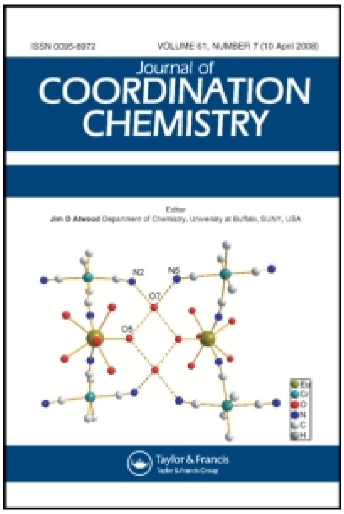

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PROTONATION CONSTANTS AND SOLVENT DEPENDENT SPIN-CROSSOVER BEHAVIOUR OF IRON(II)-2-(2'-PYRIDYL)BENZIMIDAZOLE COMPLEXES

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PROTONATION CONSTANTS AND SOLVENT DEPENDENT SPIN-CROSSOVER BEHAVIOUR OF IRON(II)-2-(2′-PYRIDYL)BENZIMIDAZOLE COMPLEXES

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Dedicated to Prof. Viktor Gutmann

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2-(2′-Pyridyl)benzimidazole (pybzim = LH) coordinates to iron(II) as a bidentate and forms the tris-ligated complex, $[Fe(pybzim)_3]^{2+}$ as isolated in the solid. Titration of $[Fe(pybzim)_3]^{2+}$ with base demonstrates the successive deprotonation of the imino hydrogens of the coordinated ligands. Protonation constants for the free ligand, pybzim ($\log_{10} K^H = 11.33$) and the complex, $[Fe(pybzim)_3]^{2+}$ ($\log_{10} K_1^H = 9.58$, $\log_{10} K_2^H = 8.13$ and $\log_{10} K_3^H = 6.97$) were measured in 30% (v/v) H_2O/EtOH. Results show that coordination to iron(II) increases the acidity of the imino hydrogen of the ligand. Spin-crossover behaviour of the complex were studied in different solvents ME, AC, AN, NM, NB, DMF, DMSO and ANL. The complex shows strong spin-crossover behaviour which is solvent dependent. Values of the spin-equilibrium constant (K_{sc}) and the associated thermodynamic parameters ($\Delta H_{sc} = 18.1$–$21.3\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S_{sc} = 69.6$–$84.4\,\mathrm{J\,K^{-1}\,mol^{-1}}$) were calculated. An increase of the enthalpy is observed with increasing donor number (DN) of the solvent.

Keywords: 2-(2′-Pyridyl)benzimidazole (pybzim); $[Fe(pybzim)_3]^{2+}$; protonation constants; spin-crossover; non-aqueous solvents; donor number

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INTRODUCTION

Studies of spin-crossover phenomena of transition metal ions of d^4–d^7 electronic configuration with diimine and triimine ligands have been shown to be of considerable importance for understanding electron transfer, dissociation and intersystem crossing in complex compounds[1] and some biologically important compounds.[2] The two electronic isomers, low-spin (LS) and high-spin (HS), of differing multiplicity, are nearly equi-energetic and become comparable to the thermal energies (kT) in certain temperature ranges. This is called the spin-crossover equilibrium between the two spin states.[3–9] Spin-crossover behaviour of tris-complexes of the diimine ligands such as 2-(aminomethyl)pyridine,[5] 2-(2′-pyridyl)imidazole[6] and 2-(2′-pyridyl)-benzimidazole[8,9] with iron(II) have been studied in detail. Bis-complexes of triimine ligands, 4-X-2,6-bis(benzimidazole-2′-yl)pyridine (X = H, Cl and OH) with iron(II) show strong spin-crossover behaviour both in solution and the solid state.[10–13] The ligands, 2-2′-bipyridine,[14] 2-(2′-pyridyl)-imidazole,[16] 4-(2′-pyridyl)imidazole[19] and 2-(2′-pyridyl)benzimidazole[26] act as bidentates with transition metal(II) ions and their stability constants are known. Accordingly, the stability constants of triimine-complexes, Fe(II)/4-X-2,6-bis(benzimidazole-2′-yl)pyridine (X = H, Cl and OH) are reported.[25] Coordination to metal ions increases the acidity of the imino hydrogen atoms of these ligands.[14–19,21,22] Furthermore, cationic complexes with divalent transition metal ions can be deprotonated by titration with alkali.[15,17,18,20–22]

The present paper describes protonation and spin-crossover behaviour of the Fe(II)-2-(2′-pyridyl)benzimidazole system in non-aqueous solvents. We have attempted a correlation between the observed spin-crossover behaviour and the donor number (DN) of the solvent.[29]

EXPERIMENTAL

Chemicals

The following chemicals were used as received: $FeCl_2 \cdot 4H_2O$ (Riedel-de-Haen), $NaClO_4 \cdot H_2O$ (Fluka), NaOH (Riedel-de-Haen), KCl (Merck), P_2O_5 (Riedel-de-Haen), $CaSO_4 \cdot 0.5H_2O$ (Merck), B_2O_3 (Merck) and CaO (tech.). Buffer solutions of pH = 2.0 and 9.0 (Merck) were used. Commercial grade methanol (ME) (Riedel-de-Haen) was refluxed over CaO for 24 h and fractionally distilled. Commercial grade acetone (AC) (Riedel-de-Haen) was distilled twice from $CaSO_4$ and once from B_2O_3. Acetonitrile (AN) (Loba) was distilled once from NaOH and twice from P_2O_5. Nitromethane (NM) (Riedel-de-Haen, 99% GC), nitrobenzene (NB) (Riedel-de-Haen, 99% GC) and *N*, *N*-dimethylformamide (DMF) (Merck, tech.) were used as received. Dimethylsulfoxide (DMSO) (Merck) was dried with molecular sieve 4 Å and subsequently distilled under reduced pressure. Absolute ethanol (EtOH) (Riedel-de-Haen, 99%) was used as received.

Synthesis

The ligand 2-(2′-pyridyl)benzimidazole (pybzim = LH) and the complex $[Fe(pybzim)_3](ClO_4)_2 \cdot H_2O$ were synthesized according to the literature[5,6] as follows: a solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (6.0 mmol) in ethanol (30 cm^3) was added to 2-(2′-pyridyl)benzimidazole (18.0 mmol) dissolved in ethanol (200 cm^3). The complex precipitated after a few minutes, then it was filtered off and washed with ethanol. The product was dried *in vacuo* to give reddish-brown crystals (yield 85–90%). Found: C: 50.20; H: 3.53 and N: 14.8%; Calc. for $C_{36}H_{29}Cl_2FeN_9O_9$: C: 50.37; H: 3.41 and N: 14.68%.

Potentiometric Titrations

Potentiometric titrations were carried out using a WTW PH 537 (Weilheim) potentiometer. Titrations of the free ligand LH (1.34×10^{-4} M) and the complex, $[Fe(LH)_3]^{2+}$ (5.34×10^{-5} M) with and without excess ligand ($[LH]/[Fe(LH)_3]^{2+} = 7.0$) were performed in 30% (v/v) H_2O/EtOH with an ionic strength of 0.2 M in KCl and at 29.3 ± 0.5°C. A uniform titration and homogeneous temperature distribution within the titration cells was ensured by using a magnetic stirrer. Nitrogen gas was passed continuously through the titration cell during the experiment. Before titrations the pH-meter was standardized with buffer solutions of pH = 2.0 and 9.0.

Spectrophotometric Measurements

Electronic absorption spectra were run on a Shimadzu UV-1601 PC spectrophotometer, equipped with a thermoelectrically temperature controlled (Shimadzu TCC-240A) cell holder for the range $7–60 \pm 0.1$°C, using a quartz sample cell (1.0 cm). The actual temperature within the sample cell was measured with a copper–constantan thermocouple. Variable temperature spectra of $[Fe(pybzim)_3]^{2+}$ ($6.0–8.0 \times 10^{-5}$ M) without and with excess ligand (*i.e.*, $[LH]/[Fe(LH)_3]^{2+} = 5.0–7.0$) were recorded out in ME, AC, AN, NM, NB, DMF, DMSO and aniline (ANL) over an extended temperature range of 8–55 ± 0.1°C. Below room temperature (< 25°C) dry nitrogen gas was passed through the cell compartment. Values of observed molar absorptivities ($\varepsilon_{obs}/M^{-1}\,cm^{-1}$) were corrected for changes in solvent density with temperature, thus changing the concentration of the solute.[23,24]

RESULTS AND DISCUSSION

Protonation Constants

The potentiometric titration curve (pH *vs* NaOH/ml) for the free ligand and the complex with excess ligand ($[LH]/[Fe(LH)_3]^{2+} = 7.0$) in 30% (v/v) H_2O/EtOH at 29.3 ± 0.5°C is shown in Figure 1. Titrations of the complex with and without excess ligand demonstrate that no hydroxyl association, hydrolysis and/or ligand dissociation occurs in case of the complex with excess ligand, even in the high pH region (> 6.5).[16,17,21] A three step, successive deprotonation reaction of the imino hydrogen of the complex is suggested,[14–20] shown in Scheme I. Values of the protonation constants ($\log_{10} K_n^H$) for the free ligand and the complex with excess ligand are

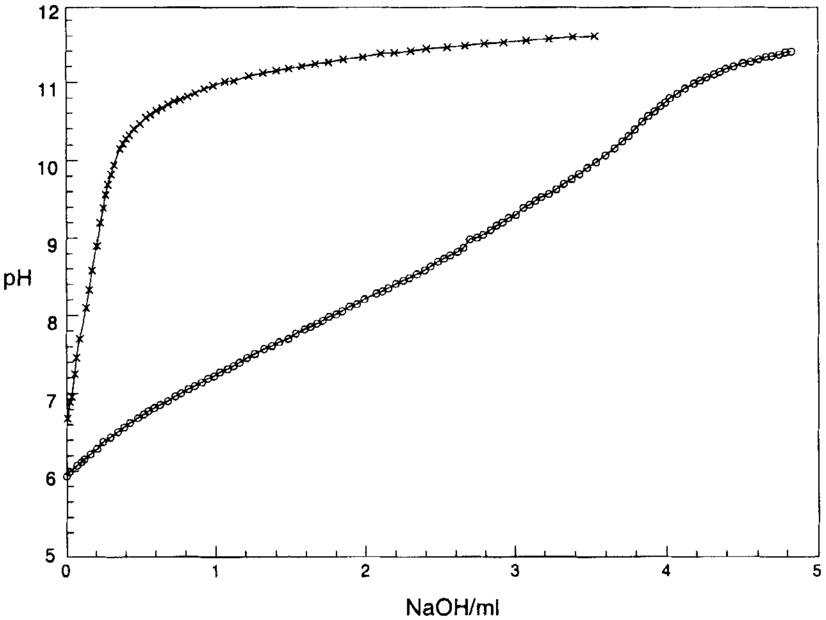

FIGURE 1 Titration curves of the free ligand, LH (1.34×10^{-4} M) and the complex, $[Fe(LH)_3]^{2+}$ (5.33×10^{-5} M) with excess ligand ($[LH]/[Fe(LH)_3]^{2+} = 7.0$) in 30% (v/v) H_2O/EtOH at I = 0.2 M and 29.3 ± 0.5°C; titrant NaOH (2.06×10^{-3} M).

TABLE I Values of protonation constants of LH (1.34×10^{-4} M) and $[Fe(HL)_3]^{2+}$ (5.33×10^{-5} M) with excess ligand ($[LH]/[Fe(LH)_3]^{2+}=7.0$) in 30% (v/v) H_2O/EtOH at $I=0.2$ M and 29.3 ± 0.5°C; titrant NaOH (2.06×10^{-3} M)

Species	$\log_{10} K_1^H$	$\log_{10} K_2^H$	$\log_{10} K_3^H$
[LH]	11.33	—	—
$[Fe(HL)_3]^{2+}$	9.58	8.13	6.97

All log values are ± 0.05; [LH] = pybzim = 2 – (2′-pyridyl)benzimidazole.

calculated using the method described by Martell and Motekaitis[27] and the values are listed in Table I. Coordination to the metal ion decreases the electron density on the imino nitrogen atom of the coordinated ligand via hyperconjugation, thereby increasing the acidity of the imino hydrogen as a function of complex stability.[14–21] Therefore, the complex shows relatively low values of protonation constants compared to the free ligand (Table I). Similar results are found for the protonation of Fe(II)-4-X-2,6-bis(benzimidazole-2′-yl)pyridine.[21]

$$Fe[L_3H_{3-n}]^{(2-n)+} + nH^+ \overset{K_n^H}{\rightleftarrows} Fe[(LH)_3]^{2+}$$

SCHEME I

Spin-Equilibria

Variable temperature electronic spectra of the complex with and without excess ligand were obtained in solvents ME, AC, AN, NM, NB, ANL, DMSO and DMF in the temperature range 8–55 ± 0.1°C and data are listed in Table II. A typical spectrum in AN (Figure 2) shows the marked spin-crossover behaviour of the complex.[4–13] A strong metal-to-ligand charge transfer band ($T_{2g}\rightarrow\pi^*$: mlct) is observed from 400 to 600 nm, as shown for similar Fe(II)-diimine and -triimine complexes.[3,8–10,25,26] The mlct band becomes less intense (i.e., the molar absorptivity decreases) and the absorption maximum (λ_{max}/nm) shifts to shorter wavelengths with increasing temperature (Table II). These results are in good agreement with observed spin-crossover behaviour of Fe(II)-imine complexes.[4–13] Values of the molar absorptivities ($\varepsilon_{500\,nm}/M^{-1}\,cm^{-1}$ for the complex with and without excess ligand decrease by 46% in ME and 42% in AN with temperature, indicating the absence of complexation equilibria in the observed spin-crossover equilibria.[28] However, complex dissociation is very likely to occur in the strong donor solvent DMSO ($DN_{DMSO}=28.8$)[29] which favours the

TABLE II Variable temperature spectroscopic data for $[Fe(LH)_3]^{2+}$ with excess ligand ($[LH]/[Fe(LH)_3]^{2+} = 5.0-7.0$) in different solvents

T (K)	λ_{max} (nm)	$\varepsilon_{500\,nm}$ ($M^{-1}cm^{-1}$)	K_{sc}	T (K)	λ_{max} (nm)	$\varepsilon_{500\,nm}$ ($M^{-1}cm^{-1}$)	K_{sc}
	ME					*DMF*	
280.7	503.5	2425	3.32	281.4	507.5	1675	1.71
284.4	504.0	2275	3.72	287.0	503.5	1488	2.02
288.3	501.0	2127	4.18	293.0	492.5	1322	2.45
292.7	501.5	1985	4.76	298.5	495.5	1203	2.88
297.4	497.5	1848	5.45	303.2	491.5	1095	3.29
302.5	497.0	1718	6.27	308.0	490.0	1000	3.75
307.2	495.0	1610	7.11	312.4	487.5	923	4.22
312.9	493.0	1503	8.24	318.1	482.5	821	4.89
316.1	490.5	1434	8.93	322.6	481.5	748	5.48
322.1	490.0	1345	10.34				
	AC				*NB*		
283.0	500.0	2416	5.20	285.3	501.5	2208	4.71
289.4	498.0	2189	6.27	290.4	500.5	2054	5.42
293.4	497.0	2042	7.01	295.2	499.5	1920	6.14
298.0	496.0	1916	7.96	299.7	498.5	1799	6.89
303.4	494.5	1795	9.18	304.9	495.5	1694	7.83
307.5	492.5	1683	10.21	309.7	493.5	1604	8.77
313.1	490.0	1593	11.72	314.9	493.0	1517	9.91
				319.8	491.5	1441	11.06
				324.9	489.0	1373	12.35
	DMSO				*NM*		
295.3	488.0	409	2.27	283.8	499.0	2254	3.96
301.4	488.0	378	2.67	288.4	497.5	2097	4.48
306.7	487.5	352	3.08	293.8	496.0	1922	5.17
312.0	485.5	328	3.53	298.4	495.0	1800	5.82
316.9	485.0	308	3.98	303.0	494.6	1689	6.53
321.8	483.0	291	4.48	307.8	493.0	1579	7.34
327.0	483.0	275	5.04	313.0	490.8	1484	8.28
331.5	482.5	260	5.60	317.9	490.2	1396	9.26
				322.9	487.2	1322	10.32
	AN				*ANL*		
283.0	498.5	2443	3.35	284.8	524.0	2065	4.66
289.1	497.5	2203	4.00	290.7	523.5	1951	5.41
294.0	495.5	2056	4.59	294.1	521.5	1871	5.90
298.6	493.5	1918	5.20	298.6	517.0	1794	6.58
303.6	491.0	1792	5.92	303.8	515.0	1718	7.44
308.5	490.0	1684	6.71	309.0	513.0	1641	8.37
313.4	488.0	1587	7.58	314.1	510.5	1577	9.36
318.1	487.5	1498	8.46	318.5	508.0	1533	10.29
323.4	484.5	1411	9.58	323.7	506.5	1488	11.46

Methanol (ME), acetone (AC), acetonitrile (AN), nitromethane (NM), nitrobenzene (NB), *N*, *N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and aniline (ANL).

mono-complex (HS-state), as shown from the relatively low values of molar absorptivities (i.e., $\varepsilon_{500\,nm} = 260-409\,M^{-1}\,cm^{-1}$) and the absorption maxima (i.e., $\lambda_{max} = 482-488\,nm$) as compared to the other solvents (Table II and Figure 3). Contrary to this finding, the complex is quite stable in aniline

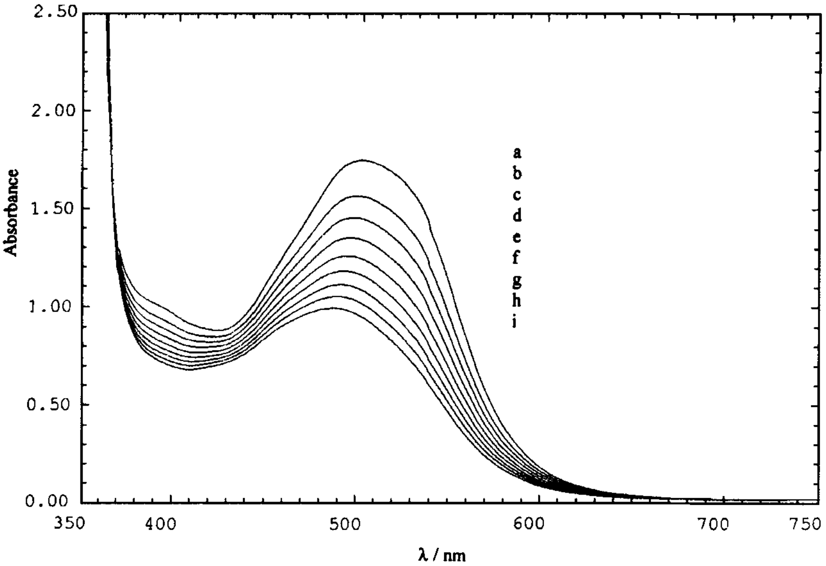

FIGURE 2 Typical electronic absorption spectra of $[Fe(pybzim)_3]^{2+}$ (1.8271×10^{-5} M) with excess ligand ($[LH]/[Fe(LH)_3]^{2+} = 6.5$.) in acetonitrile at different temperatures: (a) 283.0 K, (b) 289.1 K, (c) 294.0 K, (d) 298.6 K, (e) 303.5 K, (f) 308.5 K, (g) 313.4 K, (h) 318.1 K and (i) 323.4 K.

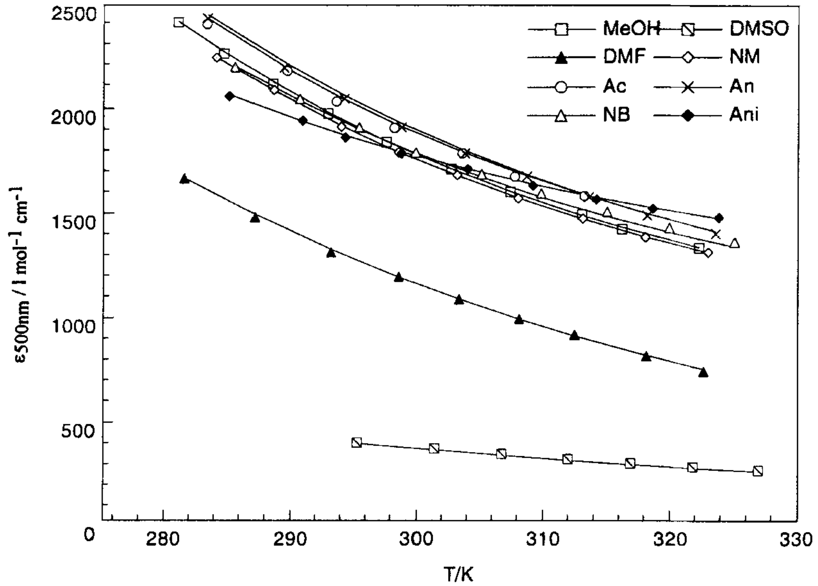

FIGURE 3 Changes of molar absorptivities with temperatures ($\varepsilon_{500\,nm}/M^{-1}cm^{-1}$ *vs* T/K) of the complex with excess ligand ($[LH]/[Fe(LH)_3]^{2+} = 5.0$–$7.0$) in different solvents; experimental points are joined by theoretical lines.

($DN_{ANL} = 33.3$)[29] and shows strong molar absorptivities ($\varepsilon_{500\,nm} = 1488$–$2065\,M^{-1}\,cm^{-1}$) with absorption maxima of $\lambda_{max} = 506$–$524\,nm$ (Table II and Figure 3).

The observed molar absorptivities at a given wavelength and temperature result from a combination of contributions from both the HS and LS isomers of the complex in solution.[10–12,21,28] Hence, the values of $\varepsilon_{HS}/M^{-1}\,cm^{-1}$ (molar absorptivities for HS isomers) and $\varepsilon_{LS}/M^{-1}\,cm^{-1}$ (for LS isomers) are estimated by means of a least-squares fitting procedure to (1) with the experimental data[10–12,21,28] and are listed in Table III. The superimposition of the theoretical curve of $\varepsilon_{500\,nm}/M^{-1}\,cm^{-1}$ *vs* T/K on the experimental data is shown in Figure 3. Accordingly, values of enthalpic and entropic parameters ($\Delta H_{sc} = 18.1$–$21.3\,kJ\,mol^{-1}$ and $\Delta S_{sc} = 69.6$–$84.4\,J\,K^{-1}\,mol^{-1}$) for the spin-equilibria are calculated and listed in (Table III). Values of the spin-equilibrium constant (K_{sc}) are found to increase with increasing temperature (Table II) as the HS-state is increasingly populated and vice versa. The present values of thermodynamic parameters (Table III) are comparable with those found from magnetic measurements ($\Delta H_{sc} = 19.7$–$21.3\,kJ\,mol^{-1}$ and $\Delta S_{sc} = 77.8$–$92.0\,J\,K^{-1}\,mol^{-1}$), reported earlier.[8]

$$K_{sc} = X_{HS}/X_{LS} = (\varepsilon_{obs} - \varepsilon_{LS})/(\varepsilon_{HS} - \varepsilon_{obs}),$$
$$\varepsilon_{obs} = (\varepsilon_{LS} + \varepsilon_{HS} \cdot \exp(\Delta S/R - \Delta H/RT))/(1 + \exp(\Delta S/R - \Delta H/RT)). \tag{1}$$

The present values of thermodynamic parameters (Table III and Figure 4) reflect similar features of the spin-crossover phenomena of these types of complexes regarding solvent influences.[4–12,21,28] The results show a good

TABLE III Values of molar absorptivities of the HS- and LS-isomers and thermodynamic parameters for the spin-crossover equlibria of $[Fe(pybzim)_3]^{2+}$ with excess ligand ($[LH]/[Fe(LH)_3]^{2+} = 5.0$–$7.0$) in different solvents

Solvents	ε_{HS}[†] ($M^{-1}cm^{-1}$)	ε_{LS}[†] ($M^{-1}cm^{-1}$)	ΔH_{sc} ($kJ\,mol^{-1}$)	ΔS_{sc} ($J\,K^{-1}\,mol^{-1}$)
ME	682 ± 17	8229 ± 495	20.6 ± 0.5	83.5 ± 1.2
DMF	100 ± 10	4372 ± 320	21.3 ± 0.7	80.2 ± 1.6
AC	794 ± 35	11037 ± 1774	19.9 ± 1.0	84.0 ± 2.1
AN	695 ± 35	8392 ± 1045	19.8 ± 1.0	79.9 ± 2.3
NM	596 ± 34	8816 ± 141	18.7 ± 0.1	77.3 ± 0.2
NB	750 ± 34	9312 ± 1807	18.7 ± 1.1	78.6 ± 2.0
DMSO	93 ± 5	1241 ± 96	18.1 ± 0.7	69.6 ± 1.5
ANL	995 ± 13	7107 ± 703	17.8 ± 0.6	75.1 ± 1.0
AC*			19.7 ± 0.4	77.8 ± 2.1
AN (20%)/ME*			21.3 ± 1.7	92.0 ± 7.1

*From magnetic measurements, Ref. [8].

[†] ε_{HS} and ε_{LS} values are estimated at $\lambda = 500\,nm$.

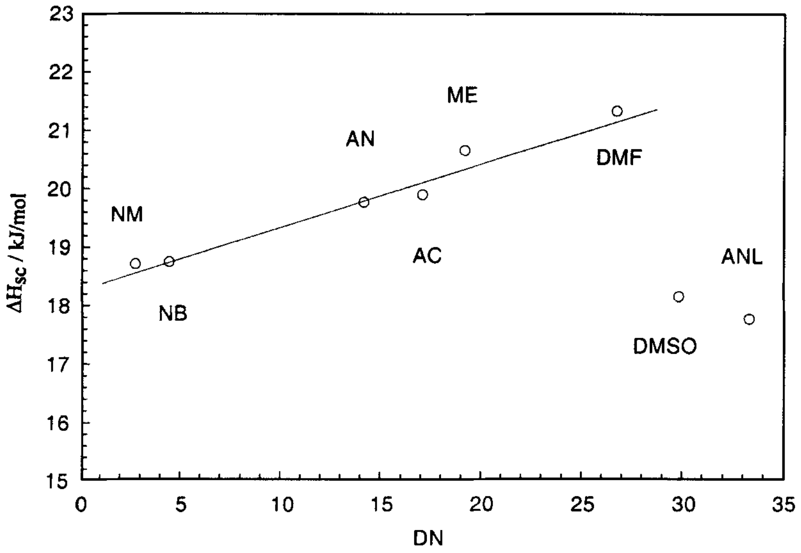

FIGURE 4 Changes of enthalpy (ΔH_{sc}/kJ mol^{-1}) with DN of solvents for the spin-crossover equilibria of $[Fe(pybzim)_3]^{2+}$ in different solvents.

correlation between the observed spin-crossover behaviour and the DN[29] of the solvent. Indeed, in some solvents, due to hydrogen-bonding interactions between the imino hydrogen atoms and the lone pair electrons of solvent, metal-ligand σ-interactions are stronger and increase in turn the $10D_q$ values, thus favouring the LS-state. Accordingly, decreasing temperature leads to a change to the LS-state. Therefore, an increase in enthalpy is observed with the DN of the solvents as shown in Figure 4.

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