest that the ligand (X-bzimpy) acts as tridentate in both the $[FeL]^{2+}$ and $[FeL_2]^{2+}$ species. Table II shows that the stability constants are hardly influenced by the presence of substituents on the ligand. However, the presence of substituents on the ligand leads to a change in the spin-state to the high-spin (HS) state for Cl-bzimpy and OH-bzimpy complexes.[4, 6–9] The influence of changes in the spin state on complex formation process is reflected in log K_3 value for phen and bipy[13] and can be explained by a drastic thermodynamic stabilisation due to an abrupt change to the ls-state on formation of the FeL_3^{2+} species.

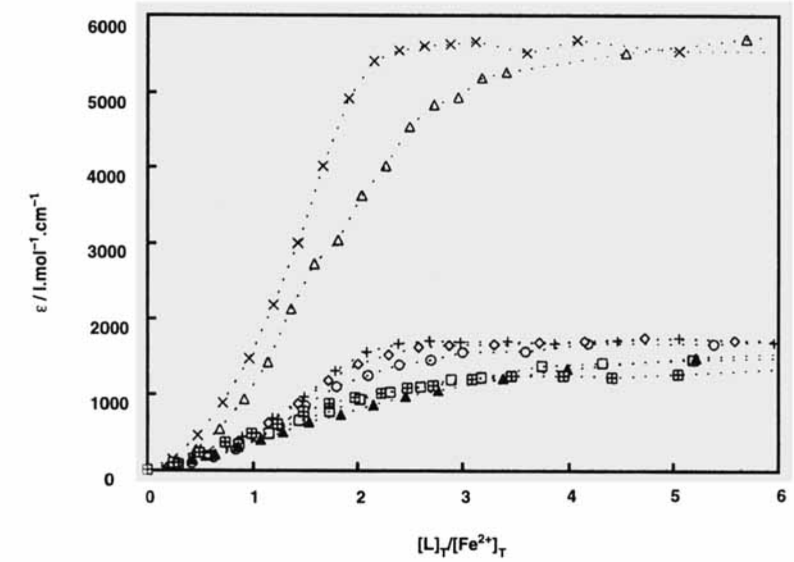

FIGURE 2 Change of molar absorptivities (ε/[l.mol⁻¹.cm⁻¹]) with increasing ligand-to-metal ratio ($[L]_T/[Fe^{2+}]_T$) for titation of $FeCl_2{,}4H_2O$ with X-bzimpy solutions in different solvents at 20°C:

Δ H-bzimpy, in MeOH, ε at 557nm, $[Fe^{2+}]_T = 1.1317 \cdot 10^{-4}$M.
× H-bzimpy, in 50% (v/v) PDC/MeOH, ε at 557nm, $[Fe^{2+}]_T = 3.1951 \cdot 10^{-4}$M.
○ OH-bzimpy, in MeOH, ε at 515nm, $[Fe^{2+}]_T = 1.1538 \cdot 10^{-4}$M.
+ OH-bzimpy, in 50% (v/v) PDC/MeOH, ε at 515nm, $[Fe^{2+}]_T = 1.1770 \cdot 10^{-4}$M.
◇ OH-bzimpy, in 10% (v/v) $CHCl_3$/MeOH, ε at 515nm, $[Fe^{2+}]_T = 1.2130 \cdot 10^{-4}$M.
▲ Cl-bzimpy, in MeOH, ε at 500nm, $[Fe^{2+}]_T = 1.0241 \cdot 10^{-4}$M.
□ Cl-bzimpy, in 50% (v/v) PDC/MeOH, ε at 500nm, $[Fe^{2+}]_T = 1.1267 \cdot 10^{-4}$M.
⊞ Cl-bzimpy, in 10% (v/v) $CHCl_3$/MeOH, ε at 500nm, $[Fe^{2+}]_T = 9.6172 \cdot 10^{-5}$M.

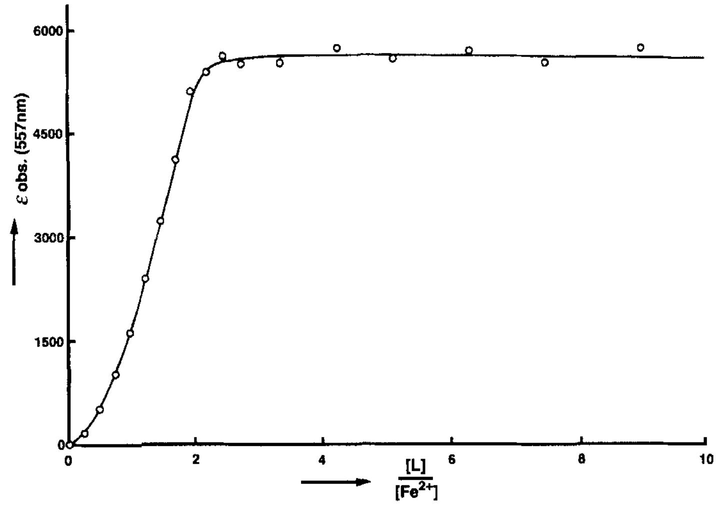

FIGURE 3 Typical formation curves of $[Fe(H\text{-}bzimpy)_2]^{2+}$ ($3.1951 \cdot 10^{-4}$M) in 50% (v/v) PDC/MeOH at l = 557nm and 20°C: (obs.: ooo ooo ooo and calc.: --- --- ---).

Solvent influence on the stability constants: The stability constants (log β_2) are higher in 50% (v/v) PDC/MeOH and in 10% (v/v) $CHCl_3$/MeOH than in pure MeOH (see Table II). These results might be explained by the donor-acceptor properties of solvents.[22] Generally, strong donor solvent ($DN_{MeOH} = 19.1 > DN_{PDC} = 15.1$) favours the dissociation of the complexes through coordination with the metal ion and thereby decreases the stability constant values. This effect is more pronouncd in $[FeL_2]^{2+}$ species than in $[FeL]^{2+}$ species.

^{1}H-NMR Studies: Changes of magnetic moments ($\mu/\mu B$) as a function of $[L]T/[Fe^{2+}]T$ are shown in Table III. The decrease of magnetic moments for free iron(II) with the addition of ligand (X-bzimpy) solution (see Figure 4) indicate the formation of mono- and bis-complex species, $[FeL]^{2+}$ and $[FeL_2]^{2+}$, in MeOH solution. A strong decrease of magnetic moment found for H-bzimpy complex compare to the OH-bzimpy and Cl-bzimpy analogues (Table III) might be due to the low-spin (LS) state of $[FeL_2]^{2+}$ specie (low magnetic moment). However, the $[FeL_2]^{2+}$ species for OH-bzimpy and Cl-bzimpy complexes are at high-spin (HS) state (high magnetic moment) in MeOH solution. These results are in good agreement with the previous studies on spin-crossover behaviour of $[Fe(X\text{-}bzimpy)_2]^{2+}$ complexes both in solution and solid state.[4, 6–9]

In conclusion, it could be said that unlike the change in spin-state behaviour of the complexes the stability constants are found to be hardly influenced by electron withdrawing substituents on the ligand. For the spin-crossover complexes of X-bzimpy, the energetic differences of the two spin-states (which is a prerequisite for spin-crossover systems) are too little to be reflected on the complexation equilibria. The complexation equilibria are complicated by the partial dissociation of the complexes as a function of solvent's donor-acceptor properties.

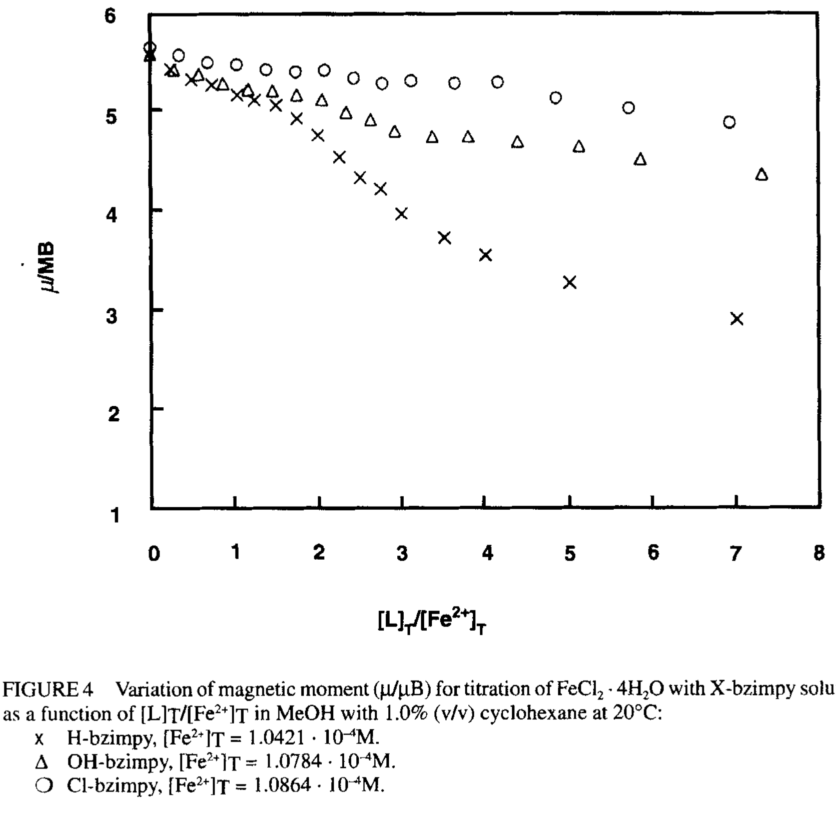

FIGURE 4 Variation of magnetic moment (μ/μB) for titration of $FeCl_2 \cdot 4H_2O$ with X-bzimpy solution as a function of $[L]T/[Fe^{2+}]T$ in MeOH with 1.0% (v/v) cyclohexane at 20°C:

X H-bzimpy, $[Fe^{2+}]T = 1.0421 \cdot 10^{-4}M$.

Δ OH-bzimpy, $[Fe^{2+}]T = 1.0784 \cdot 10^{-4}M$.

O Cl-bzimpy, $[Fe^{2+}]T = 1.0864 \cdot 10^{-4}M$.

TABLE I The absorbtion maxima and molar absorbtivities of $[FeL]^{2+}$ and $[FeL_2]^{2+}$ species in different solvents at 20°

Ligands	*Solvents*	λ $[FeL]^{2+}$ [*nm*]	ε $[FeL]^{2+}$ [$l.mol^{-1}.cm^{-1}$]	λ $[FeL_2]^{2+}$ [*nm*]	ε $[FeL_2]^2$ [$l.mol^{-1}.cm^{-1}$]
H — bzimpy	MeOH	505	300 ± 50	557	5800 ± 300
OH — bzimpy	MeOH	~445	250 ± 50	~519	1800 ± 100
Cl — bzimpy	MeOH	~443	250 ± 50	~500	1550 ± 100
H — bzimpy	PDC/MeOH[a]	500	300 ± 50	556	5600 ± 300
OH — bzimpy	PDC/MeOH[a]	~443	300 ± 50	~515	1650 ± 100
Cl — bzimpy	PDC/MeOH[a]	~440	300 ± 50	~503	1550 ± 100
OH — bzimpy	$CHCl_3$/MeOH[b]	~440	300 ± 50	~521	1750 ± 100
Cl — bzimpy	$CHCl_3$/MeOH[b]	~433	350 ± 50	~490	1350 ± 100

[a] 50% (v/v) PDC/MeOH and [b] 10% (v/v) $CHCl_3$/MeOH.

TABLE II Stability constants of $[FeL]^{2\pm}$ ($LogK_1$) and $[FeL_2]^{2\pm}$ ($LogK_2$) species in different solvents at 20°C

Ligands (L)	*Solvents*	$\lambda/[nm]^a$	$LogK_1$	$LogK_2$	$log_{10}\beta_2$
H — bzimpy	MeOH	557	5.90	4.80	10.70
OH — bzimpy	MeOH	515	6.70	4.40	11.10
Cl — bzimpy	MeOH	500	7.00	4.00	11.00
H — bzimpy	PDC/MeOH*	557	6.15	5.30	11.45
OH — bzimpy	PDC/MeOH*	515	7.00	5.05	12.05
Cl — bzimpy	PDC/MeOH*	500	7.10	4.85	11.95
OH — bzimpy	$CHCl_3/MeOH^+$	515	6.70	4.80	11.50
Cl — bzimpy	$CHCl_3/MeOH^+$	500	7.30	4.35	11.65

[a] wave length at which stability constants were calculated.
* 50% (v/v) PDC/MeOH and + 10% (v/v) $CHCl_3$/MeOH.
All values are ± 0.05.

TABLE III Magnetic moment datas for titration of $FeCl_2 \cdot 4H_2O$ with ligands (X–bzimpy) solution in MeOH at 20°C

$[L^a]T/[Fe^{2+}]T$	$\mu/\mu B$	$[L^b]T/[Fe^{2+}]T$	$\mu/\mu B$	$[L^c]T/[Fe^{2+}]T$	$\mu/\mu B$
0	5.55	0	5.62	0	5.55
0.25	5.41	0.35	5.55	0.29	5.40
0.50	5.31	0.69	5.48	0.58	5.37
0.75	5.25	1.04	5.45	0.87	5.27
1.05	5.16	1.39	5.41	1.18	5.21
1.25	5.11	1.74	5.39	1.46	5.20
1.51	5.05	2.08	5.40	1.75	5.16
1.76	4.92	2.43	5.33	2.05	5.11
2.01	4.75	2.78	5.28	2.34	4.98
2.26	4.53	3.13	5.30	2.65	4.91
2.51	4.33	3.65	5.28	2.93	4.80
2.76	4.21	4.17	5.30	3.37	4.74
3.01	3.97	4.86	5.15	3.81	4.75
3.52	3.73	5.73	5.04	4.40	4.70
4.02	3.56	6.95	4.91	5.13	4.66
5.02	3.28	8.68	4.79	5.87	4.53
7.03	2.91	-	-	7.33	4.38

[a] L = H–bzimpy, [b] L = Cl–bzimpy and [c] L = OH–bzimpy.

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