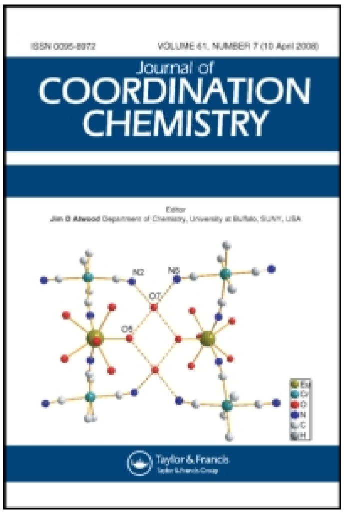

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STABILITY CONSTANTS FOR [2-(2′-PYRIDYL)BENZIMIDAZOLATO]IRON(II)

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The bidentate ligand, 2-(2′-pyridyl)benzimidazole (pybzim) coordinates to iron(II) and forms $[FeLS_4]^{2+}$, $[FeL_2S_2]^{2+}$ and $[FeL_3]^{2+}$ in solution. These complexes are characterized by electronic spectroscopy. The complexes show strong absorption bands (mlct) at 450 nm ($\epsilon_1 = 200 \pm 10\,M^{-1}cm^{-1}$), 470 nm ($\epsilon_2 = 700 \pm 20$) and 500 nm ($\epsilon_3 = 2100 \pm 100$), respectively. Stability constants were calculated in MeOH ($\log K_1 = 5.47$, $\log K_2 = 4.36$ and $\log K_3 = 3.15$) and in 50% (v/v) PDC/MeOH ($\log K_1 = 5.65$, $\log K_2 = 4.75$ and $\log K_3 = 4.30$) at 20°C. The values decrease on going from mono- to tris-complexes as a result of steric effects. Partial dissociation of the tris-complex occurs in the presence of excess ligand in MeOH and complete complexation is only found in 50% (v/v) PDC/MeOH.

Keywords: Iron(II); 2-(2′-pyridyl)benzimidazole (pybzim); stability constants

INTRODUCTION

α-Diimine ligands such as 2-2′-bipyridine,[1,2] 2-(aminomethyl)pyridine,[3] 2-(2′-pyridyl)imidazole,[4-6] 2-(2′-pyridyl)imidazoline,[2,6] 4-(2′-pyridyl)imidazole,[7] and 2-(2′-pyridyl)benzimidazole[2,6] coordinate to divalent transition metal ions as bidentates and form mono-, bis- and tris-complexes in solution. Tris-complexes of 2-(aminomethyl)pyridine, 2-(2′-pyridyl)imidazole and 2-(2′-pyridyl)benzimidazole with iron(II) show marked spin-crossover behaviour in solution and the solid state.[3,8-10] Other related triimine ligands such as 2,6-(dibenzothiazole-2′-yl)pyridine, 1,3-bis-(2′-pyridyl)-2,3-diaza-1-propane and their derivatives coordinate to transition metal ions to form mono- and bis-complexes.[11-13] However, recent investigations of

4-X-2,6-bis(benzimidazole-2′-yl)pyridine (X = H, Cl and OH) with iron(II) indicate the formation of both mono- and bis-complexes in solution.[14,15] The bis-complexes were isolated as solids and show pronounced spin-crossover behaviour in solution and solid state.[15–18] Coordination to metal ions increases the acidity of the imino-hydrogen atom of these ligands as a function of complex stability.[1,2,4–7,16,19] Further, the cationic complexes of diimines[2,5–6,11] and triimines[16,19–20] can be deprotonated with base to give neutral complexes.

However, coordination of 2-(2′-pyridyl)benzimidazole (L = pybzim) with iron(II) yields $[FeLS_4]^{2+}$, $[FeL_2S_2]^{2+}$ and $[FeL_3]^{2+}$ as shown in Scheme 1. It was planned to determine the stability constants ($\log K_1$, $\log K_2$ and $\log K_3$) of these species in MeOH and in 50% (v/v) PDC/MeOH at 20°C. Solvent donor–acceptor properties might influence the stability constants.

$$[FeS_6]^{2+} + L \underset{-2S}{\overset{K_1}{\rightleftharpoons}} [FeLS_4]^{2+} + L \underset{-2S}{\overset{K_2}{\rightleftharpoons}} [FeL_2S_2]^{2+} + L \underset{-2S}{\overset{K_3}{\rightleftharpoons}} [FeL_3]^{2+}$$

Scheme 1 (S = solvent, L = pybzim)

EXPERIMENTAL

$FeCl_2 \cdot 4H_2O$ (Aldrich) was used as received. Commercial grade MeOH was refluxed over CaO for 24 hours and fractionally distilled. Propanediolcarbonate (PDC) (Loba) was refluxed for 24 hours under reduced pressure and fractionally distilled. The ligand 2-(2′-pyridyl)benzimidazole (L = pybzim) was prepared according to the literature.[6,9]

Spectrophotometric Measurements

Electronic spectra were obtained with a Hitachi U-2000 spectrophotometer, equipped with an electronically thermostatted cell holder (Hitachi). The temperature was recorded using a Copper–Constantan thermocouple mounted within the 1 cm quartz cell and homogeneous temperature distribution within the cell was ensured by use of a magnetic stirrer. Spectrophotometric titrations of $FeCl_2 \cdot 4H_2O$ with 2-(2′-pyridyl)benzimidazole solution were carried out at ligand-to-iron ($[L]_T/[Fe^{2+}]_T$) ratio of 0 to 20 in MeOH and in 50% (v/v) PDC/MeOH at 20 ± 0.1°C. All measurements were performed under nitrogen with solvents deoxygenated by nitrogen to avoid any oxidation.

RESULTS AND DISCUSSION

Electronic titration spectra of $FeCl_2 \cdot 4H_2O$ with 2-(2′-pyridyl)benzimidazole in MeOH at 20 ± 0.1°C are shown in Figure 1. With increasing $[L]_T/[Fe^{2+}]_T$ ratio the light yellowish solution becomes gradually light red, and finally red, and an increase of absorptivities of the spectra is observed. The molar absorptivity *vs* ligand-to-iron ratio plot (Figure 2) suggests that $[FeLS_4]^{2+}$, $[FeL_2S_2]^{2+}$ and $[FeL_3]^{2+}$ are formed consecutively at stoichiometric amounts of pybzim to iron(II) according to Scheme 1. Strong metal-to-ligand charge transfer ($T_{2g} \rightarrow \pi^*$: mlct) bands for these complexes are observed in the range of 400 to 600 nm as for other α-diimine ligands with iron(II).[3,8-10,14,15] Absorption maxima (λ_{max}) and molar absorptivities ($\epsilon_{max}/M^{-1}\,cm^{-1}$) are listed in Table I. $[FeLS_4]^{2+}$ shows a strong mlct band

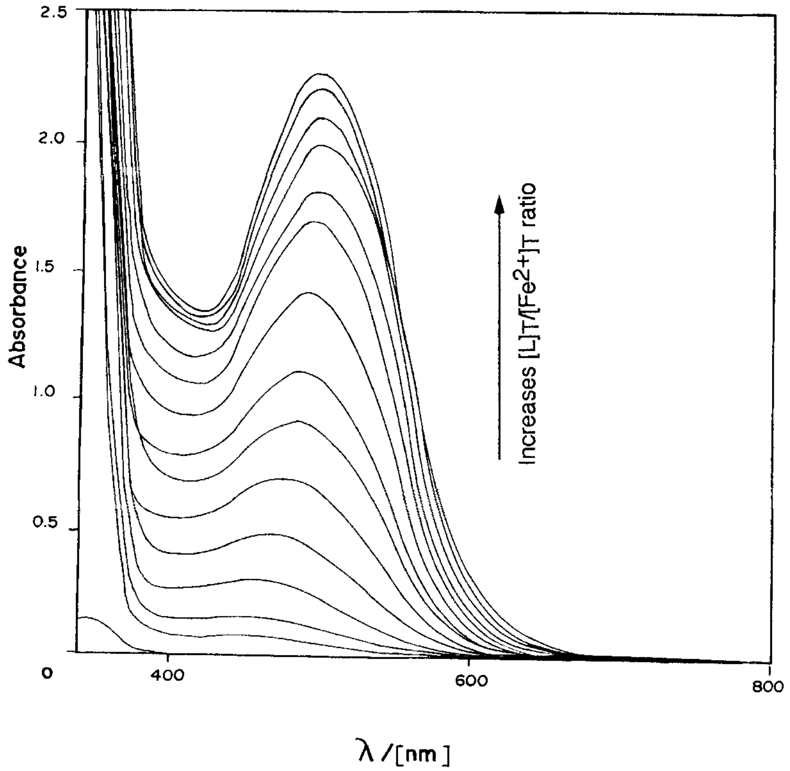

FIGURE 1 Electronic titration spectra of $FeCl_2 \cdot 4H_2O$ (2.026×10^{-4} M) with pybzim in MeOH at $[L]_T/[Fe^{2+}]_T = 0.0, 0.21, 0.43, 0.85, 1.28, 1.64, 1.97, 2.29, 2.62, 2.95, 3.60, 4.26, 5.57,$ 9.50 and 14.74, respectively, at 20°C.

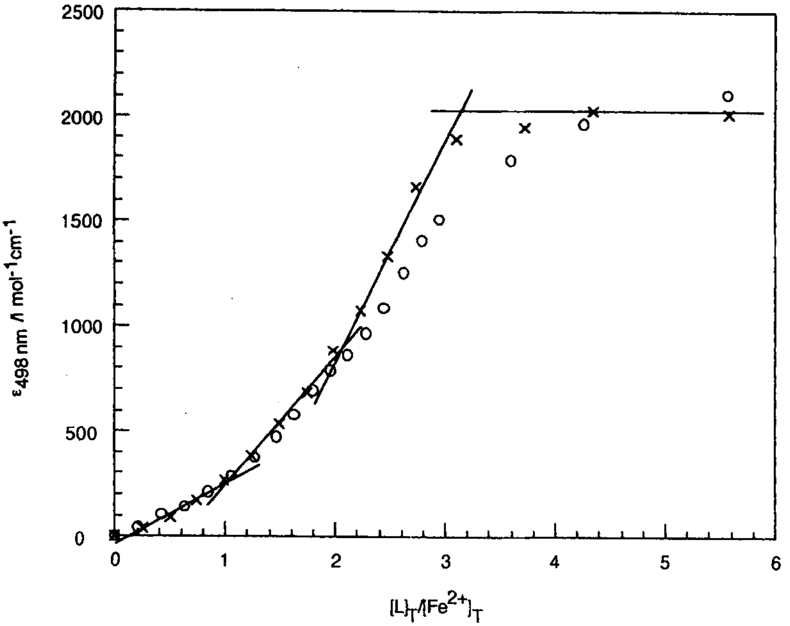

FIGURE 2 Changes of molar absorptivities (ϵ/M^{-1} cm^{-1}) at 498 nm with increasing ligand-to-iron ratio for titration of $FeCl_2 \cdot 4H_2O$ with pybzim solution at 20°C: (o o o) in MeOH, $[Fe^{2+}]_T = 2.026 \times 10^{-4}$M; (× × ×) in 50% (v/v) PDC/MeOH, $[Fe^{2+}]_T = 7.080 \times 10^{-5}$M.

at about 450 nm ($\epsilon_{max} = 200 \pm 10$) at very low ligand-to-iron ratio. With increasing ligand-to-iron ratio, the band shifts to longer wavelength as $[FeL_2S_2]^{2+}$ and $[FeL_3]^{2+}$ form. Absorption maxima ($\lambda_{max} \approx 500 \pm 0.5$ nm) and molar absorptivities ($\epsilon_{max} \approx 2050 \pm 50$) of the mlct bands remain almost unchanged at ligand-to-iron ratios of 3.0 to 20 and indicating the formation of the tris-complex in 50% (v/v) PDC/MeOH. However, the tris-complex shows an absorption maximum at about 498 nm ($\epsilon_{max} \approx 2200 \pm 50$) which changes with further addition of ligand in MeOH. The bis-complex has an absorption maximum at about 470 nm ($\epsilon \approx 700 \pm 20$) at a ligand-to-iron ratio of 1.0 to 2.0. The mlct band consists of both low-spin (LS) and high-spin (HS) contributions for this complex.[8–10] The very strong absorption bands at higher energies (< 400 nm) are essentially due to $\pi \rightarrow \pi^*$ electron transitions in the ligand.[3,8,9] The d-d transition ($t_{2g} \rightleftharpoons e_g$) bands, usually observed for most spin-crossover iron(II)-imine complexes,[3,16] are obscured by the mlct.[8,10]

Comparable studies of the equilibria in MeOH and in 50% (v/v) PDC/MeOH suggest that phenomena are influenced by partial dissociation of the tris-complex even in the presence of excess ligand in MeOH, as can be seen from the molar absorptivity *vs* $[L]_T/[Fe^{2+}]_T$ curve (Figure 2). Indeed, complete complexation at stoichiometric amounts of pybzim to iron(II) at $[L]_T/[Fe^{2+}]_T = 3.0$ is only found in 50% (v/v) PDC/MeOH (Figure 2). The formation curve obtained from curve fitting of titration data of iron(II) with pybzim is shown in Figure 3A.[14,15] Values of molar absorptivities used for curve fitting are listed in Table I. The formation curve only can be fitted satisfactorily by a model involving at least three species, as shown from the coincidence of the theoretically calculated curve with the experimental data. These results confirm that $[FeLS_4]^{2+}$, $[FeL_2S_2]^{2+}$ and $[FeL_3]^{2+}$ are formed at $[L]_T/[Fe^{2+}]_T = 1.0$, 2.0 and 3.0, respectively, according to Scheme 1. Corresponding distribution curves are shown in Figure 3B. Values of stability constants ($\log K_1$, $\log K_2$ and $\log K_3$), evaluated from curve fitting, are listed in Table II and show a decrease on going from $[FeLS_4]^{2+}$ to $[FeL_3]^{2+}$; this might be due to steric effects.[13-15] Results ($\log_{10}\beta_3 = 12.98$ and 14.70) are similar in magnitude to those found for comparable α-diimine ligands, such as 2-2′-bipyridine ($\log_{10}\beta_3 = 17.50$),[1] 2-(2′-pyridyl)imidazole ($\log_{10}\beta_3 = 11.60$)[4] and 4-(2′-pyridyl)imidazole ($\log_{10}\beta_3 = 13.76$)[7] with iron(II). Further, the mono- and bis-species show low values of stability constants ($\log K_1$ and $\log K_2$) compared to corresponding species of 2,6-bis(benzimidazole-2′-yl)pyridine (bzimpy) with iron(II) (Table II), suggesting that pybzim acts as a bidentate.

Results in Table II show no influence of change in spin-state on complex formation, as reflected in the significant increase of $\log K_3$ values for phen and bipy,[1] explained by thermodynamic stabilization due to an abrupt change to the low-spin state on formation of $[FeL_3]^{2+}$. However, it may be mentioned that the energetic differences between the two spin-states of the iron(II)-2-(2′-pyridyl)benzimidazole complex are too small to be reflected in the stability constants, as with iron(II)-2,6-bis(benzimidazole-2′-yl)-pyridine.[14,15]

Table II shows that the stability constants are influenced by the solvent. $\log K_1$ and $\log K_2$ values are slightly changed, whereas $\log K_3$ increases by

TABLE I Absorption maxima and molar absorptivities of the complexes ($[FeLS_4]^{2+}$, $[FeL_2S_2]^{2+}$ and $[FeL_3]^{2+}$) in MeOH and in 50% (v/v) PDC/MeOH at 20°C

	$[FeLS_4]^{2+}$		$[FeL_2S_2]^{2+}$		$[FeL_3]^{2+}$	
	λ_{max} [nm]	ϵ_{max} [$l\,mol^{-1}\,cm^{-1}$]	λ_{max} [nm]	ϵ_{max} [$l\,mol^{-1}\,cm^{-1}$]	λ_{max} [nm]	ϵ_{max} [$l\,mol^{-1}\,cm^{-1}$]
MeOH	~450	200 ± 10	~470	700 ± 20	498	2200 ± 50
PDC/MeOH	~450	200 ± 10	~470	700 ± 20	500	2050 ± 50

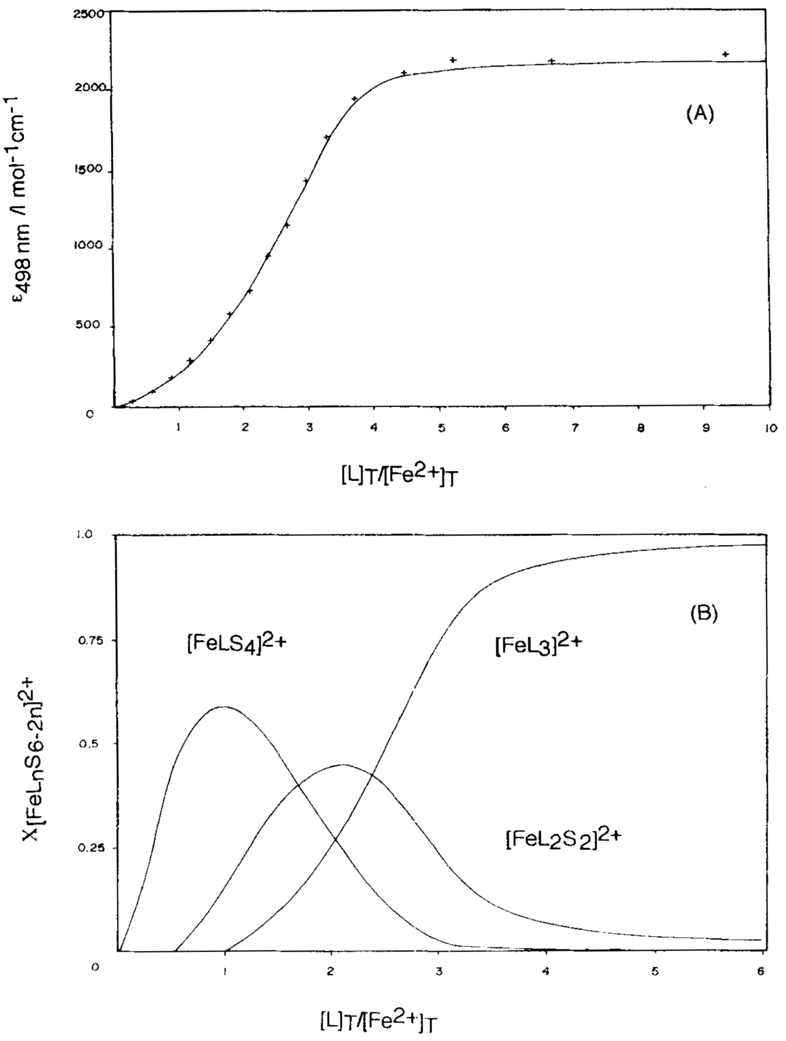

FIGURE 3 (A) Typical formation curves for $[FeLS_4]^{2+}$, $[FeL_2S_2]^{2+}$ and $[FeL_3]^{2+}$ in 50% (v/v) PDC/MeOH: (exptl. +++ and cald. ——) at $\lambda = 498$ nm and 20°C; (B) their corresponding distribution curves.

more than one unit in 50% (v/v) PDC/MeOH compared to MeOH. These results might be explained by Gutmann donor–acceptor properties of the solvents.[21] Generally, a strong donor solvent favours dissociation of complex through coordination with iron(II) and thereby decreases the stability constant. As a result, the complex shows lower stability in MeOH ($DN_{MeOH} = 19.1 > DN_{PDC} = 15.1$). These results are in good agreement

TABLE II Stability constants for the complexes of pybzim and bzimpy with iron(II) in MeOH and in 50% (v/v) PDC/MeOH at 20°C

Ligand	$\log K_1$	$\log K_2$	$\log K_3$	$\log_{10}\beta_2$	$\log_{10}\beta_3$	*Ref.*
pybzim*	5.47	4.36	3.15	9.83	12.98	this work
pybzim†	5.65	4.75	4.30	10.40	14.70	this work
bzimpy*	5.90	4.80	—	10.70	—	14
bzimpy†	6.15	5.30	—	11.45	—	14

*In MeOH and †in 50% (v/v) PDC/MeOH; pybzim = 2-(2′-pyridyl)benzimidazole: $\log K_{1-3}$ calculated at 498 nm; bzimpy = 2,6-bis(benzimidazole-2′-yl)pyridin: $\log K_{1-2}$ calculated at 557 nm; all $\log K$ values are ±0.10.

with studies of solvent influence on the stability of complexes of 2,6-bis (benzimidazole-2′-yl)pyridine with iron(II).[14]

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