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Formation constants and thermodynamic properties of the spin-crossover Fe(II)-2,6-bis-(benzimidazol-2′-yl)pyridine complex

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Abstract

The tridentate ligand, 2,6-bis-(benzimidazol-2′-yl)pyridine (bzimpy) coordinates to iron(II) and forms the mono- and bis-complexes, $[FeLS_3]^{2+}$ (S = solvent) and $[FeL_2]^{2+}$ in 50% (v/v) PC/MeOH (PC = propanedilo-1,2-carbonate). The complexes are characterized by observed metal-to-ligand charge transfer (MLCT) bands with absorption maximum at 500.0 ± 5.0 nm ($\varepsilon_{max} = 200$–$700\ l\ mol^{-1}\ cm^{-1}$) for $[FeLS_3]^{2+}$ and at 555.0 ± 1.0 nm ($\varepsilon_{max} = 5100$–$7500\ l\ mol^{-1}\ cm^{-1}$) for $[FeL_2]^{2+}$. The complexation equilibria are studied at an extended temperature range of 4, 13, 20 and 32 ± 1 °C in 50% (v/v) PC/MeOH. The values of formation constants ($\log_{10}\beta_2 = 10.90$–11.47) are calculated and found to decrease with increasing temperature. The thermodynamic parameters (ΔH and ΔS) for complexation equilibria are 50.52 kJ mol^{-1} and 43.28 J $mol^{-1}\ K^{-1}$, respectively. Study at low temperature (4 °C) reveals the likely formation of a tris-complex, $[FeL_3]^{2+}$ in addition to $[FeLS_3]^{2+}$ and $[FeL_2]^{2+}$ in solution. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The tridentate ligand, 2,6-bis-(benzimidazol-2′-yl)pyridine (bzimpy) coordinates to Fe(II) and forms the mono- and bis-ligated complex species, $[FeLS_3]^{2+}$ (S = solvent, L = bzimpy) and $[FeL_2]^{2+}$ at room temperatures [1,2]. The complexation equilibria are influenced by the partial dissociation of the bis-complex even in the presence of excess ligand in MeOH. In fact, the complete complexation at stoichiometric amounts of $[bzimpy]/[Fe]^{2+} = 2{:}1$ is only found in 50% (v/v) PC/MeOH (PC = propanedilo-1,2-carbonate). [1,2] Substituent- and solvent-effects on the formation of 4-X-bzimpy (X = H, OH and Cl) with Fe(II) are also reported. [1] The bis-complex $[FeL_2]^{2+}$ is isolated as a solid and found to exhibit strong spin-crossover behaviour both in solution and in the solid state. Low temperatures favour the low-spin (LS)-state, while high temperatures favour the high-spin (HS)-state of the bis-complex [2–9]. Coordination of the ligand, bzimpy to the metal ions increases the acidity of the imino-hydrogen in 4-X-bzimpy. [6,8] Furthermore, deprotonation of the imino-hydrogen of the complex in base solution results in a change in the spin-state to the LS-state. [6,8,9] However, the complexation equilibria and the spin-crossover equilibria

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of the complex might well be closely related to each other, as both are temperature dependent.

In view of this consideration, it is planned to determine the formation constant values of bzimpy with Fe(II) at the extended temperature range of 4, 13, 20 and 32 ± 1 °C in 50% (v/v) PC/MeOH, and to evaluate the values of the thermodynamic parameters (ΔH and ΔS), in order to compare these results with those observed for spin-crossover behaviours of the complex in solution. The technique of UV–VIS absorption spectroscopy was employed to determine the values of formation constants [1,2].

2. Experimental

Commercial grade MeOH (Fa. Riedel) was refluxed over CaO for 24 h and fractionally distilled. PC (Loba) was refluxed for 24 h under reduced pressure and was fractionally distilled. $FeCl_2{\cdot}4H_2O$ (99.99%, Aldrich) was used as received. The ligand, bzimpy was prepared according to the literature [4,5,10].

2.1. Spectrophotometric measurements

The UV–VIS absorption spectra were obtained with a Hitachi U-2000 Spectrophotometer, equipped with an electronically thermostated cell holder (Hitachi) for the range of temperature 0–100 ± 0.5 °C; the quartz cell had a path length of 1.0 cm. The actual 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. All measurements were carried out in a nitrogen atmosphere, with solvents being deoxygenated by passing nitrogen gas to avoid oxidation effects. Below room temperature (20 °C) dry nitrogen gas was blown into the cell compartment. Spectrophotometric titrations of $FeCl_2{\cdot}4H_2O$ (2.98×10^{-4} to 3.2×10^{-5} M) with bzimpy solution were carried out in the presence of excess ligand (i.e. $[\text{bzimpy}]/[\text{Fe}]^{2+} = 7\text{–}10$) in 50% (v/v) PC/MeOH at temperatures of 4, 13, 20 and 32 ± 1 °C, respectively. The values of the observed molar extinction co-efficients (ε_{obs}) were corrected for changes in solvent density, changing the concentration of solute, with temperature. [11].

3. Results and discussion

The UV–VIS absorption spectra for titration of $FeCl_2{\cdot}4H_2O$ with bzimpy in 50% (v/v) PC/MeOH at 20 °C are shown in Fig. 1 and the spectral data are listed in Table 1. In the course of titration the iron solution gradually changes to light red, then wine red and finally, to an intense red violet. The spectra show different characteristic bands of: (i) very strong absorption bands due to internal ligand transitions ($\pi \rightarrow \pi^*$) at higher energies (<420 nm), (ii) strong broad metal-to-ligand charge transfer (MLCT) ($t_{2g} \rightarrow \pi^*$, MLCT) bands at 420–600 nm and (iii) weak d–d transition ($t_{2g} \rightleftarrows e_g$) bands at 600–800 nm (Fig. 1) [1–5,12]. It has been suggested that the strong broad MLCT band might result from the contribution of a combination of both LS- and HS-isomer bands of the complex [2–7]. With the addition of bzimpy to the iron solution, the MLCT band becomes increasingly populated and shifts to the longer wavelength, suggesting the formation of the mono- and bis-ligated-species, $[FeLS_3]^{2+}$ and $[FeL_2]^{2+}$ according to reaction Scheme 1 [1,2,13]. At the very low ratio of $[\text{bzimpy}]_T/$

Table 1
Absorption maxima and the molar extinction co-efficient of mono-, bis- and tris-complexes in 50% (v/v) PC/MeOH at different temperatures

Temperature[a] (°C)	$[FeLS_3]^{2+}$		$[FeL_2]^{2+}$		$[FeL_3]^{2+}$	
	λ_{max} (nm)	ε_{max} (l mol^{-1} cm^{-1})	λ_{max} (nm)	ε_{max} (l mol^{-1} cm^{-1})	λ_{max} (l mol^{-1} cm^{-1})	ε_{max} (l mol^{-1} cm^{-1})
4	500 ± 5.0	700 ± 50	556.0 ± 0.5	7500 ± 100	556.0 ± 0.5	7500 ± 100
13	500 ± 5.0	600 ± 50	555.5 ± 0.5	6650 ± 100		
20	500 ± 5.0	300 ± 50	555.0 ± 0.5	5650 ± 100		
32	500 ± 5.0	200 ± 50	554.0 ± 0.5	5100 ± 100		

[a] All readings are ±1 °C.

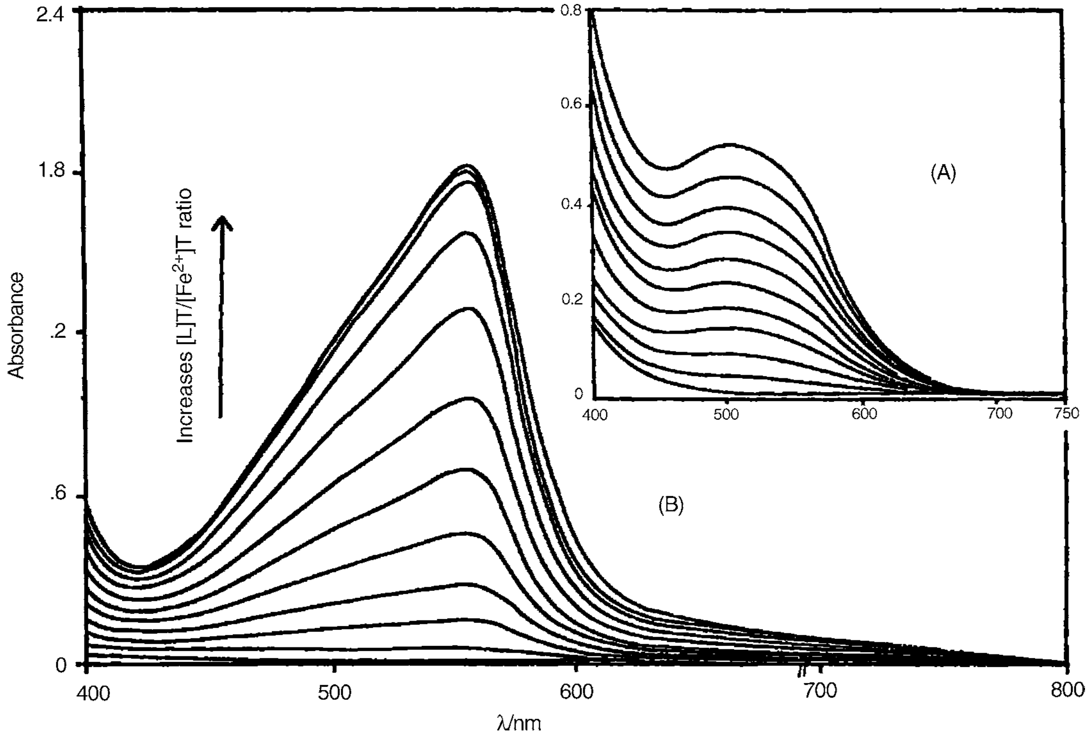

Fig. 1. (A) UV–VIS absorption spectra for titration of $FeCl_2 \cdot 4H_2O$ (2.9861×10^{-4} M) with bzimpy (L) in 50% (v/v) PC/MeOH at 20 ± 1 °C: $[L]_T/[Fe^{2+}]_T = 0.0$, 0.02, 0.05, 0.08, 0.12, 0.15, 0.18, 0.21, 0.24, 0.28 and 0.31, respectively. (B) UV–VIS absorption spectra for titration of $FeCl_2 \cdot 4H_2O$(3.1951×10^{-5} M) with bzimpy (L) in 50% (v/v) PC/MeOH at 20 ± 1 °C: $[L]_T/[Fe^{2+}]_T = 0.0$, 0.24, 0.49, 0.73, 0.97, 1.21, 1.46, 1.70, 1.94, 2.43, 2.91 and 4.13, respectively.

$[Fe^{2+}]_T < 0.4$, the mono-species $[FeLS_3]^{2+}$ is formed which shows the MLCT band with absorption maximum at 500 ± 5 nm (λ_{max}) and the molar extinction coefficient of $\varepsilon_{max} = 200–700\ l\ mol^{-1}\ cm^{-1}$ (Fig. 1(A) and Table 1). On further addition of bzimpy into the metal solution, the MLCT band shifts to the longer wavelength with an increase of molar extinction coefficient and finally, remains almost unchanged at the extended ratios >2.0–10.0 (Fig. 1(B)). The result suggests the formation of the bis-complex, $[FeL_2]^{2+}$ which shows the MLCT bands with $\lambda_{max} = 555.0 \pm 1.0$ nm and $\varepsilon_{max} = 5100–7500\ l\ mol^{-1}\ cm^{-1}$) (Table 1). Indeed, the ε_{max} versus $[L]_T/[Fe^{2+}]_T$ curve (Fig. 2, experimental data points) indicates the complete formation of $[FeLS_3]^{2+}$ and $[FeL_2]^{2+}$ at stoichiometric amounts of $[L]_T/[Fe^{2+}]_T = 1.0$ and 2.0, respectively. The ligand coordinates to Fe(II) in a tridentate manner in the $[FeLS_3]^{2+}$ and $[FeL_2]^{2+}$ complexes [1,2]. However, the curve in Fig. 2 (experimental data points) at low temperature (4 °C) suggests that the formation of a tris-ligated complex, $[FeL_3]^{2+}$, at a ratio of $[L]_T/[Fe^{2+}]_T = 3.0$, in addition to $[FeLS_3]^{2+}$ and $[FeL_2]^{2+}$ is more likely. Here, the ligand seems to coordinate in a bidentate fashion in to the Fe(II). No clear distinction was observed between the spectra of $[FeL_3]^{2+}$ and $[FeL_2]^{2+}$, and the spectral data found for $[FeL_2]^{2+}$ are also used for $[FeL_3]^{2+}$ in determining the values of formation constants (Table 1).The values of formation constants ($\log_{10} \beta_2$) are calculated using a curve fitting procedure, as described in earlier papers [1,2,13], and are listed in Table 2. The formation curves, ε_{max} versus $[L]_T/[Fe^{2+}]_T$ obtained from the curve fitting of the

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

Scheme 1. L = bzimpy, S = solvent.

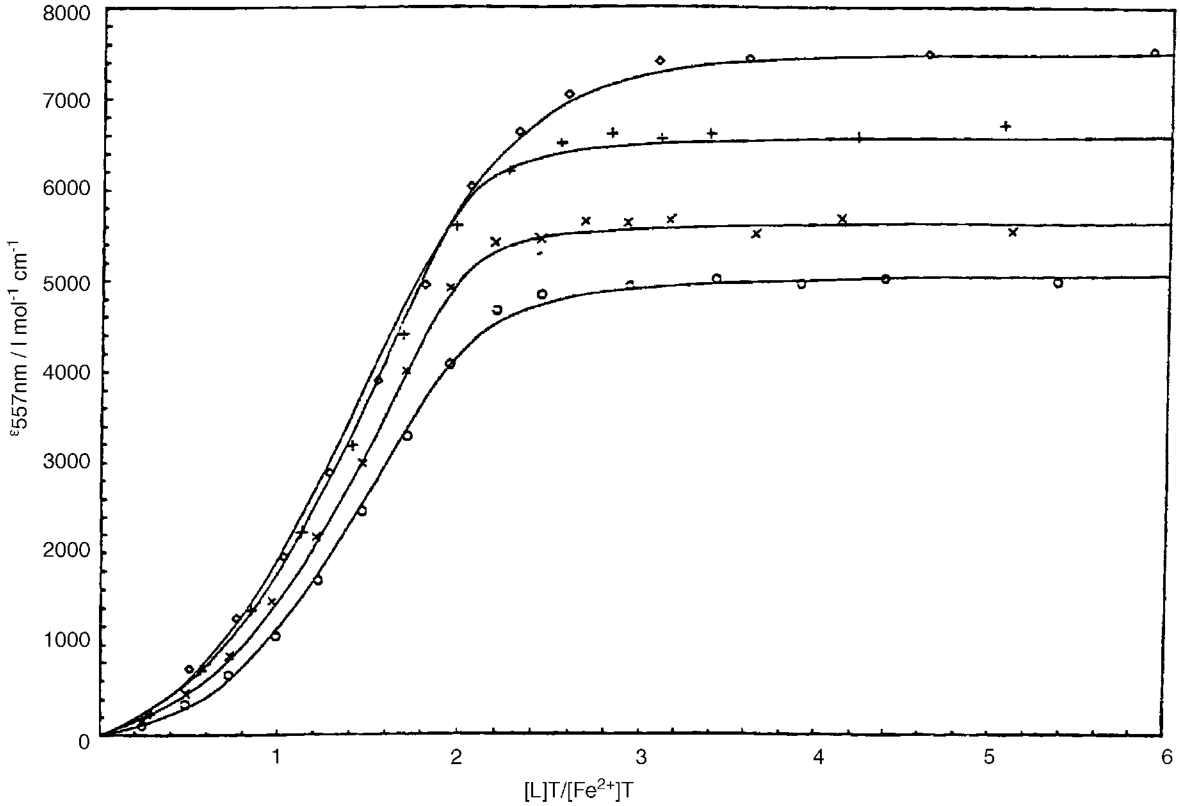

Fig. 2. Formation curves of the $[FeLS_3]^{2+}$, $[FeL_2]^{2+}$ and $[FeL_3]^{2+}$ (L = bzimpy) at $\lambda = 557$ nm and at different temperatures in 50% (v/v) PC/MeOH—at 4 °C: $[Fe^{2+}]_T = 2.0704 \times 10^{-5}$ M, experimental (◇) and theoretical (—); at 13 °C: $[Fe^{2+}]_T = 2.0895 \times 10^{-5}$ M, experimental (+) and theoretical (—); at 20 °C: $[Fe^{2+}]_T = 3.1951 \times 10^{-5}$ M, experimental (×) and theoretical (—); at 32 °C: $[Fe^{2+}]_T = 2.2804 \times 10^{-5}$ M, experimental (○) and theoretical (—).

respective experimental data for titration of Fe(II) with bzimpy, are shown in Fig. 2. The values of molar extinction co-efficients (ε_{max}) for the mono-species, $[FeLS_3]^{2+}$ are calculated from the experimental data at the very low ratio of $[L]_T/[Fe^{2+}]_T < 0.4$ and at a high concentration of Fe(II) ion. Accordingly, the values of ε_{max} for $[FeL_2]^{2+}$ are obtained with a large excess of bzimpy to Fe(II) ion (i.e. $[L]_T/[Fe^{2+}]_T > 2.0$–10.0), where the values are found to be almost same. The values of ε_{max} for $[FeLS_3]^{2+}$ and $[FeL_2]^{2+}$, used in the

Table 2
Formation constants and thermodynamic parameters of the $[FeLS_3]^{2+}$, $[FeL_2]^{2+}$ and $[FeL_3]^{2+}$ (L = bzimpy) in 50% (v/v) PC/MeOH at different temperatures

Temperature (°C)[a]	$\log_{10} K_1$[b]	$\log_{10} K_2$[b]	$\log_{10} K_3$[b]	$\log_{10} \beta_2$	$\log_{10} \beta_3$
4	5.90	5.05	4.0	10.95	14.95
13	6.11	5.36		11.47	
20	6.00	5.26		11.26	
32	5.88	5.03		10.90	

$\Delta H = 50.52$ kJ mol^{-1}, $\Delta S = 43.28$ J mol^{-1} K^{-1}.

[a] All readings are ± 1.0.

[b] All values are calculated at $\lambda = 557$ nm and are±0.05.

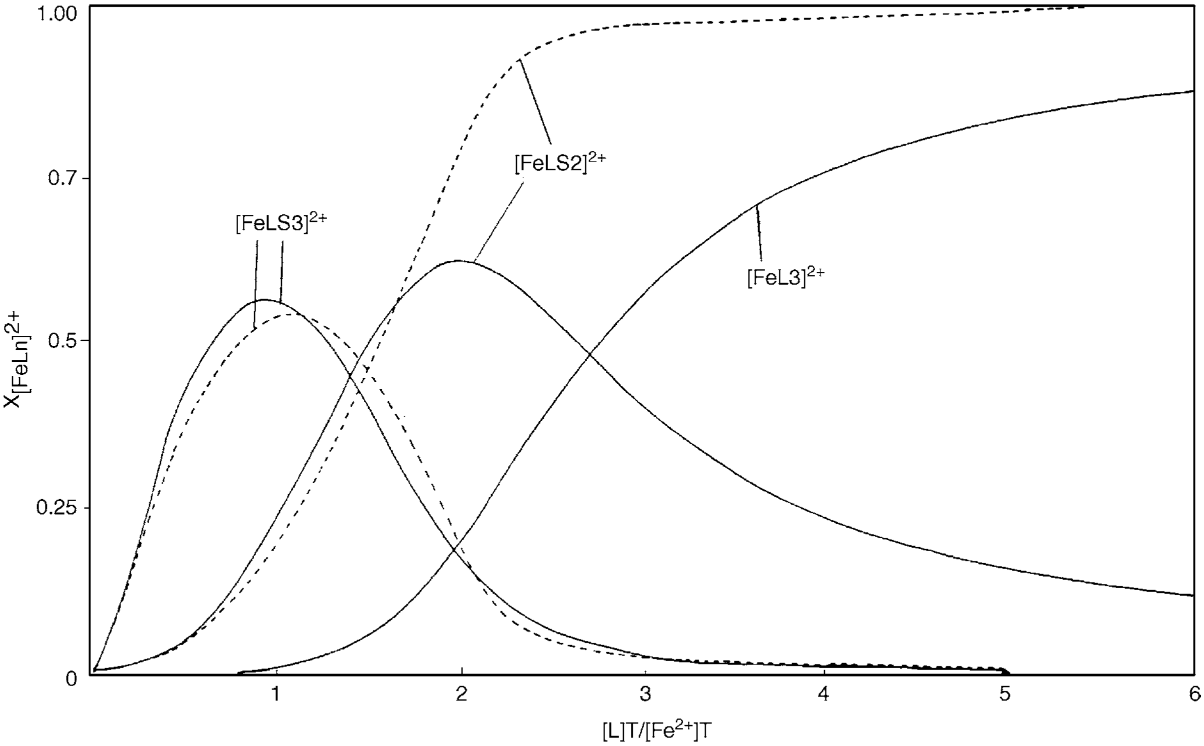

Fig. 3. The corresponding distribution curves of the $[FeLS_3]^{2+}$, $[FeL_2]^{2+}$ and$[FeL_3]^{2+}$ species at 4 °C (—) and 20 °C (- - -) in 50% (v/v) PC/MeOH.

curve fitting procedure, are listed in Table 1. However, the formation curve modelled for the two ligated-species, $[FeLS_3]^{2+}$ and $[FeL_2]^{2+}$, fits satisfactorily to the experimental data at 13, 20 and 32 °C (Fig. 2). This is clearly shown from superimposition of the theoretical curve (solid line) to the experimental data points (scattered points). These results further confirm the formation of $[FeLS_3]^{2+}$ and $[FeL_2]^{2+}$ as suggested in the reaction Scheme 1. The formation curve for the experimental data at low temperatures (4 °C) can be fitted quite well by a model involving the three ligated-species, $[FeLS_3]^{2+}$ and $[FeL_2]^{2+}$, $[FeL_3]^{2+}$. Hence, at low temperature it is likely that a new tris-complex in addition to the mono- and bis-complexes is formed in solution. The corresponding distribution curves of $X[FeL_n]^{2+}$ versus $[L]_T/[Fe^{2+}]_T$ of these complexes at 4 and 20 °C are shown in Fig. 3.

Table 2 shows that the value of formation constants decreases from mono-to bis-complex which might be due to the steric effects experienced by this kind of bulky ligand. The relatively large values of formation constants ($\log_{10}\beta_2 = 10.90$–11.47) in comparison to bidentate ligands such as 2-2′-bipyridine ($\log_{10}\beta_2 = 8.0$) [14], 2-(2′-pyridyl)imidazole ($\log_{10}\beta_2 = 7.9$) [15], 4-(2′-pyridyl)imidazole ($\log_{10}\beta_2 = 9.0$) [16] and 2-(2′-pyridyl)benzimidazole ($\log_{10}\beta_2 = 10.40$) [13] with Fe(II) suggest that bzimpy acts as a tridentate in both mono- and bis-complexes. However, the value of the formation constant for tris-complex ($\log_{10}\beta_3 = 14.95$) (where the ligand acts as a bidentate at 4 °C) is comparable with the corresponding one found for the bidentate ligand, 2-(2′-pyridyl)benzimidazole with Fe(II) ($\log_{10}\beta_3 = 14.70$ [13]). The relatively large values of formation constants in 50% (v/v) PC/MeOH ($\log_{10}\beta_2 = 10.90$–11.47) rather than in MeOH ($\log_{10}\beta_2 = 10.70$ [1]) might be explained by Gutmann's donor–acceptor properties of solvents.[1,17] The strong donor MeOH (DNMeOH = 19.1 > DNPC = 15.1 [17]) causes a partial dissociation of the complex via coordination to the iron and results in a small formation constant value. This effect might be more pronounced in $[FeL_2]^{2+}$ than in $[FeLS_3]^{2+}$.

The effect of temperature on complexation equilibria are reflected from Table 2, which shows that the values of formation constants decrease with increasing temperature and vice versa. These results are in good agreement with the finding that low temperature favors the LS-state of the complex and the observed strong ligand field (Δ°_{LS}) leads to a large formation value of the complex [1,2,5,14,18,19]. On the other hand, the high temperature results in the less stable (i.e. weak ligand field, Δ°_{HS}) HS-state of the complex. Hence, it could be said that the observed effect of temperature on complexation equilibria might have some contribution from the change in the spin-state of the complex with temperature. The present values of enthalpy and entropy (ΔH and ΔS) associated with complexation equilibria are calculated from the linear plot of $\log_{10} \beta_2$ versus $1/T$ and are found to be 50.52 kJ mol^{-1} and 43.28 J mol^{-1} K^{-1} (Table 2), respectively. The enthalpy value is obviously higher than that found for the spin-crossover equilibria of this complex in 50% (v/v) PC/MeOH [18] (14.73 kJ mol^{-1}) and in PC [19] (17.45 KJ mol^{-1}), where no complexation equilibria are involved. Hence, the enthalpy value involved for the complexation equilibrium of the complex is (50.52–14.73) 35.79 kJ mol^{-1}.

In conclusion, it could be said that the complexation equilibria and the spin-crossover equilibria of the complex are closely related to each other.

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References

[1] M. Enamullah, W. Linert, J. Coord. Chem. 40 (1996) 193.
[2] M. Enamullah, Spin-crossover behaviour of transition metal(II) ions, Ph.D. thesis, Institute of Inorganic Chemistry, Technical University of Vienna, 1994.
[3] S. Rüttimann, C.M. Moreau, A.F. Williams, G. Bernardinelli, A.W. Addison, Polyhedron 11 (1992) 635.
[4] A.W. Addison, S. Burman, C.G. Wahlgren, O.A. Rajan, T.M. Rowe, E. Sinn, J. Chem. Soc., Dalton Trans. (1987) 2621.
[5] M. Enamullah, W. Linert, V. Gutmann, R.F. Jameson, Monatsh. Chemie 125 (1994) 661.
[6] M. Enamullah, W. Linert, V. Gutmann, R.F. Jameson, Monatsh. Chemie 125 (1994) 1301.
[7] M. Enamullah, W. Linert, V. Gutmann, Vibrat. Spectrosc. 9 (1995) 265.
[8] M. Enamullah, W. Linert, J. Coord. Chem. 35 (1995) 325; M. Enamullah, W. Linert, J. Coord. Chem. 38 (1996) 337.
[9] M. Enamullah, F. Renz, U. El-Ayaan, G. Wiesinger, W. Linert, Vibrat. Spectrosc. 14 (1997) 95.
[10] A.W. Addison, P.J. Burke, J. Heterocycl. Chem. 20 (1983) 1481.
[11] R.F. Brunel, K.V. Bibber, International Critical Table, McGraw-Hill, New York, 1926; D. Ostfeld, I.A. Cohen, J. Chem. Educ. 49 (1972) 829.
[12] P. Krumholz, Inorg. Chem. 4 (1965) 612.
[13] M. Enamullah, J. Coord. Chem. 45 (1998) 23.
[14] H. Irving, D.P. Mellor, J. Chem. Soc. (1962) 5222.
[15] W.J. Eilbeck, F. Holmes, J. Chem. Soc. A (1967) 1777.
[16] W.J. Eilbeck, F. Holmes, G.G. Phillips, A.E. Underhill, J. Chem. Soc. A (1967) 1161.
[17] V. Gutmann, The Donor–Acceptor Approach to Molecular Interactions, Plenum Press, New York, 1978.
[18] M. Enamullah, J. Bangladesh Acad. Sci. 22 (1998) 63.
[19] M. Enamullah, J. Coord. Chem. 43 (1997) 231.