

Spin-Crossover Complexes in Solution. III. Substituent- and Solvent Effects on the Spin-Equilibrium of 4-substituted Iron(II)-2,6- bis-(benzimidazol-2'-yl)-pyridine systems

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Summary. Transition metal complexes of the composition $[\text{Fe}(4\text{-X-bzimpy})_2](\text{ClO}_4)_2$ [*bzimpy* = 2,6-bis-(benzimidazol-2'-yl)pyridine and X = H, OH, Cl] show thermally accessible spin-crossover behaviour in solution that depends on both the ligand and the solvent. ¹H-NMR spectroscopy and UV-visible spectroscopy measurements suggest that ligand substituent effects, solvent donor-acceptor properties and hydrogen-bonding may be employed to "fine-tune" the ligand field strength and hence to affect the spin-crossover behaviour. The ligand substitution changes in solution are reflected by the magnetic data (X = H: $\mu_{\text{exp}} = 2.50 \mu_{\text{B}}$; X = OH: $\mu_{\text{exp}} = 4.20 \mu_{\text{B}}$ and X = Cl: $\mu_{\text{exp}} = 4.30 \mu_{\text{B}}$ at 294 K in MeOH), and by the shift of metal-to-ligand *charge-transfer* band (X = H, $\lambda = 557 \text{ nm}$; X = OH, $\lambda = 520 \text{ nm}$; X = Cl, $\lambda = 500 \text{ nm}$). $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$ exhibits a pronounced spin-crossover equilibrium (¹A₁ → ⁵T₂) in solution ($K_{\text{sc}} = 0.26$ at 293 K; $\mu_{\text{exp}} = 1.30 \rightarrow 3.40 \mu_{\text{B}}$ for 213 → 328 K in MeOH). A small variation of magnetic moments of $[\text{Fe}(4\text{-OH-bzimpy})_2](\text{ClO}_4)_2$ ($\mu_{\text{exp}} = 3.77 \rightarrow 4.73 \mu_{\text{B}}$ at 220 → 332 K) might indicate either the existence of (temperature dependent) hydrogen bonding between the ligand and solvent molecules or a temperature dependent variation in the population of the ⁵E_g sublevel. The presence of strong donor solvents ($DN \geq 30$) shifts the spin-state of the complexes.

Keywords. 4-Substituted 2,6-bis(benzimidazol-2'-yl)pyridine complexes; Solvent-effects; Spin-crossover; Thermochromism.

Spin-Crossover Komplexe in Lösung, 3. Mitt.: Substituenten- und Lösungsmiteleinflüsse auf das Spin-Gleichgewicht von 4-substituierten Eisen(II)-2,6-bis-(benzimidazol-2'-yl)-pyridinsystemen

Zusammenfassung. Übergangsmetallkomplexverbindungen der Form $[\text{Fe}(4\text{-X-bzimpy})_2](\text{ClO}_4)_2$ [*bzimpy* = 2,6-bis-(benzimidazol-2'-yl)-pyridin und X = H, OH, Cl] zeigen thermisch anregbare Spinübergänge in Lösung, welche sowohl vom Liganden als auch vom Lösungsmittel beeinflusst werden. ¹H-NMR- und UV-Vis-spektroskopische Messungen zeigen, daß Substituenteneffekte, Donor- und Acceptor-Eigenschaften der Lösungsmittel und Wasserstoffbrückenbindungen herangezogen werden

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können, um die Ligandenfeldstärke und damit das Spinübergangsverhalten zu verändern. Substituentenvariation führt zu Änderungen der magnetischen Momente in Lösung ($X = \text{H}$: $\mu_{\text{exp}} = 2.50 \mu_{\text{B}}$; $X = \text{OH}$: $\mu_{\text{exp}} = 4.20 \mu_{\text{B}}$; $X = \text{Cl}$: $\mu_{\text{exp}} = 4.30 \mu_{\text{B}}$ bei 294 K in MeOH) und zu einer Verschiebung der charge-transfer – Bande ($X = \text{H}$, $\lambda = 557 \text{ nm}$; $X = \text{OH}$, $\lambda = 520 \text{ nm}$; $X = \text{Cl}$, $\lambda = 500 \text{ nm}$). $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2$ zeigt ein thermisch stark verschiebbares Spin-Gleichgewicht ($^1A_1 \rightarrow ^5T_2$) in Lösung ($K_{\text{sc}} = 0.26$ bei 293 K; $\mu_{\text{exp}} = 1.30 \rightarrow 3.40 \mu_{\text{B}}$ für 213 \rightarrow 328 K in MeOH). Die relativ geringe Veränderung des magnetischen Moments von $[\text{Fe}(4\text{-OH-bzimpy})_2](\text{ClO}_4)_2$ ($\mu_{\text{exp}} = 3.77 \rightarrow 4.73 \mu_{\text{B}}$ bei 220 \rightarrow 332 K) deutet auf die Existenz (temperaturabhängiger) Wasserstoffbrückenbindungen zwischen Liganden und Lösungsmittelmolekülen oder auf eine temperaturabhängige Änderung der Besetzung der 5E_g -Zustände. Die Anwesenheit von starken Donor-Lösungsmitteln ($DN \geq 30$) beeinflusst den Spinübergang.

Introduction

Thermally induced spin-state equilibria between low-spin (*ls*) and high-spin (*hs*) states of transition metal complexes are usually accompanied by thermochromism and can be observed in the case of octahedral d^5 ions when the potential minima of the 1A_1 and the 5T_2 surfaces are so similar in energy that both can be thermally populated [1]. Previous studies on $[\text{Fe}(\text{bzimpy})_2(\text{ClO}_4)_2]$ (*bzimpy* = 2,6-bis-(benzimidazol-2'-yl)-pyridine) have shown [2, 3] that this complex and possibly also species derived from it by substitution are promising candidates for the investigation of spin-crossover phenomena in solution [3–10]. We investigated therefore the effect of substituent variation on the spin-crossover behaviour of these complexes in various solvents. Substitution on the 4-position was chosen as most likely to influence the spin equilibrium by electronic rather than steric effects.

Experimental

Solvents: Commercial grade methanol was refluxed over CaO for 24 hours and fractionally distilled. Acetone (*Ac*) was twice distilled after refluxing over CaSO_4 . The water content of methanol was analyzed by *Karl Fischer* titration and was found to be below 30 mg l^{-1} . Nitromethane (*NM*) (Riedel, 99% (GC)) and N,N-Dimethylformamide (*DMF*) was used as received. Acetonitrile (*An*) was refluxed over NaOH for 24 hours and collected over P_2O_5 through a distillation for 12 hours. 1,2-propanediol-carbonate (*PDC*) was fractionally distilled under reduced pressure (1.3 mbar) for 10 hours.

Solutions: Spectrophotometric titrations with ligand solution were performed at a Fe^{2+} -concentration range of 1 to $5 \cdot 10^{-4} \text{ mol dm}^{-3}$ with a L: Fe^{2+} ratio between 0 and 20 for *bzimpy* and with $8 \cdot 10^{-5} - 2 \cdot 10^{-4} \text{ M}$ with a L: Fe^{2+} ratio between 0 and 15 for the 4-Cl-*bzimpy* and the 4-OH-*bzimpy* species. The solubilities of Cl-*bzimpy* and OH-*bzimpy* in methanol are lower than that of *bzimpy* itself. Both spectroscopic and magnetic properties were investigated with complex concentrations of 2 to $5 \cdot 10^{-4} \text{ mol dm}^{-3}$ adding excess ligand (saturated ligand solution in the case of nitromethane) to avoid extensive ligand dissociation at higher temperatures.

Spectrophotometric Measurements: UV-Visible spectra were run on a Hitachi U-2000 Spectrophotometer, equipped with a electronic thermostatted cell holder (Hitachi) for the range of $0 - 100 \pm 0.5 \text{ }^\circ\text{C}$. The temperatures were recorded with a copper-constantan thermocouple in the cell. A homogeneous temperature distribution within the cells was ensured by using a magnetic stirrer. Below room temperature ($\leq 20 \text{ }^\circ\text{C}$), dry nitrogen gas was blown into the cell compartment. Due to the thermochromism of the system under study, temperature-constancy could be easily followed on an

absorbance *versus* time plot; a constant value was usually attained after *ca.* 6 minutes. Molar absorptions, ϵ_{obs} , were corrected for changes in the solvent density due to the temperature variation.

Magnetic Measurements: $^1\text{H-NMR}$ 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 as instrument lock. Magnetic susceptibilities in solution were measured by the *Evans* $^1\text{H-NMR}$ method [11] using the solvent methanol for temperature calibration [12]. The results were corrected for changes in the solvent density with temperature [13]. 0.5% dioxane (v/v) was used as internal reference compound.

Preparation of Ligands and Complexes: All complexes were prepared in a nitrogen atmosphere with solvents (methanol) deoxygenated by nitrogen gas. 2,6-bis-(benzimidazol-2'-yl)-pyridin (*bzimpy*) was prepared by a method analogous to that of *A. W. Addison* and *P. J. Burke* [2, 3, 10] and recrystallized three times from methanol.

4-Hydroxy-2,6-bis(imidazol-2'-yl)pyridine (*OH-bzimpy*)

14.66 g (80 mmol) 4-hydroxypyridine-2,6-dicarboxylic acid and 19.04 g (172 mmol) 1,2-phenylenediamine were suspended in 160 ml phosphoric acid (85%) and kept with vigorous stirring at 210–220 °C for 6 hours [10]. The blue coloured melt so obtained was poured, after cooling, into 3 liter cold water, the precipitate collected by filtration and transferred to 1 liter hot 10% aqueous sodium carbonate solution. The resulting solid was filtered off and dried *in vacuo* at 100 °C. The product was dissolved in 30 ml hot methanol saturated with sodium carbonate, diluted with water to 300 ml and acidified with 15% hydrochloric acid to *pH* 1. The white product was filtered off and extracted several times with 1 liter boiling methanol. The collected extracts were evaporated until beginning precipitation (*ca.* 500 ml). Cooling overnight yielded colourless crystals which were filtered off, washed with methanol and ether, and finally dried *in vacuo* at 120 °C. 17.1 g, 65%, *m.p.* > 250 °C. Found: C, 64.89%; H, 4.55%; N, 19.68%; calc. for $\text{C}_{19}\text{H}_{13}\text{N}_5\text{O}\cdot 1.5\text{H}_2\text{O}$: C, 64.40%; H, 4.35%; N, 19.76%. $^1\text{H-NMR}$ (EtOH- d_6): 7.36 (s, pyridine ring), 7.15–7.30, 6.82–6.86 (m, benzene ring).

4-Chloro-2,6-bis(imidazol-2'-yl)pyridine (*Cl-bzimpy*)

16.13 g (80 mmol) 4-Chloropyridine-2,6-dicarboxylic acid [10] and 19.04 g (172 mmol) 1,2-phenylenediamine were suspended in 160 ml 85% phosphoric acid and stirred at 210 °C for 8 hours. When cool, the green coloured melt was poured into 3 liter cold water, the precipitate was collected by filtration and transferred in 1 liter hot 10% aqueous sodium carbonate solution. The resulting solid was filtered off and dried *in vacuo* at 100 °C. The product was dissolved in 30 ml hot methanol saturated with sodium carbonate, diluted with water to 300 ml and acidified with 15% hydrochloric acid to *pH* = 1. The white coloured product was filtered off and extracted several times with 1 liter boiling methanol. The volume of collected extracts was reduced at boiling temperature until beginning precipitation (*ca.* 700 ml), cooled overnight, and the colourless crystals were filtered off and washed with methanol and ether. The crystals thus obtained were dried *in vacuo* at 120 °C yielding 18.5 g (67%), *m.p.* > 250 °C. Found: C, 60.39%; H, 4.07%; N, 18.01%; Cl, 8.67%; calc. for $\text{C}_{19}\text{H}_{12}\text{N}_5\text{Cl}\cdot 2\text{H}_2\text{O}$: C, 59.77%; H, 3.96%; N, 18.34%; Cl, 9.24%. $^1\text{H-NMR}$ ($\text{D}_2\text{O-NaOD}$): 7.11 (s, pyridine ring); 7.37–7.45; 6.89–6.98 (m, benzene ring).

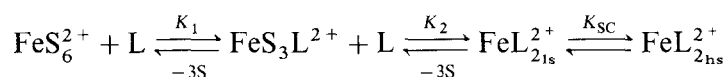
$[\text{Fe}(\text{X-bzimpy})_2](\text{ClO}_4)_2$

A hot oxygen free solution of the free ligand (6 mmol) in methanol (1000 cm^3) was combined with 20 cm^3 of a saturated solution of $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ (3 mmol) in methanol to give a deep red solution [6].

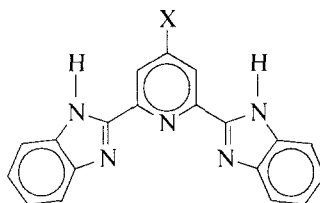
The solution was reduced *in vacuo* to about 150 cm³. Solid NaClO₄·H₂O (12 mmol) was added and the solution cooled overnight. The magenta coloured crystals so obtained were filtered off, washed twice with 10 ml cooled methanol and 20 ml ethyl ether, dried *in vacuo* and stored over CaCl₂ under reduced pressure. Yield, 92–95%. [Fe(*bzimpy*)₂](ClO₄)₂: found: C, 51.94%; H, 2.96%; N, 15.93%; calc. for C₃₈H₂₆Cl₂FeN₁₀O₈: C, 52.02%; H, 2.99% and N, 15.91%. [Fe(OH-*bzimpy*)₂](ClO₄)₂, found: C, 47.17%; H, 3.12% and N, 14.25%; calc. for C₃₈H₂₆Cl₂FeN₁₀O₁₀·3H₂O: C, 47.37%; H, 3.35% and N, 14.53%. [Fe(Cl-*bzimpy*)₂](ClO₄)₂, found: C, 45.36%; H, 2.92% and N, 13.60%; calc. for C₃₈H₂₄Cl₄FeN₁₀O₈·3.5H₂O: C, 45.21%; 3.00% and N, 13.88%.

Results and Discussion

A generalized reaction scheme to describe the complex-formation equilibria and the thermochromic behaviour of these complexes is given in the Scheme below (S = solvent; L = X-*bzimpy*).



where the structure of the ligand L is



L = X-2,6-bis-(benzimidazol-2'-yl)-pyridine, X = H, OH and Cl

The scheme shows that *mono*- and *bis*-complexes are formed successively and that a spin-crossover-equilibrium involving the *bis*-complexes occurs. The scheme is simpler than that proposed earlier [2, 3] as the present results suggest that FeL₃ (with X-*bzimpy* acting as a bidentate ligand) is only formed in MeOH solution and then in negligible concentration. From the observed thermochromism of the complex in solution and its magnetic properties the equilibrium constants (K_1 and K_2), the spin-equilibrium constants (K_{SC}), and the associated thermodynamic parameters (ΔH_{SC} , ΔS_{SC}) of the spin-state equilibria between *ls* and *hs* states can be evaluated.

UV-Visible spectra

UV-Visible spectral data of [Fe(X-*bzimpy*)₂]²⁺ complexes dissolved in MeOH, *Ac*, *An*, *PDC*, *NM*, *DMF*/MeOH and Et₃N/MeOH with excess ligand (to reduce ligand dissociation) are listed in Table 1. The solvent dependent spin-crossover behaviour of the complexes is evident from the Table 1 as the absorption maxima of the *charge-transfer* bands [14, 15] are shifted accompanied by colour changes dependent on the nature of the solvent. At 600 to 800 nm d-d absorption bands are found [6, 7]. With ligand substitution from X = H to X = OH and Cl the colour of the solution changes at room temperature from red-violet to bluish-violet and finally

to light brown. The *CT* band shifts towards shorter wavelengths whereas the d–d transition band shifts to longer wavelengths and the molar absorbances become gradually smaller (upto one fourth or less). This can be explained by assuming that the energy of the lowest unfilled π -orbital of the ligand is increased leading to relatively higher energies for the *CT* band whereas the ligand field splitting is decreased [7] (*i.e.* a hyperconjugative effect arises due to the substituent). This results

Table 1. The UV-Visible spectral data of $[\text{Fe}(4\text{-X-bzimpy})_2][\text{ClO}_4]_2$ with and without excess ligands in non-aqueous solutions

Solvent	L/Fe ²⁺	Color	λ_{max} (nm)	ϵ_{max} (L mol ⁻¹ cm ⁻¹)
[Fe(H-bzimpy) ₂][ClO ₄] ^a				
MeOH	28.0	red violet	557.0	7000 ± 20
MeOH	2.0	red violet	557.0	4330 ± 20
Ac	24.0	red	555.0	5940 ± 20
Ac	2.0	red	555.0	5560 ± 20
An	5.7	red	552.0	4970 ± 20
An	2.0	red	552.0	4550 ± 20
NM	saturated	light rose	554.0	6320 ± 20
NM	2.0	light rose	554.0	5080 ± 20
PDC	40.0	red violet	554.5	5930 ± 20
PDC	2.0	red violet	554.5	5180 ± 20
PDC/MeOH ^c	30.0	red violet	556.0	5650 ± 20
PDC/MeOH ^c	2.0	red violet	556.0	4880 ± 20
DMF/MeOH ^d	7.0	red violet	555.0	5200 ± 20
[Fe(4-OH-bzimpy) ₂][ClCO ₄] ^b				
MeOH	8.7	red violet	513.5	1800 ± 20
MeOH	2.0	light red	503.0	1440 ± 20
Ac	2.0	wine red	502.0	1490 ± 20
AN	2.0	light rose	498.0	1700 ± 20
NM	2.0	rose	502.5	2270 ± 20
PDC	2.0	wine red	501.0	1580 ± 20
DMF	2.0	blue	585.0	3300 ± 20
DMF/MeOH ^d	5.8	bluish red	541.0	2160 ± 20
[Fe(4-Cl-bzimpy) ₂][ClO ₄] ^b				
MeOH	6.9	wine red	502.0	980 ± 20
MeOH	2.0	light red	486.5	620 ± 20
Ac	2.0	light red	489.5	750 ± 20
AN	2.0	light rose	487.0	1820 ± 20
NM	2.0	rose	500.0	2250 ± 20
PDC	2.0	light rose	492.5	1320 ± 20
DMF	2.0	light yellow	–	–
DMF/MeOH ^d	5.3	light red	490.0	850 ± 20

^a T = 294 K, ^b T = 298 K

MeOH Methanol, NM Nitromethane, Ac Acetone, An Acetonitril, PDC Propanediolcarbonate, DMF N,N-Dimethylformamide

^c 50% (v/v) PDC/MeOH and ^d 20% (v/v) DMF/MeOH

in almost pure *hs*-states at room temperature for the Cl- and OH-substituted species. The lowering of symmetry from O_h to D_{2d} causes a splitting of the degenerate t_{2g} level into a single and a double degenerated level ($b_2 + e$). It is assumed that this splitting ($d_{\pi}(b_2) \rightarrow \pi_1^*$ and $d_{\pi}(e) \rightarrow \pi_1^*$) is responsible for the broader peaks [8, 15, 16] found for the Cl- and OH-substituted species compared to those of the unsubstituted complex.

The spin-crossover equilibrium of the $[\text{Fe}(\text{X-bzimpy})_2]^{2+}$ is paralleled in the UV-Visible spectra by a variation of the intense *charge-transfer* band in the investigated temperature range of 276–331 K. With increasing temperatures, molar absorption decreases as the high-spin state is increasingly populated, and the shape of the d–d bands of $[\text{Fe}(\text{bzimpy})_2]^{2+}$ at high temperature are almost identical to those of $[\text{Fe}(\text{X-bzimpy})_2]^{2+}$ ($\text{X} = \text{OH}, \text{Cl}$) which are in their high-spin state at all temperatures. The value of the molar absorbances of pure high spin-component ($\epsilon_{\text{hs}} = 750 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) can be estimated from of high temperature spectra of $[\text{Fe}(\text{Cl-bzimpy})_2]^{2+}$. Due to the experimentally limited temperature range, the value for the pure low-spin isomer (ϵ_{ls}) is not accessible directly and was evaluated by means of a least square fitting procedure ($\epsilon_{\text{ls}} = 13000 \pm 500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The values of ϵ_{hs} and ϵ_{ls} were found to be in agreement with literature values [1–3].

$^1\text{H-NMR}$ Spectra

The solution-state magnetic behavior of the complexes was measured by applying *Evan's* method based on NMR-shifts [11] over a wide temperature range. Magnetic

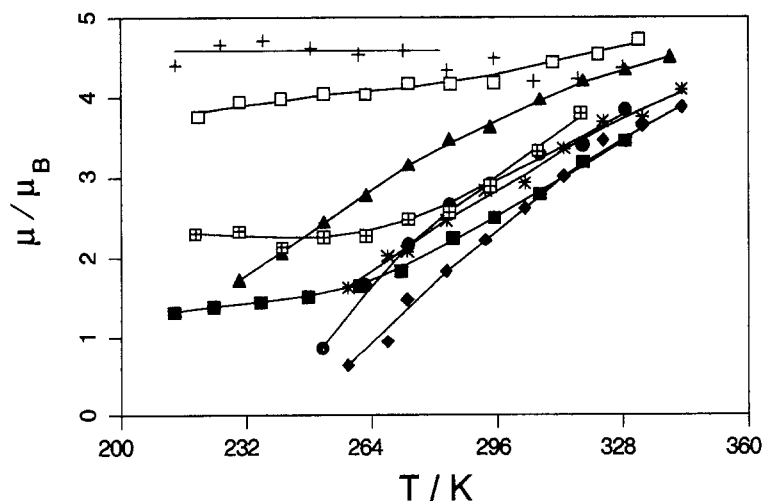


Fig. 1. Magnetic moments of $[\text{Fe}(\text{4-X-bzimpy})_2(\text{ClO}_4)_2]$ with excess ligands in nonaqueous solution versus temperature:

- $[\text{Fe}(\text{H-bzimpy})_2]^{2+}$ in MeOH: $5.580 \cdot 10^{-4} \text{ M}$ and $[\text{L}]/[\text{Fe}^{2+}] = 8.3$
- * $[\text{Fe}(\text{H-bzimpy})_2]^{2+}$ in NM: $3.437 \cdot 10^{-4} \text{ M}$ and $[\text{L}]/[\text{Fe}^{2+}] = 5.2$
- ▲ $[\text{Fe}(\text{H-bzimpy})_2]^{2+}$ in Ac: $3.0634 \cdot 10^{-4} \text{ M}$ and $[\text{L}]/[\text{Fe}^{2+}] = 7.32$
- $[\text{Fe}(\text{H-bzimpy})_2]^{2+}$ in An: $3.966 \cdot 10^{-4} \text{ M}$ and $[\text{L}]/[\text{Fe}^{2+}] = 7.4$
- ◆ $[\text{Fe}(\text{H-bzimpy})_2]^{2+}$ in PDC: $5.5525 \cdot 10^{-4} \text{ M}$ and $[\text{L}]/[\text{Fe}^{2+}] = 7.1$
- $[\text{Fe}(\text{OH-bzimpy})_2]^{2+}$ in MeOH: $2.870 \cdot 10^{-4} \text{ M}$ and $[\text{L}]/[\text{Fe}^{2+}] = 5.0$
- + $[\text{Fe}(\text{bzimpy})_2]^{2+}$ in MeOH: $2.473 \cdot 10^{-4} \text{ M}$ and $[\text{L}]/[\text{Fe}^{2+}] = 7.3$

Table 2. Magnetic moment data of $[\text{Fe}(\text{X-bzimpy})_2(\text{ClO}_4)_2]$ at different temperatures in nonaqueous solvents

$[\text{Fe}(\text{H-bzimpy})_2(\text{ClO}_4)_2]$ in MeOH		$[\text{Fe}(\text{OH-bzimpy})_2(\text{ClO}_4)_2]$ in MeOH		$[\text{Fe}(\text{Cl-bzimpy})_2(\text{ClO}_4)_2]$ in MeOH	
T (K)	μ (μ_B)	T (K)	μ (μ_B)	T (K)	μ (μ_B)
213.7	1.31	219.8	3.76	214.0	4.41
223.8	1.38	230.4	3.95	225.5	4.66
235.8	1.43	240.9	3.99	236.3	4.72
247.7	1.50	251.7	4.05	248.5	4.62
261.0	1.64	262.4	4.04	260.7	4.54
271.5	1.83	273.3	4.18	272.2	4.59
284.8	2.24	284.0	4.17	283.3	4.34
295.4	2.50	295.1	4.19	295.3	4.49
306.9	2.79	310.3	4.44	305.4	4.20
317.9	3.19	321.7	4.54	316.7	4.24
328.7	3.45	332.0	4.73	328.1	4.38
$[\text{Fe}(\text{H-bzimpy})_2(\text{ClO}_4)_2]$ in Ac		$[\text{Fe}(\text{H-bzimpy})_2(\text{ClO}_4)_2]$ in An		$[\text{Fe}(\text{H-bzimpy})_2(\text{ClO}_4)_2]$ in PDC	
T (K)	μ (μ_B)	T (K)	μ (μ_B)	T (K)	μ (μ_B)
251.7	0.85	230.2	1.72	230.2	0.64
262.5	1.65	241.1	2.06	241.1	0.94
273.4	2.15	251.7	2.45	251.7	1.47
283.8	2.65	262.5	2.78	262.5	1.83
294.3	2.91	273.3	3.16	273.3	2.22
306.9	3.28	283.8	3.48	283.8	2.61
317.9	3.40	294.2	3.63	294.3	3.01
328.8	3.84	306.9	3.98	306.9	3.46
317.9	4.21	317.8	3.65		
328.8	4.35	328.7	3.88		
340.0	4.51				
$[\text{Fe}(\text{H-bzimpy})_2(\text{ClO}_4)_2]$ in NM		$[\text{Fe}(\text{H-bzimpy})_2(\text{ClO}_4)_2]$ 20% (v/v) DMF in MeOH			
T (K)	μ (μ_B)	T (K)	μ (μ_B)		
258	1.62	219.0	2.30		
268	2.02	230.3	2.33		
273	2.08	241.1	2.13		
283	2.47	251.7	2.26		
293	2.84	262.5	2.27		
303	2.93	273.3	2.48		
313	3.36	283.8	2.57		
323	3.70	294.3	2.89		
333	3.75	306.4	3.33		
343	4.10	317.4	3.80		

moments of the complexes in solution were calculated from eqs. 1 and 2,

$$\chi_{\text{exp}} = (3\Delta\nu \cdot 0.001/4\pi \cdot M) \quad (1)$$

$$\mu_{\text{exp}} = 2.84\sqrt{\chi} \cdot T \quad (2)$$

where $\Delta\nu$ (in ppm) is the paramagnetic shift of a reference compound, corrected for the diamagnetic contribution of the ligand, and M is the molarity of the paramagnetic ion. The diamagnetic correction for the ligand had been determined experimentally, *i.e.* using free ligand, and the respective Zn-species [3].

Magnetic susceptibilities of the complexes in solution were measured in the temperature range of 220 to 330 K (cf. Table 2). The non-Curie magnetic behavior of the $[\text{Fe}(\text{bzimpy})_2]^{2+}$ complex in different solvents reflects the spin-transition equilibria. The magnetic moments vary between $1.50 \mu_{\text{B}}$ (223 K) and $3.40 \mu_{\text{B}}$ (328 K) and clearly fall into the range between pure low-spin ($S = 0$, *i.e.* $0-0.5 \mu_{\text{B}}$) and pure high-spin ($S = 2$, $5.0-5.5 \mu_{\text{B}}$) found for similar six coordinated iron(II)-imine complexes [1, 4-8, 17].

The temperature dependence is much less pronounced for the Cl- and OH-species (Fig. 1). Magnetic moments vary between $4.0-4.5 \mu_{\text{B}}$ for the former and $3.7-4.7 \mu_{\text{B}}$ for the latter, showing that these complexes are in their high-spin state. The slight temperature dependence of $[\text{Fe}(\text{OH-bzimpy})_2]^{2+}$ may be explained by a variation of hydrogen-bonding between OH-groups of the ligand and the solvent MeOH with temperature variation. An alternative explanation would be a variable population of the sublevels of the ${}^5E_{\text{g}}$ component within the split ${}^5T_{2\text{g}}$ ground state as has been suggested for iron(II)poly(1-pyrazolyl)borates [8]. Similar magnetic behaviour due to the change of the substituent on the ligand has been reported for [iron(II)tris{4-((6-R)-2-pyridyl)-3-aza-3-butenyl}amine](PF₆)₂ complexes [17] (R = H or CH₃) and for [Co(II)bis(N-R-2,6-pyridinedicarboxaldimine)](PF₆)₂ complexes [5] (R = C(CH₃)₃, CH(CH₃)₂, NH(CH₃), *p*-PhCH₃, and CH₂Ph).

From the observed magnetic behavior in solution, the spin-crossover equilibrium constant (K_{SC}) of $\text{Fe}(\text{H-bzimpy})_2(\text{ClO}_4)_2$ has been evaluated by eq. (3),

$$K_{\text{SC}} = x_{\text{hs}}/x_{\text{ls}} = (\mu_{\text{exp}}^2 - \mu_{\text{ls}}^2)/(\mu_{\text{hs}}^2 - \mu_{\text{exp}}^2) \quad (3)$$

where x_{hs} and x_{ls} are the mole fractions of the respective spin isomers and μ_{hs} and μ_{ls} are the effective magnetic moments for the high-spin and low-spin forms, respectively. The values of spin-equilibrium constants (K_{SC}) were determined by using $\mu_{\text{hs}} = 5.5 \mu_{\text{B}}$ and $\mu_{\text{ls}} = 0$ [4]. Thermodynamic parameters (ΔS_{SC} and ΔH_{SC}) were estimated from plots of free energy ($\Delta G = -RT \ln K_{\text{SC}}$) versus T. The obtained spin equilibria (Table 3) are in good agreement with the comparable spin-crossover behavior of Fe(II)-imine complexes [2-4, 6].

It is seen that the K_{SC} values found from earlier spectrophotometric measurements [2, 3] are significantly larger. We analyzed the present results in the same way and also found large values ($\Delta H_{\text{SC}} = 3.9 \text{ kcal/mol}$, $\Delta S_{\text{SC}} = 12.95 \text{ cal K}^{-1} \text{ mol}^{-1}$, $K_{\text{SC}} = 0.85$). These high values appear to stem from the fact that only a restricted temperature range is available for the spectroscopic determination coupled with a lack of exact values of the molar absorbances. The relatively high ΔH_{SC} and ΔS_{SC} values of the complex in 20% (v/v) DMF/MeOH in contrast to that in MeOH, may be explained by solvation of the imidazole proton which would be expected to

Table 3. Spin-equilibrium constants and thermodynamic parameters of some iron(II)-imine complexes in different solvents

Complex	Solvent	ΔH (kcal mol ⁻¹)	ΔS (cal K ⁻¹ mol ⁻¹)	K_{sc}^T	Reference
[Fe(H- <i>bzimpy</i>) ₂ (ClO ₄) ₂] ^m	MeOH	4.90 ± 0.1	14.00 ± 0.1	0.26	This work
[Fe(H- <i>bzimpy</i>) ₂ (ClO ₄) ₂] ^m	DMF (20%)/MeOH	7.03 ± 0.1	22.23 ± 0.1	0.38	This work
[Fe(H- <i>bzimpy</i>) ₂ (ClO ₄) ₂] ^m	NM	4.87 ± 0.1	14.53 ± 0.1	0.36	This work
[Fe(H- <i>bzimpy</i>) ₂ (ClO ₄) ₂] ^m	Ac	5.38 ± 0.1	16.26 ± 0.1	0.39	This work
[Fe(H- <i>bzimpy</i>) ₂ (ClO ₄) ₂] ^m	An	4.15 ± 0.1	13.68 ± 0.1	0.77	This work
[Fe(H- <i>bzimpy</i>) ₂ (ClO ₄) ₂] ^m	PDC	5.71 ± 0.1	17.65 ± 0.1	0.43	This work
[Fe(H- <i>bzimpy</i>) ₂ (ClO ₄) ₂] ^s	MeOH	3.95 ± 0.1	12.95 ± 0.1	0.85	This work
[Fe(H- <i>bzimpy</i>) ₂ (ClO ₄) ₂] ^s	DMF	10.22 ± 0.1	33.71 ± 0.1	0.57	[6]
[Fe(<i>pybzim</i>) ₃ (BPh ₄) ₃] ^m	CH ₃ COCH ₃	4.70 ± 0.1	18.60 ± 0.1	3.62	[4]
[Fe(<i>pybzim</i>) ₃ (BPh ₄) ₃] ^m	An (20%)/MeOH	5.10 ± 0.1	22.00 ± 0.1	10.0	[4]

^m From magnetic measurement, T = 293 K

^s From spectroscopic measurement at $\lambda_{max} = 557$ nm

stabilize the *ls* form. This effect appears to increase with increasing donor number of the solvent.

In conclusion it can be said that the pronounced spin crossover behaviour found for the parent complex, [Fe(*bzimpy*)₂]²⁺, in solution is strongly reduced by electron withdrawing substituents resulting in pure high spin states for the FeL₂²⁺ species at room temperature in MeOH. This suggests, in agreement with the ligand field parameters evaluated from the Ni²⁺ complexes that, despite strong withdrawing properties of the substituted ligands, the ligand field splitting in the FeL₂²⁺ species must be lower (possibly due to the loss in symmetry).

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