

20. Synthesis and Electronic Properties of Intensely Coloured Iron(II) Complexes with New 4-Substituted Planar Tridentate Nitrogen Ligands Analogous to 2,2':6',2''-Terpyridine

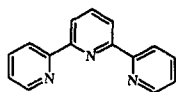
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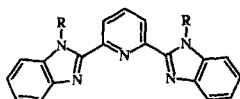
(27.VIII.92)

The *para*-substituted tridentate ligands 2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]-4-(4'-X-phenyl)-pyridine (X = H: L^3 ; X = NO_2 : L^4 ; X = NEt_2 : L^5) have been synthesized in six steps using *Kröhnke* reactions. Spectroscopic results show that the electronic properties of the ligands are strongly influenced by the nature of the substituent bound to the pyridine ring and extended *Hückel* calculations performed on 4-(X-phenyl)pyridine fragments give a qualitative insight into the factors responsible for the striking differences observed in the absorption spectra. Upon complexation to Fe^{II} , the ligands L^2 – L^5 give intensely coloured pseudo-octahedral low spin $[\text{Fe}(\text{L}^n)_2]^{2+}$ ($n = 2$ –5) complexes in acetonitrile solution. Electrochemical and spectroscopic measurements show that the particular electronic characteristics associated with each substituent strongly influence the properties of the resulting Fe^{II} complexes as demonstrated by the very intense MLCT transition ($\epsilon > 50000 \text{ M}^{-1} \text{ cm}^{-1}$) observed in the green complex $[\text{Fe}(\text{L}^5)_2]^{2+}$.

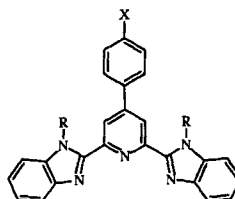
Introduction. – Two themes of current interest in coordination chemistry are the synthetic modification of multidentate ligands in such a way as to vary in a predictable fashion the properties of their complexes, and the linking of multidentate ligands together in such a way as to favour the formation of structured polynuclear complexes. We have recently been studying the complexes of the ligand 2,6-bis(1-methyl-benzimidazol-2-yl)-pyridine (L^1), a rigid tridentate ligand which is structurally [1] [2] and chemically [1] [3] analogous to 2,2':6',2''-terpyridine (terpy). L^1 forms a double-stranded helicate with Cu^{I} [4], and two L^1 units may be linked together to give a bis-tridentate ligand which forms a triple-stranded helicate with Eu^{III} [5]. In contrast to terpy, L^1 may readily be derivatised at the benzimidazole groups to give soluble ligands [6]. It has been shown that derivatisation of terpy in the 4'-position can lead to the formation of a branched polyterpyridyl ligand



terpy



R = CH_3 : L^1
R = $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{CH}_2$: L^2



R = $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{CH}_2$; X = H: L^3
R = $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{CH}_2$; X = NO_2 : L^4
R = $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{CH}_2$; X = $\text{N}(\text{C}_2\text{H}_5)_2$: L^5

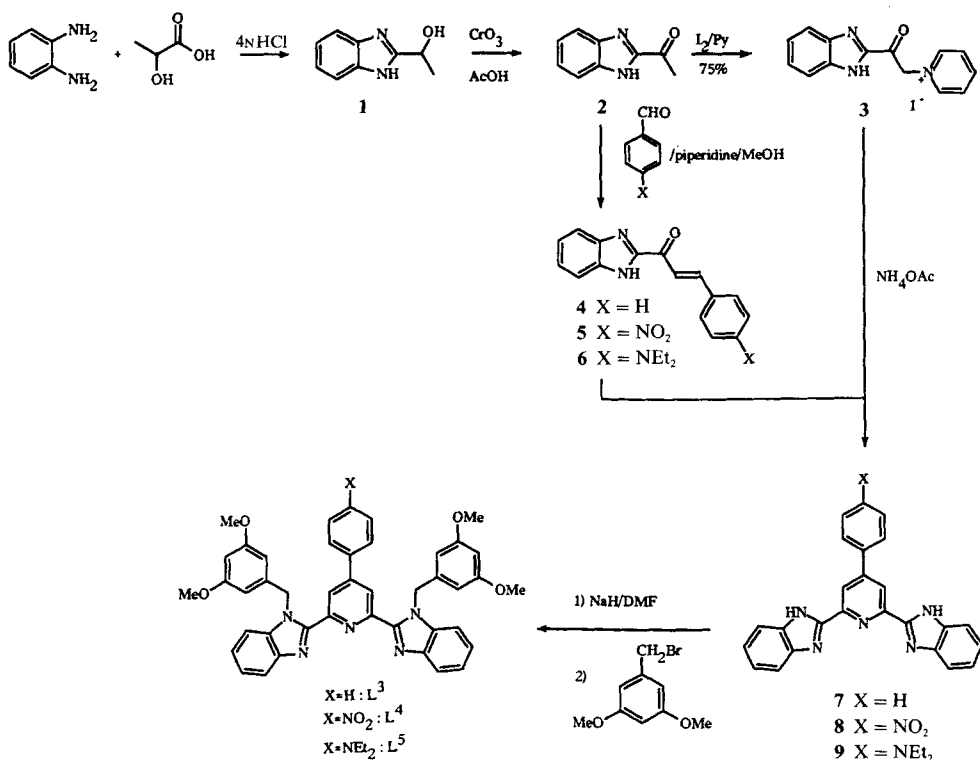
[7], and allows modification of the photophysical properties of the ligand [8], and the synthesis of coloured complexes with Fe^{II} which have been used for the spectrophotometric determination of iron [9]. These results, coupled with our recent observations of the photophysical properties of the lanthanide complexes $[\text{Ln}(\text{L}^1)(\text{NO}_3)_3(\text{CH}_3\text{OH})]$ [10], prompted us to design new ligands, analogous to L^1 , but substituted in the 4-position of the pyridine ring by groups which might modify both the energy of the excited states centred on the ligand, and the complexation properties of the ligand.

In this paper, we report the preparation of the new ligands 2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]-4-(4'-X-phenyl)pyridine ($\text{X} = \text{H}$: L^3 ; $\text{X} = \text{NO}_2$: L^4 ; $\text{X} = \text{NEt}_2$: L^5). Data are presented to show that the nature of the substituent strongly modifies the electronic properties of the ligands leading to the formation of intensely coloured pseudo-octahedral low spin $[\text{Fe}(\text{L}^n)_2]^{2+}$ ($n = 2-5$) complexes.

Experimental. – Solvents and starting materials were purchased from Fluka AG (Buchs, Switzerland) and used without further purification, unless otherwise stated. Aluminium oxide (Merck act. II–III, 0.063–0.200 mm) and silica gel (Merck 60, 0.040–0.060 mm) were used for preparative column chromatography.

Preparation of the Ligands (Scheme). The ligand 2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]pyridine (L^2) was prepared as described in [6]. 2-Acetylbenzimidazole (**2**) [11] and 2-[3-(4'-X-phenyl)acryloyl]benzimidazole ($\text{X} = \text{H}$: **4**, $\text{X} = \text{NO}_2$: **5**; $\text{X} = \text{NEt}_2$: **6**) [12] were obtained according to published literature procedures.

Scheme



1-[(Benzimidazol-2-yl)carbonyl]methyl-1-pyridinium Iodide (**3**) [13]. 2-Acetylbenzimidazole (**2**; 2 g, 12.5 mmol) and 3.17 g (12.5 mmol) of I_2 were dissolved in dry distilled pyridine (40 ml) under an inert atmosphere. The mixture was heated at 100° for 15 h, then cooled to r.t., and the resulting brown precipitate was filtered, washed with pyridine/Et₂O 1:1 (50 ml) and Et₂O (2 × 100 ml). The dried crude product was carefully recrystallized from EtOH with charcoal to give 3.28 g (8.98 mmol; 72%) of **3** as dark yellow needles. M.p. 205° (dec.). TLC (silica gel; CH₂Cl₂/MeOH 1:1): R_f 0.07. ¹H-NMR ((D₆)DMSO): 6.54 (s, 2 H); 7.38 (t, ³J = 8, 1 H); 7.46 (t, ³J = 8, 1 H); 7.64 (d, ³J = 8, 1 H); 7.90 (d, ³J = 8, 1 H); 8.30 (t, ³J = 7, 2 H); 8.76 (t, ³J = 7, 1 H); 9.06 (d, ³J = 7, 2 H). ¹³C-NMR ((D₆)DMSO): 65.82 (secondary C); 113.06, 121.10, 123.72, 126.37, 127.77, 145.32, 146.51 (tertiary C); 134.42, 142.64, 146.51, 183.70 (quaternary C). FAB-MS: 238 ([M–I]⁺).

2,6-Bis(benzimidazol-2-yl)-4-phenylpyridine (**7**) and 2,6-Bis(benzimidazol-2-yl)-4-(4'-nitrophenyl)pyridine (**8**) [14]. Compound **3** (4 g, 10.95 mmol), 2.47 g (9.96 mmol) of 2-(3-phenylacryloyl)benzimidazole (**4**), and 30 g (389 mmol) of ammonium acetate were dissolved in EtOH (250 ml). The mixture was refluxed for 24 h under N₂ and then slowly cooled to r.t. The resulting white crystals were separated by filtration and recrystallized from MeOH to give 2.20 g (5.68 mmol; 57%) of **7**. M.p. > 230°. TLC (silica gel, MeOH): R_f 0.64. ¹H-NMR ((D₆)DMSO): 7.30 (m, 4 H); 7.5–7.6 (m, 3 H); 7.7–7.8 (m, 4 H); 8.0 (m, 2 H); 8.58 (s, 2 H); 13.0 (s, 2 H). ¹³C-NMR ((D₆)DMSO): 111.76, 118.38, 119.69, 122.23, 123.72, 127.03, 129.40, 129.90 (tertiary C); 136.49, 144.14, 148.53, 149.98, 150.43 (quaternary C). EI-MS: 387 (M⁺).

The same procedure was followed for the synthesis of **8**, but its very low solubility in MeOH did not allow recrystallization. The crude product was extracted with boiling MeOH (50 ml), filtered, and dried to give 72% of **8**. M.p. > 230°. TLC (silica gel, MeOH): R_f 0.69. ¹H-NMR ((D₆)DMSO): 7.30 (m, 4 H); 7.7 (m, 4 H); 8.2–8.4 (m, AA'BB', 4 H); 8.59 (s, 2 H); 12.99 (s, 2 H). ¹³C-NMR ((D₆)DMSO): 111.74, 118.48, 119.66, 122.17, 123.74, 124.11, 128.32 (tertiary C); 134.32, 142.34, 144.06, 147.34, 147.89, 148.62, 150.07 (quaternary C). EI-MS: 432 (M⁺).

2,6-Bis(benzimidazol-2-yl)-4-[4'-(diethylamino)phenyl]pyridine (**9**) [14]. Compound **3** (4 g, 10.95 mmol), 3.18 g (9.96 mmol) of 2-[3-[p-(diethylamino)phenyl]acryloyl]benzimidazole (**6**), and 30 g (389 mmol) of ammonium acetate were heated at 90° in AcOH (60 ml) until complete disappearance of **6** (TLC; silica gel, CH₂Cl₂/MeOH 9:1). The resulting dark mixture was poured into H₂O (300 ml) and the precipitate was filtered, washed with H₂O (50 ml), and recrystallized from MeOH to give 2.56 g (5.59 mmol; 56%) of **9** as yellow needles. M.p. > 230°. TLC (silica gel; CH₂Cl₂/MeOH 9:1): R_f 0.45. ¹H-NMR ((D₆)DMSO): 1.14 (t, ³J = 7, 6 H); 3.46 (q, ³J = 7, 4 H); 6.82 (m, AA'MM', 2 H); 7.28 (m, 4 H); 7.76 (m, 4 H); 7.85 (m, AA'MM', 2 H); 8.48 (s, 2 H); 13.7 (s, 2 H). ¹³C-NMR ((D₆)DMSO): 12.43 (primary C); 43.71 (secondary C); 111.70, 115.6 (br.), 116.40, 123.05, 127.90 (tertiary C); 121.6, 139.05 (br.), 148.76, 149.74, 150.74 (quaternary C). EI-MS: 458 (M⁺).

2,6-Bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]-4-(4'-X-phenyl)pyridine (X = H: L³; X = NO₂: L⁴; X = NEt₂: L⁵). The compounds **7–9** were alkylated with 3,5-dimethoxybenzyl bromide according to a previously published method [6] to give the ligands L^{3–5} which were purified by column chromatography (Al₂O₃; CH₂Cl₂) and then crystallized from CH₂Cl₂/hexane (L³, L⁴) or EtOH (L⁵) to give 86–93% yield of white (L³) and yellow (L⁴, L⁵) crystals.

2,6-Bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]-4-(4-phenyl)pyridine (L³): M.p. 198–200°. TLC (Al₂O₃, CH₂Cl₂): R_f 0.54. ¹H-NMR (CDCl₃): 3.55 (s, 12 H); 5.59 (s, 4 H); 6.01 (d, ⁴J = 2, 4 H); 6.30 (t, ⁴J = 2, 2 H); 7.28–7.40 (m, 6 H); 7.48–7.58 (m, 3 H); 7.90 (m, 4 H); 8.72 (s, 2 H). ¹³C-NMR (CDCl₃): 55.06 (primary C); 48.07 (secondary C); 99.11, 104.16, 110.85, 120.17, 123.04, 123.40, 123.88, 127.33, 129.09, 129.68 (tertiary C); 136.58, 136.88, 139.56, 142.58, 150.09, 150.77, 161.09 (quaternary C). EI-MS: 687 (M⁺).

2,6-Bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]-4-(4'-nitrophenyl)pyridine (L⁴): M.p. 208–210°. TLC (Al₂O₃; CH₂Cl₂): R_f 0.51. ¹H-NMR (CDCl₃): 3.57 (s, 12 H); 5.61 (s, 4 H); 6.00 (d, ⁴J = 2, 4 H); 6.31 (t, ⁴J = 2, 2 H); 7.29 (dd, ³J = 8, ⁴J = 1, 2 H); 7.32 (td, ³J = 8, ⁴J = 1, 2 H); 7.37 (td, ³J = 8, ⁴J = 1, 2 H); 7.91 (d, ³J = 8, 2 H); 8.1 (m, AA'BB', 2 H); 8.4 (m, AA'BB', 2 H); 8.72 (s, 2 H). ¹³C-NMR (CDCl₃): 55.07 (primary C); 48.08 (secondary C); 99.98, 104.18, 110.93, 120.24, 123.25, 123.41, 124.17, 124.31, 128.35 (tertiary C); 136.63, 139.39, 142.55, 143.22, 148.23, 148.53, 149.51, 150.62, 161.13 (quaternary C). EI-MS: 732 (M⁺).

2,6-Bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]-4-[4'-(diethylamino)phenyl]pyridine (L⁵): M.p. 191–192°. TLC (Al₂O₃; CH₂Cl₂): R_f 0.57. ¹H-NMR (CDCl₃): 1.24 (t, ³J = 7, 6 H); 3.44 (q, ³J = 7, 4 H); 3.54 (s, 12 H); 5.59 (s, 4 H); 6.02 (d, ⁴J = 2, 4 H); 6.29 (t, ⁴J = 2, 2 H); 6.77 (d, ³J = 8, 2 H); 7.25–7.36 (m, 6 H); 7.86 (d, ³J = 8, 2 H); 7.90 (d, ³J = 8, 2 H); 8.62 (s, 2 H). ¹³C-NMR (CDCl₃): 12.56, 55.04 (primary C); 44.36, 48.04 (secondary C); 99.14, 104.15, 110.76, 115.50, 120.06, 121.48, 122.82, 123.60, 128.34 (tertiary C); 122.44, 136.55, 139.72, 142.65, 148.95, 149.79, 150.26, 150.64, 161.01 (quaternary C). EI-MS: 758 (M⁺).

$[Fe(L^2)](ClO_4)_2$ and $[Fe(L^3)](ClO_4)_2$. $Fe(ClO_4)_2 \cdot 6H_2O$ (71.8 mg, 0.198 mmol) in EtOH (5 ml) was slowly added to a soln. of 242 mg (0.396 mmol) of L^2 in EtOH (65 ml) at 50°. The resulting mixture was maintained at 50° for 1 h, cooled to –20°, and the violet crystals were filtered, dissolved in MeCN, and Et₂O was allowed to diffuse into the soln. for 1 d to give 260 mg (0.176 mmol; 89%) of $[Fe(L^2)](ClO_4)_2$ as dark violet needles. ¹H-NMR (CD₃CN): 3.36 (s, 24 H); 5.80 (d, ³J = 8, 4 H); 5.84 (d, ⁴J = 2, 8 H); 5.98 (s, 8 H); 6.30 (t, ⁴J = 2, 4 H); 6.87 (t, ³J = 8, 4 H); 7.24 (t, ³J = 8, 4 H); 7.46 (d, ³J = 8, 4 H); 8.76 (‘t’, AB₂, ³J = 8, 2 H); 8.88 (‘d’, AB₂, ³J = 8, 4 H). Anal. calc. for FeC₇₄H₆₆N₁₀O₁₆Cl₂: Fe 3.78; C 60.13, N 9.48, H 4.50; found: Fe 3.75, C 59.61, N 9.68, H 4.51.

The same procedure was used for the preparation of $[Fe(L^3)](ClO_4)_2$, but EtOH was slowly diffused instead of Et₂O to give violet needles of $[Fe(L^3)](ClO_4)_2 \cdot H_2O$ in 88% yield. ¹H-NMR (CD₃CN): 3.37 (s, 24 H); 5.93 (d, ⁴J = 2, 8 H); 5.95 (d, ³J = 8, 4 H); 6.09 (s, 8 H); 6.38 (t, ⁴J = 2, 4 H); 6.87 (t, ³J = 8, 4 H); 7.28 (t, ³J = 8, 4 H); 7.55 (d, ³J = 8, 4 H); 7.8 (m, 6 H); 8.0 (m, 4 H); 8.96 (s, 4 H). Anal. calc. for FeC₈₆H₇₄N₁₀O₁₆Cl₂ · H₂O: Fe 3.39, C 62.66, N 8.50, H 4.65; found: Fe 3.26, C 62.71, N 8.47, H 4.60.

$[Fe(L^4)](ClO_4)_2$ and $[Fe(L^5)](ClO_4)_2$. $Fe(ClO_4)_2 \cdot 6H_2O$ (61.9 mg, 0.17 mmol) in MeCN (10 ml) was slowly added to a soln. of 250 mg (0.34 mmol) of L^4 in 40 ml MeCN/CH₂Cl₂ 1:3. The resulting deep blue soln. was evaporated to dryness and the crude precipitate suspended in EtOH (30 ml) at 50° for 1 h. After cooling to r.t., the precipitate was filtered, dissolved in MeCN, and Et₂O was allowed to diffuse for 15 h to give 201 mg (0.116 mmol; 71%) of $[Fe(L^4)](ClO_4)_2$ as violet crystals. ¹H-NMR (CD₃CN): 3.36 (s, 24 H); 5.92 (d, ⁴J = 2, 8 H); 5.95 (d, ³J = 8, 4 H); 6.08 (s, 8 H); 6.35 (t, ⁴J = 2, 4 H); 6.90 (t, ³J = 8, 4 H); 7.29 (t, ³J = 8, 4 H); 7.52 (d, ³J = 8, 4 H); 8.18 (m, AA’BB’, 4 H); 8.53 (m, AA’BB’, 4 H); 8.91 (s, 4 H). Anal. calc. for FeC₈₆H₇₂N₁₂O₂₀Cl₂: Fe 3.25, C 60.04, N 9.77; H 4.22; found: Fe 3.15, C 59.76, N 9.73, H 4.21.

A similar procedure was used for the synthesis of $[Fe(L^5)](ClO_4)_2$, but EtOH was diffused for 3 d to give dark green crystals of $[Fe(L^5)](ClO_4)_2 \cdot 2H_2O$ in 87% yield. ¹H-NMR (CD₃CN): 1.32 (t, ³J = 7, 12 H); 3.40 (s, 24 H); 3.62 (q, ³J = 7, 8 H); 5.95 (d, ⁴J = 2, 8 H); 6.09 (d, ³J = 8, 4 H); 6.12 (s, 8 H); 6.35 (t, ⁴J = 2, 4 H); 6.85 (t, ³J = 8, 4 H); 6.95 (d, ³J = 8, 4 H); 7.23 (t, ³J = 8, 4 H); 7.62 (d, ³J = 8, 4 H); 7.92 (d, ³J = 8, 4 H); 9.12 (s, 4 H). Anal. calc. for FeC₉₄H₉₂N₁₂O₁₆Cl₂ · 2H₂O: Fe 3.09, C 62.43, N 9.29, H 5.35; found: Fe 3.00, C 62.51, N 9.16, H 5.31.

Caution! Perchlorate salts with org. ligands are potentially explosive and should be handled with the necessary precautions [15].

Physical Measurements. Electronic spectra in the UV/VIS range were recorded in soln. with Perkin-Elmer Lambda 5 and Perkin-Elmer Lambda 2 spectrophotometers at 20° using quartz cells of 1, 0.1, and 0.01 cm path length. IR Spectra were obtained from KBr pellets with a Perkin-Elmer IR 597 spectrophotometer. ¹H- and ¹³C-NMR spectra were recorded on Varian XL 200 and Bruker AMX 400 spectrometers. Chemical shifts are given in ppm, relative to TMS; EI-MS (70 eV) were recorded with VG 7000E and Finnigan 4000 instruments. FAB-MS (9 kV, positive mode from nitrobenzyl alcohol matrix) were recorded at the Laboratories of the CMU (Geneva). Cyclic voltammograms were recorded using a Tacussel PRGE-DEC potentiostat connected to a function generator and a XY plotter. A 3-electrode system consisting of a stationary Pt disk working electrode, a Pt counter electrode, and a non-aq. Ag/Ag⁺ reference electrode was used. NBu₄PF₆ (0.1M in MeCN) served as inert electrolyte and MeCN was distilled from P₂O₅ and then passed through an Alox column (activity I). The reference potential ($E^\circ = 0.41$ (V) vs. SCE) was standardized against the known complex [Ru(bipy)₃](ClO₄)₂ [16]. The scan speed used was 0.2 V/s, and voltammograms were analyzed according to established procedures [16]. All the given potentials are expressed vs. SCE. Elemental analyses were performed by Dr. H. Eder of the Microchemical Laboratory of the University of Geneva. Iron was determined by atomic absorption (Pye Unicam SP9) after acidic oxidative mineralization of the complex. Extended Hückel calculations [17] were performed with a modified version of program ICON8 [18] using the standard parameters given in Table 1.

Table 1. Parameters Used for the EHMO Calculations [18]

Atoms	Orbitals	H_{ii} [eV]	Exponent	Atoms	Orbitals	H_{ii} [eV]	Exponent
H	1s	–13.60	1.300	N	2s	–26.00	1.950
C	2s	–21.40	1.625		2p	–13.40	1.950
	2p	–11.40	1.625	O	2s	–32.30	2.275
					2p	–14.80	2.275

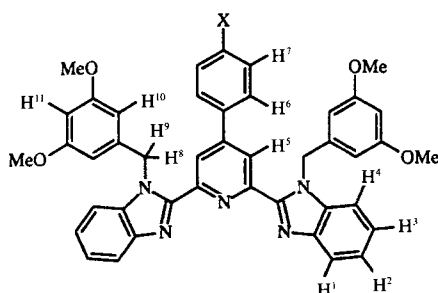
Results and Discussion. – *Preparation of the Ligands.* The unsubstituted ligand 2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]pyridine (L^2) is obtained in two steps according to a strategy based on a modified *Philips* reaction [3] [6]. The analogous substituted ligands 2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]-4-(4'-X-phenyl)-pyridine ($X = H$: L^3 ; $X = NO_2$: L^4 ; $X = NEt_2$: L^5) are synthesized in six steps using a *Kröhnke* reaction for the construction of the 4-substituted central pyridine ring [14]. The required pyridinium salt **3** is prepared via an *Ortoleva-King* reaction [13] from 2-acetylbenzimidazole [11], while the 2-[3-(4'-X-phenyl)acryloyl]benzimidazoles **4–6** are obtained by *Knoevenagel* condensations [12]. *Kröhnke* reactions lead to the poorly soluble compounds **7–9** which are alkylated with 3,5-dimethoxybenzyl bromide [6] to give the soluble ligands L^3 – L^5 in good yields.

Preparation of Fe^{II} Complexes. The Fe^{II} complexes are obtained by mixing ligands L^2 – L^5 with stoichiometric amounts of $Fe(ClO_4)_2 \cdot 6 H_2O$ in EtOH or $CH_2Cl_2/MeCN$ mixtures. The perchlorate salts can be easily crystallized in good yield by slow diffusion of Et_2O or EtOH into an MeCN solution to give intensely coloured crystals whose elemental analyses are compatible with the formulations $[Fe(L^2)_2](ClO_4)_2$, $[Fe(L^3)_2](ClO_4)_2 \cdot H_2O$, $[Fe(L^4)_2](ClO_4)_2$, and $[Fe(L^5)_2](ClO_4)_2 \cdot 2 H_2O$. Upon complexation to Fe^{II} , the IR spectra show small shifts of the C=C and C=N stretching vibrations in the 1600–1500 cm^{-1} region as previously observed for Fe^{II} [1], Cu^I [4], Cu^{II} , and Zn^{II} complexes [3] with ligands L^1 and L^2 . The ClO_4^- anions all show the two expected symmetrical vibrations (1095, 625 cm^{-1}) typical of ionic perchlorates. To establish the structure of the complexes in solution and to study the effects of the substitution on the electronic properties of the ligands, we have studied the 1H -NMR and electronic spectra and the cyclic voltammograms for the free ligands L^n and the complexes $[Fe(L^n)_2](ClO_4)_2$ ($n = 2–5$).

Table 2. 1H -NMR Shifts (with respect to TMS) for Ligands L^2 – L^5 in $CDCl_3$ and $[Fe(L^n)_2]^{2+}$ ($n = 2–5$) Complexes in CD_3CN

Compound	H ¹	H ²	H ³	H ⁴	H ⁵	H ⁶	H ⁷	H ⁸ , H ⁹	H ¹⁰	H ¹¹
L^2	7.82		7.22–7.38		8.39	–	–	5.54	5.97	6.27
L^3	7.90		7.28–7.40		8.72		7.5–7.9	5.59	6.01	6.30
L^4	7.91		7.29–7.37		8.72	8.10	8.40	5.61	6.00	6.31
L^5	7.90		7.25–7.36		8.62	7.86	6.77	5.59	6.02	6.29
$[Fe(L^2)_2]^{2+}$	5.80	6.87	7.24	7.46	8.86	–	–	5.98	5.84	6.30
$[Fe(L^3)_2]^{2+}$	5.95	6.87	7.28	7.55	8.96		7.8–8.0	6.09	5.93	6.38
$[Fe(L^4)_2]^{2+}$	5.95	6.90	7.29	7.52	8.91	8.18	8.53	6.08	5.92	6.35
$[Fe(L^5)_2]^{2+}$	6.09	6.85	7.23	7.62	9.12	7.92	6.95	6.12	5.95	6.35

1H -NMR Spectra. The aromatic part of the 1H -NMR spectra of ligands L^2 – L^5 (Table 2) show pseudo-first order spectra for the pyridine protons H^5 giving a *doublet* (from an AM_2 spin system) for ligand L^2 and a *singlet* (A_2 spin system) at lower field for the ligands L^3 – L^5 ($\Delta\delta = 0.2–0.3$ ppm) due to the deshielding effect of the substituted Ph rings in the vicinity of H^5 [19]. The benzimidazole protons give a complicated $ABCD$ spin system with H^1 giving a *multiplet* around 7.8 ppm and the three other protons a *multiplet* between 7.2–7.4 ppm [4] [6] [20]. The 1H -NMR signals of the Ph protons (H^6, H^7) strongly depend on the nature of the substituent giving a complicated $AA'BB'C$ spin system for L^3 and $AA'MM'$ for L^4 and L^5 .



Upon complexation to Fe^{II} , the ^1H -NMR signals are significantly modified, but the resulting spectra are typical for low spin diamagnetic $[\text{Fe}(\text{L}^n)_2]^{2+}$ ($n = 2-5$) complexes [21] showing two equivalent ligands on the NMR time scale (Fig. 1). The pyridine protons H^5 still display first-order spectra, but a lower field ($\Delta\delta = 0.2-0.4$ ppm) which is typical for N-coordination of the pyridine ring [4] [6] [22]. As previously described for complexes of L^1 with Cu^{I} [4] [6], the benzimidazole protons H^3 and H^4 are slightly shifted upon complexation, but the two remaining protons H^1 and H^2 are significantly shielded in the $[\text{Fe}(\text{L}^n)_2]^{2+}$ ($n = 2-5$) complexes (1.0–1.3 and 0.5 ppm, respectively). Similar upfield shifts have been observed for the H^6 protons of terpyridine in $[\text{Fe}(\text{terpy})_2]^{2+}$ [21] and

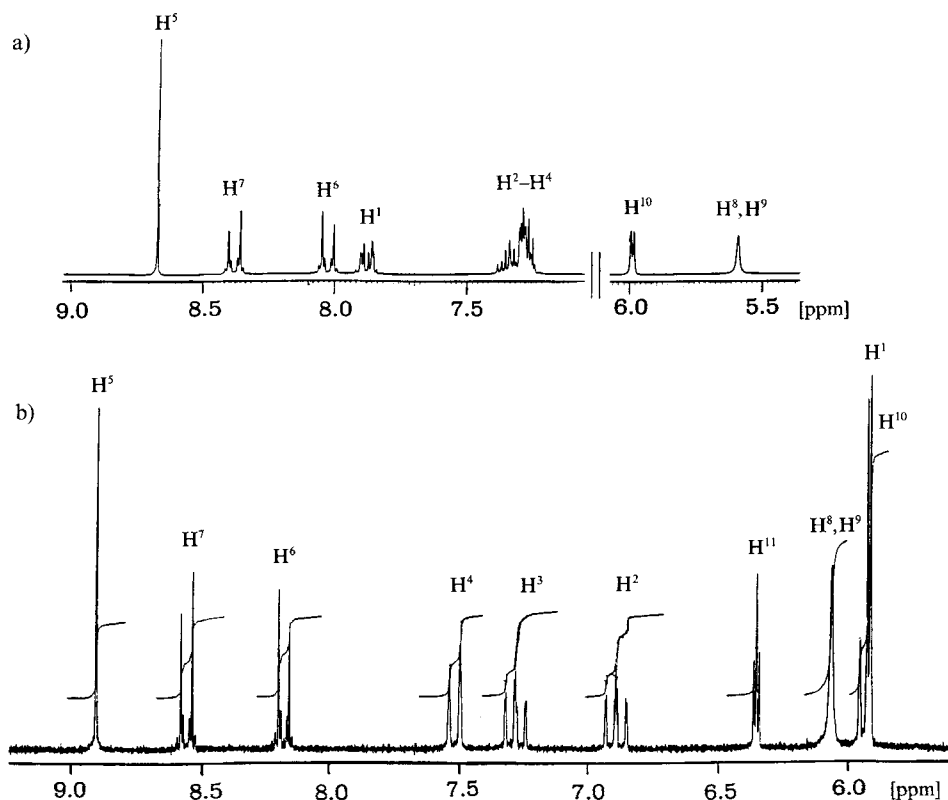


Fig. 1. ^1H -NMR Spectra of a) ligand L^4 in CDCl_3 and b) complex $[\text{Fe}(\text{L}^4)_2]^{2+}$ in CD_3CN

[Mg(terpy)₂]²⁺ [23], and are ascribed to the shielding experienced by these protons lying above the plane of the central pyridine ring of the second ligand as a result of the perpendicular arrangement of the two tridentate donors around the pseudo-octahedral metal ion. Finally, the signals of the aromatic protons of the 3,5-dimethoxybenzyl groups are not significantly modified upon complexation to Fe^{II}, but the methylene protons H⁸ and H⁹ still remain enantiotopic confirming the achiral nature of the [Fe(Lⁿ)₂]²⁺ (*n* = 2–5) complexes [6]. The ¹H-NMR results strongly suggest that all the [Fe(Lⁿ)₂]²⁺ (*n* = 2–5) complexes adopt a *D*_{2d} symmetry in MeCN solution giving a pseudo-octahedral coordination of the low-spin Fe^{II} ions in complete agreement with the pseudo-*D*_{2d} structures found in the solid state for [Fe(terpy)₂](ClO₄)₂ [24] and [Fe{2,6-bis(benzimidazol-2-yl)-pyridine}](CF₃SO₃)₂ · 2 C₂H₅OH [1].

Electronic Spectra. The electronic spectrum of the unsubstituted ligand L² in solution displays a broad band centred at 30980 cm⁻¹ which is attributed to π₁ → π* according to L¹ [3] [4] [6] and terpyridine [25] where this transition appears at 30400 cm⁻¹ and 35700 cm⁻¹, respectively. The weak shoulder observed at higher energy (35185 cm⁻¹ for L²), missing for L¹, can be reasonably assigned to an internal π → π* transition centred on the 3,5-dimethoxybenzyl groups (Fig. 2). Although the great similarity between the electronic properties of L¹ and terpyridine has been firmly established [10], we were unable to find in the spectra of L¹ and L² the weaker n → π* transitions expected at lower energy [26] suggesting that these transitions (*ε* ≤ 300 M⁻¹ cm⁻¹ for terpy in hexane) are masked by the intense π₁ → π* as previously reported for terpyridine in CHCl₃ [26]. The substitution in the 4-position of the pyridine ring by Ph groups to give ligands L³–L⁵ significantly

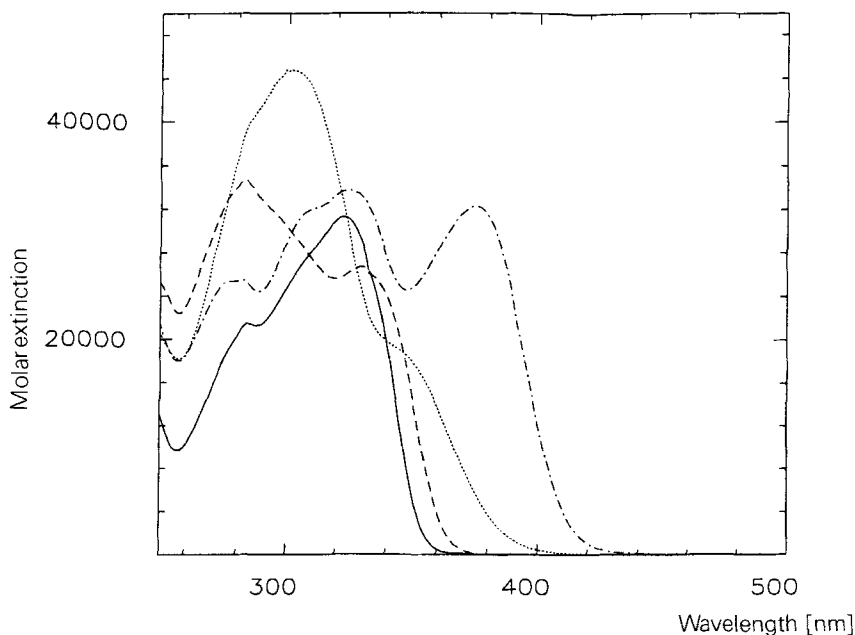


Fig. 2. Electronic spectra of ligands L²–L⁵ in CHCl₃ at 20°. L² (full line), L³ (dashed line), L⁴ (dotted line), and L⁵ (alternated line).

modifies the absorption spectrum (Fig. 2). The electronic spectrum of L^3 clearly shows some similarity with that of L^2 , but the $\pi_1 \rightarrow \pi^*$ transitions are shifted to lower energy ($\sim 770 \text{ cm}^{-1}$) and a new broad band appears in the UV region (35290 cm^{-1}). Adding a NO_2 electron-attractor group to the 4-position of the Ph group to give ligand L^4 leads to a very broad absorption at 33400 cm^{-1} with a shoulder at lower energy, while the electron-donor NEt_2 group in L^5 gives an unexpected spectrum whose UV part is very similar to L^3 , but displays a new intense absorption in the VIS region (26710 cm^{-1} ; Table 3).

Table 3. *Electronic Spectral Data for the Ligands L^2 – L^5 in CHCl_3 and Complexes $[\text{Fe}(\text{L}^n)_2]^{2+}$ ($n = 2$ – 5) in MeCN^a) and Electrochemical Reduction Potentials in MeCN^b) at 20°*

Compound	$\pi \rightarrow \pi^*$	MLCT	$E_{1/2}$	$E_{\text{pa}} - E_{\text{pc}}$
L^2	35185 (21450, sh) 30980 (31220)		–1.98	70
L^3	35290 (34640) 30210 (26650)		–1.84	80
L^4	35200 (39500, sh) 33400 (44790)		–0.95 –1.45	90 95
L^5	28800 (18640, sh) 35410 (25440, sh) 30770 (33710)		+1.01 –1.94	90 80
$[\text{Fe}(\text{L}^2)_2]^{2+}$	26710 (32290) 35560 (42000) 31850 (43400) 28490 (47930) 27190 (55500)	18520 (8100, sh) 17390 (10090)	+0.97 –0.99 –1.39	70 80 80
$[\text{Fe}(\text{L}^3)_2]^{2+}$	35550 (62500) 32240 (92900) 28170 (51800) 26900 (58030)	18200 (12000, sh) 16780 (21950)	+0.93 –0.92 –1.30	70 70 80
$[\text{Fe}(\text{L}^4)_2]^{2+}$	35335 (66020) 31625 (77950) 28990 (44000) 26455 (48700)	17700 (12100, sh) 16350 (24800)	+1.00 –0.72 –0.91 –1.30	80 irrev. 80 80
$[\text{Fe}(\text{L}^5)_2]^{2+}$	26455 (48700) 35540 (53290) 31370 (64550) 28950 (56190) 27640 (55070) 23040 (42050)	17780 (12100, sh) 16250 (50860)	+1.19 +0.82 –1.04 –1.40	90 ^c 80 ^d 80 70

^a) Energies are given for the maximum of the band envelope in cm^{-1} and ϵ (in parentheses) in $\text{M}^{-1}\text{cm}^{-1}$; sh = shoulder.

^b) Electrochemical potentials are given in V vs. SCE and $E_{\text{pa}} - E_{\text{pc}}$ in [mV]. Estimated error on $E_{1/2}$ is ± 0.01 V.

^c) Oxidation centred on the ligand.

^d) Oxidation centred on the metal.

Recently, the EHMO method [17] has been applied to 2,2'-bipyridine and was shown to give good qualitative agreement with spectroscopic results [27] and, to rationalize qualitatively our observations, we have performed EHMO calculations on the 4-(X-phenyl)pyridine fragments ($X = \text{H}, \text{NO}_2, \text{NH}_2$). The two aromatic rings and the substituent (if any) were maintained coplanar, and C_{2v} symmetry was assumed. Bond dis-

tances and angles were taken from the crystal structure of 4-phenylpyridine [19] and from standard reported values [28]. The results show that two allowed transitions are expected for 4-phenylpyridine at rather similar energy: $n(A_1) \rightarrow \pi^*(B_1)$ ($n(A_1)$ is essentially the lone pair on the N-atom) and $\pi(B_1) \rightarrow \pi^*(B_1)$ at slightly higher energy which qualitatively corresponds to the observed pattern in the spectra of pyridine [29], 2,2'-bipyridine [30], and 2,2':6',2''-terpyridine [26]. However, the intensity of the $n \rightarrow \pi^*$ is very weak compared to the $\pi \rightarrow \pi^*$, since it is an overlap forbidden transition [26] [31] and may be neglected for our purpose. The substitution with a NO_2 group to give 4-(4'-nitrophenyl)pyridine leads to the stabilization of both $\pi(B_1)$ and $\pi^*(B_1)$ orbitals due to the interactions with the low-lying empty B_1 orbital located on the NO_2 fragment. This effect is more pronounced for the π^* orbital leading to an expected shift of the $\pi \rightarrow \pi^*$ transitions to lower energy which is observed in the spectra when going from L^3 to L^4 . On the other hand, the substitution with a NH_2 donor group to give 4-(4'-aminophenyl)pyridine strongly destabilizes the $\pi(B_1)$ orbital which becomes the HOMO of the fragment (Fig. 3)

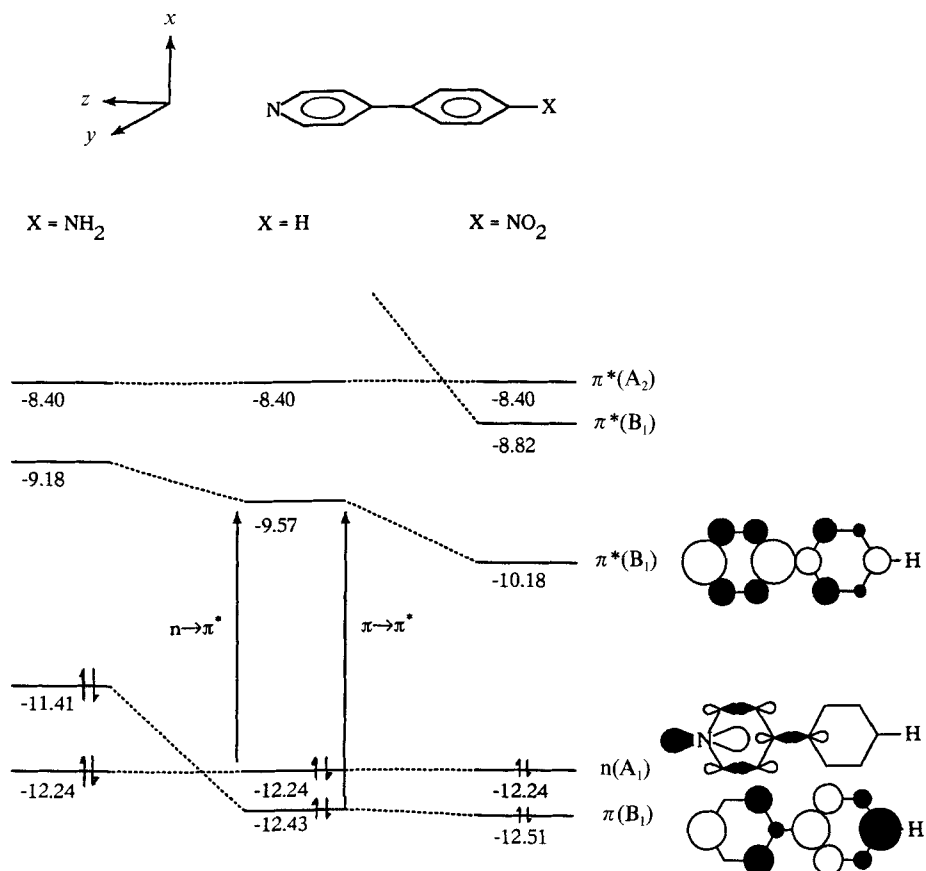


Fig. 3. Schematic representation of frontier orbitals calculated with EHMO [18] for the 4-(X-phenyl)pyridine fragments (X = H, NO_2 , NH_2) assuming C_{2v} symmetry. Energies are given in eV and projections along the x direction for the $\pi^*(B_1)$, $n(A_1)$, and $\pi(B_1)$ orbitals of 4-phenylpyridine are shown on the right.

resulting in a greater shift of the $\pi \rightarrow \pi^*$ transitions to lower energy than that expected for the NO_2 group. These results qualitatively correspond to the tendency observed in the electronic spectra of $\text{L}^3\text{--L}^5$ (Fig. 2) and strongly suggest that the nature of the 4-(X-phenyl) substituent, by influencing the energy of the π and π^* orbitals, is mainly responsible for the striking change observed in the UV region as recently reported by *Sauvage* and coworkers for substituted 4-phenylterpyridine [8].

Our simple approach using 4-(X-phenyl)pyridine fragments and EHMO calculations is inadequate to give a quantitative and even a qualitative description of the modifications of the electronic structure which results from the complexation of Fe^{II} to ligands L^2 to L^5 . However, we expect some change in energy for the $\pi(\text{B}_1)$, $\pi^*(\text{B}_1)$, and $n(\text{A}_1)$ orbitals as a result of π and σ interactions with the metal orbitals. Upon complexation to Fe^{II} , the intraligand $\pi_1 \rightarrow \pi^*$ transitions of the ligand L^2 are split in two main components $\pi_a^1 \rightarrow \pi^*$ and $\pi_b^1 \rightarrow \pi^*$ [25] showing further structure as previously described for $[\text{Fe}(\text{L}^1)_2]^{2+}$ [1] (Fig. 4, Table 3). A similar splitting is observed for all the ligands $\text{L}^2\text{--L}^5$, but the features

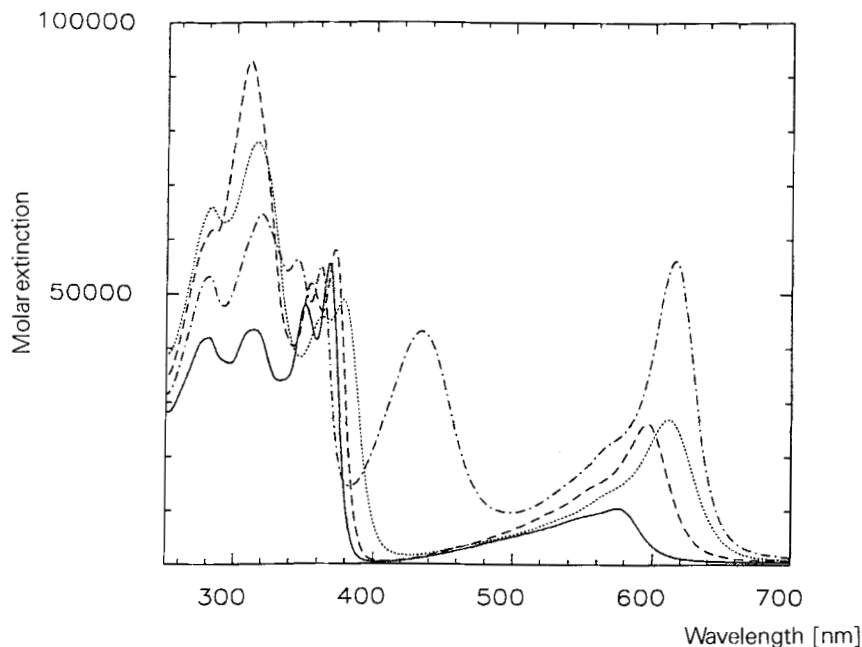


Fig. 4. Electronic spectra of complexes $[\text{Fe}(\text{L}^n)_2]^{2+}$ ($n = 2\text{--}5$) in CH_3CN at 20° . $[\text{Fe}(\text{L}^2)_2]^{2+}$ (full line), $[\text{Fe}(\text{L}^3)_2]^{2+}$ (dashed line), $[\text{Fe}(\text{L}^4)_2]^{2+}$ (dotted line), and $[\text{Fe}(\text{L}^5)_2]^{2+}$ (alternated line).

associated with each substituent bound to the pyridine ring are essentially maintained in the pseudo-octahedral $[\text{Fe}(\text{L}^n)_2]^{2+}$ ($n = 3\text{--}5$) complexes. A new intense transition, attributed to a metal-to-ligand charge transfer ($\text{Fe}^{\text{II}} \rightarrow \pi^*$ MLCT) [32], is exhibited in the 400–600-region (Table 3). For the low spin complexes $[\text{Fe}(\text{L}^n)_2]^{2+}$ ($n = 2\text{--}5$), the MLCT bands appear as unsymmetrical triangles with a rather sharp cut-off at low energy (the d–d transitions in these complexes are very weak [1]), but with a broad shoulder to high

energy associated with a vibrational progression [32] as previously reported for the analogous pseudo-octahedral complexes $[\text{Fe}(\text{terpy})_2]^{2+}$ (18120 cm^{-1} ; $\epsilon = 11900\text{ M}^{-1}\text{ cm}^{-1}$) [33] and $[\text{Fe}(\text{L}^1)_2]^{2+}$ (17360 cm^{-1} ; $\epsilon = 8800\text{ M}^{-1}\text{ cm}^{-1}$) [1] in MeCN. Although the shift of the MLCT transitions to lower energy is well-documented for the ligands 4-phenylterpyridine [9] and 4-tolylterpyridine [34], there is apparently no simple relation between the nature of the substituent and the position of the MLCT bands in 4-substituted $[\text{Fe}^{\text{II}}(\text{diimine})_3]^{2+}$ or $[\text{Fe}(\text{triamine})_2]^{2+}$ compounds [32]. Our results confirm this, and we observe a significant shift to lower energy for the MLCT in $[\text{Fe}(\text{L}^3)_2]^{2+}$ (610 cm^{-1} compared to $[\text{Fe}(\text{L}^2)_2]^{2+}$) associated with the better σ -donor and π -acceptor properties of the Ph group [9] [34], but $[\text{Fe}(\text{L}^4)_2]^{2+}$ and $[\text{Fe}(\text{L}^5)_2]^{2+}$ give rather similar energy for the maximum of the MLCT band, although NO_2 and NEt_2 substituents lie on opposite sides of the *Hammett* scale [35]. This probably results from the opposing effect of the substituent on the energy of the π^* orbital and on the oxidation potential of Fe^{II} for these complexes (*vide infra*). The most striking feature of the MLCT transitions in $[\text{Fe}(\text{L}^n)_2]^{2+}$ ($n = 2-5$) complexes is the considerable increase in intensity observed when going from L^2 to L^5 . As expected [9], the molar absorption coefficient at the maximum of the transition (ϵ) approximately doubles, when a Ph group is attached to the central pyridine ring in $[\text{Fe}(\text{L}^3)_2]^{2+}$, which can be explained by an increase of the transition dipole length [36]. Following the reasoning of *Phifer* and *McMillin* [36], the substitution with a NO_2 group to give $[\text{Fe}(\text{L}^4)_2]^{2+}$ should slightly increase the separation between the centroids of the donor and acceptor orbitals leading to a greater value of ϵ which is indeed observed (*Table 3*). However, the substitution with a NEt_2 group in the green coloured $[\text{Fe}(\text{L}^3)_2]^{2+}$ gives an unexpected $\epsilon \approx 50000\text{ M}^{-1}\text{ cm}^{-1}$, the largest value observed, to our knowledge, for this type of transition in pseudo-octahedral Fe^{II} complexes. The origin of this effect is not obvious: EHMO calculations with the 4-(4'-aminophenyl)pyridine fragments do not show any significant change in the repartition of the atomic orbital coefficients in the π^* orbitals, but a mixing with the $\pi\pi^*$ excited state, closer in energy for $[\text{Fe}(\text{L}^3)_2]^{2+}$, could increase the intensity of the MLCT transition [37]. However, as pointed out by *Jørgensen* [38], the introduction of *para*- NR_2 groups is well-known to give intense colorants, particularly when Ph groups are bound to an electron-deficient C-atom as demonstrated by Crystal Violet or Malachite Green.

Cyclic Voltammograms. The electrochemical potentials (in V vs. SCE) as well as the separation between anodic and cathodic peaks are summarized in *Table 3*. In MeCN, the cyclic voltammetry shows the ligands L^2 and L^3 to be reduced in a single reversible mono-electronic wave at -1.98 and -1.84 V , respectively, to give the corresponding radical anion. These values can be compared to those measured for terpyridine (-2.09 V) and 4-phenylterpyridine (-2.00 V) in very similar conditions [9]. In both cases, the 4-Ph-substituted ligands are easier to reduce due to the ability of the Ph group to function as a π acceptor [9] [34]. The cyclic voltammogram of L^4 shows two reversible mono-electronic reduction waves at less negative potentials. The first wave (-0.95 V) is very similar to that found for nitrobenzene (-1.15 V [16]) and probably implies a reduction mainly centred on the 4-nitrophenyl substituent while the second wave (-1.45 V) is associated with the formation of the dianion $(\text{L}^4)^{2-}$. L^5 also displays two mono-electronic waves, but the first one is associated with an oxidation centred on the 4-(diethylaminophenyl) group, as reported by *Sauvage* and coworkers for a 10-methylphenothiazine donor group bound to 4-tolylterpyridine ($+0.75\text{ V}$ [8]), and the second wave corresponds to the formation of the radical anion $(\text{L}^5)^{\cdot-}$. Since the half-wave potential ($E_{1/2}$) of the reduction centred on the

ligand reflects the LUMO energy [39], the observed increasing order $E_{1/2}(L^2) < E_{1/2}(L^3) < E_{1/2}(L^4)$ confirms the π -acceptor properties of the ligands predicted by our EHMO calculations. The cyclic voltammograms of the pseudo-octahedral complexes $[\text{Fe}(L^n)_2]^{2+}$ ($n = 2-5$) show two separate reversible mono-electronic reduction waves corresponding to the successive reduction of each coordinated ligand [40]. The measured potentials still reflect the properties of the different ligands but are shifted to less negative potentials as a result of the coordination to Fe^{II} . The complexes $[\text{Fe}(L^n)_2]^{2+}$ ($n = 2-5$) also exhibit a mono-electronic oxidation wave at positive potentials (+0.82 to +1.00 V vs. SCE) which is centred on the metal and assigned to the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple [9] [40]. The measured half-wave potentials for these oxidation processes in $[\text{Fe}(L^n)_2]^{2+}$ ($n = 2-5$) complexes show that the stabilization of Fe^{III} follows the order $L^4 < L^2 < L^3 < L^5$ which corresponds to the order deduced from the electron-donor properties of the substituents [9] [34] [35] and from the EHMO-calculated net charge on the pyridine N-atom for the 4-(X-phenyl)pyridine fragments ($X = \text{NO}_2$: -0.844; $X = \text{H}$: -0.856; $X = \text{NH}_2$: -0.893). The electrochemical results clearly confirm the dual role played by the Ph substituent in L^3 which stabilizes both higher oxidation states by σ -donor effect and lower oxidation states by π -acceptor effect [9]. Further substitution of the Ph ring by electro-active groups (NO_2 : L^4 or NEt_2 : L^5) modifies the electrochemical properties according to our qualitative approach based on EHMO calculations performed on the 4-(X-phenyl)pyridine fragments: an acceptor group, like NO_2 , lowers the LUMO and also destabilizes Fe^{III} , while a donor group, like NEt_2 , raises the LUMO and stabilizes Fe^{III} . These observations could qualitatively explain the apparent lack of direct intelligible correlation between the MLCT energies and the nature of the substituent.

Conclusions. – As for terpyridine derivatives [41], the use of *Kröhnke* reactions [14] leads to the efficient syntheses of the 4-substituted tridentate ligands **7–9**, but the introduction of lipophilic groups on the benzimidazole side arms is easier giving the ligands L^3 – L^5 suitably designed for the study of coordination properties in solution [6]. The substitution in the 4-position of the central pyridine ring by *para*-(X-phenyl) groups to give L^3 – L^5 does not strongly modify the complexation properties of the ligands, but significantly changes the electronic properties. Our results suggest that the energy levels of the $^1\pi\pi^*$ excited states, which are mainly responsible for the observed electronic spectra in the UV range, can be adjusted through the judicious choice of the substituent. This effect could play a major role in the design of new chromophores for efficient light conversion with lanthanide ions [10]. The detailed studies of the complexes $[\text{Fe}(L^n)_2]^{2+}$ ($n = 2-5$) show the possibility of tuning the electrochemical potentials and the energy of the MLCT bands by varying the substituent. However, the most striking feature is the very high intensity of the MLCT transitions found for the complex $[\text{Fe}(L^5)_2]^{2+}$ which could be used for the analytical spectrophotometric determination of iron.

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