

Structure and Properties of New Pyridyltriazine Low-spin Iron(II) Complexes

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Abstract

A number of low-spin iron(II) complexes of formula $[\text{Fe}(\text{LL})_3](\text{PF}_6)_2$ with LL = a substituted 3-(pyridin-2-yl)-1,2,4-triazine ligand have been prepared. NMR spectroscopy has been used to identify the structure of the complexes; in all cases the ligands bind didentately via N1 of the triazine ring and the pyridyl-nitrogen atom. With the asymmetrical pyridyltriazine ligands, two geometrical isomers have been observed, viz. *facial* (*fac*) and *meridional* (*mer*). Electrochemical measurements (CV and DPP) revealed that the triazine ligands have low-lying empty π^* levels and as a result all complexes are easily reduced. Comparison with analogous ruthenium complexes, revealed that the oxidation potentials of the iron(II) complexes are about 200 mV lower, while the reduction potentials are very similar.

Introduction

Iron(II) compounds with various chelating ligands have been studied extensively because of the spin-state transition phenomenon [1–5]. While some complexes are in the high-spin (HS) state at all temperatures, others occur solely in the low-spin (LS) form and the third group shows HS–LS transitions at temperatures between 50 and 400 K. The ligand-field strength of such systems can be tuned by (slightly) changing the ligands [6]. An example is $[\text{Fe}(\text{phen})_3]\text{X}_2$ for which a low-spin species is isolated, while the analogous 2-methyl-substituted ligand only yields high-spin complexes [4, 5].

Most systems have been studied using magnetic measurements and Mössbauer spectroscopy [1–5, 7]. The structures of the complexes have been elucidated mostly using X-ray crystallography. However, very few reports have appeared concerning NMR spectroscopy of low-spin iron(II) complexes [8, 9]. Because of the fast relaxation of the HS species in the NMR experiments, usually no high quality spectra

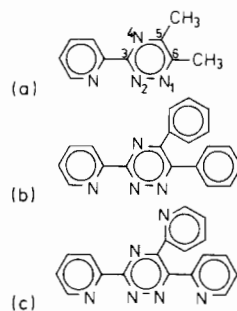


Fig. 1. Schematic representation of the ligands used: (a) 5,6-dimethyl-3-(pyridin-2-yl)-1,2,4-triazine (dmpt); (b) 5,6-diphenyl-3-(pyridin-2-yl)-1,2,4-triazine (dppt); (c) 3,5,6-tri(pyridin-2-yl)-1,2,4-triazine (tpt).

can be obtained. Even for LS complexes, the reports of NMR spectra of iron(II) complexes are scarce [7, 8], probably due to the fact that traces of HS Fe(II) and rapid electron transfer reactions cause line broadening.

For the isoelectronic low-spin ruthenium(II) complexes, NMR spectroscopy has been used extensively to elucidate the structure of the compounds [8, 10–19].

One of the studied systems was ruthenium compounds with substituted (pyridin-2-yl)-1,2,4-triazines [18]. Iron(II) complexes with 3-(pyridin-2-yl)-5,6-diphenyl-1,2,4-triazine (dppt) have also been reported [20]. This ligand has been used to determine quantitatively the iron contents in acidic solutions [20].

In this paper we report the synthesis, structure and properties of a number of low-spin iron(II) complexes with various substituted 1,2,4-triazine ligands (Fig. 1). It will be shown that NMR spectroscopy can be used to analyse the structure as well as the formation of isomers of the complexes.

Experimental

Materials

The starting material 2-pyridyl-amidrazone was synthesised by mixing equimolar amounts of 2-cyanopyridine and hydrazine monohydrate, after which a small amount of ethanol was added until a clear

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solution was visible. Upon standing overnight at room temperature, the almost colourless crystals of 2-pyridinecarboxamidrazone were filtered off, washed with a small amount of ether and dried in the air. Yield 90%.

5,6-Dimethyl-3-(pyridin-2-yl)-1,2,4-triazine (dmpt)

Dmpt was prepared by refluxing 0.1 mol 2-pyridyl-amidrazone with 0.1 mol 2,3-butanedione and 0.2 M of triethylamine in 200 cm³ ethanol for 3 h. After evaporation, the dark oil was extracted with hot diisopropylether, which was cooled until -20 °C for 2 h. A dark-yellow crystalline product was obtained, which was used without further purification; melting point (m.p.) 197–200 °C. ¹H NMR: 8.76 (d; H6), 8.36 (d; H3), 7.99 (t; H4), 7.55 (t; H5), 2.66 (s; CH₃(6)), 2.57 (s; CH₃(5)) ppm. Yield 70%.

5,6-Diphenyl-3-(pyridin-2-yl)-1,2,4-triazine (dppt)

This ligand was prepared as described for the dmpt ligand, but benzyl was refluxed with 2-pyridyl-amidrazone and 50 ml ethanol for 1 h. After cooling to room temperature, a yellow precipitate was isolated; m.p. 181–184 °C (lit. 179–180 °C [21]). ¹H NMR: 8.85 (d; H6), 8.55 (d; H3), 8.07 (t; H4), 7.64 (t; H5), 7.37–7.61 (m; phenyl) ppm. Yield 40%.

3,5,6-Tri-(pyridin-2-yl)-1,2,4-triazine (tpt)

This ligand was prepared as described for the analogous phenyl substituted ligand, except that here 2,2'-pyridil was used. M.p. 183–185 °C (lit. 191–192 °C [21]). ¹H NMR: 8.87 (d; H6), 8.59 (d; H3), 8.08 (t; H4), 7.65 (t; H5), 8.32–8.37 (t; H6' + H6''), 8.10–8.22 (m; H3' + H3''), 7.94–8.05 (m; H4' + H4''), 7.40–7.49 (m; H5' + H5'') ppm. Yield 30%.

Preparation of the Iron(II) Complexes

[Fe(tpt)₃](PF₆)₂·H₂O

One mmol FeCl₂·4H₂O and 3 mmol NH₄PF₆ were dissolved in 10 ml water. This solution was filtered into a 10 ml EtOH/H₂O (1:1) solution containing 4 mmol tpt. The dark coloured precipitate was filtered off and recrystallised from acetonitrile/water (1/2; 20 ml). Yield 1100 mg, 86%. *Anal. Calc.* for [Fe(C₁₈H₁₂N₆)₃](PF₆)₂·H₂O: C, 49.86; H, 2.94; N, 19.38; P, 4.76. *Found:* C, 49.65; H, 3.16; N, 19.45; P, 4.45%.

[Fe(dppt)₃](PF₆)₂·2H₂O

This complex was prepared and isolated as described for [Fe(tpt)₃](PF₆)₂. Yield 550 mg, 43%. *Anal. Calc.* for [Fe(C₂₀H₁₄N₄)₃](PF₆)₂·2H₂O: C, 54.89; H, 3.51; N, 12.81; P, 4.73. *Found:* C, 54.85; H, 3.57; N, 13.84; P, 4.46%.

[Fe(dmpt)₃](PF₆)₂

This complex was prepared and isolated as described for [Fe(tpt)₃](PF₆)₂. Yield 380 mg, 42%.

Anal. Calc. for [Fe(C₁₀H₁₀N₄)₃](PF₆)₂: C, 39.83; H, 3.34; N, 18.58; P, 6.85. *Found:* C, 40.05; H, 3.49; N, 18.55; P, 6.93%.

Equipment

Electronic spectra were recorded in ethanol on a Perkin-Elmer 330 spectrophotometer. Proton NMR spectra were obtained on a Bruker 300 MHz spectrometer with (CD₃)₂CO as solvent. All peak positions are relative to TMS. Electrochemical measurements were carried out using an E.G. and G. Par C model 303 polarographic analyser with an E.G. and G. Par 384B Universal Programmer. A saturated calomel electrode was used as reference electrode. Measurements were carried out in analytical grade CH₃CN, dried over molecular sieves. Tetrabutylammonium perchlorate (TBAP) was used as supporting electrolyte. A glassy carbon electrode was used as working electrode and a platinum electrode was used as auxiliary electrode. The values reported here were obtained with a scan rate of 100 mV s⁻¹.

Results and Discussion

Nuclear Magnetic Resonance Spectra

The proton chemical shifts of the compounds are displayed in Table 1. Using 2-D COSY NMR spectroscopy, the protons of the pyridyl groups of the ligands could be assigned. An example of a COSY spectrum is depicted in Fig. 2. As reported previously for ruthenium(II) complexes with three asymmetric didentate ligands, *facial* (*fac*) and *meridional* (*mer*) geometrical isomers would be expected [14]. In the *fac* isomer, the three ligands are magnetically equivalent, because the isomer possesses a C₃-axis of symmetry (Fig. 3). Therefore, a very simple NMR spectrum would be expected. The three ligands in the *mer* isomer are magnetically inequivalent and a more complex NMR spectrum is expected.

TABLE 1. ¹H NMR data of the iron(II) complexes with the 1,2,4-triazine ligands. All values in ppm vs. TMS, measured in d⁶-acetone

	H3	H4	H5	H6	R
[Fe(tpt) ₃] ²⁺	9.00	8.49	7.99	8.64 ^a	7.22–8.54 ^d
[Fe(dppt) ₃] ²⁺	9.15	8.49	7.88	8.84 ^b	7.09–7.76 ^c
	8.95	8.38	7.65	8.30 ^b	
	8.79	8.35	7.71	7.91 ^b	
	8.97	8.47	7.97	8.60 ^a	
[Fe(dmpt) ₃] ²⁺	8.80	8.38	7.80	8.20 ^b	2.76 + 2.78 ^e
	8.72	8.25	7.54	7.82 ^b	
	8.62	8.25	7.63	7.68 ^b	
	8.89	8.38	7.74	8.29 ^a	

^aFrom *fac* isomer.

^bFrom *mer* isomer.

^cR = phenyl.

^dR = pyridyl.

^eR = methyl.

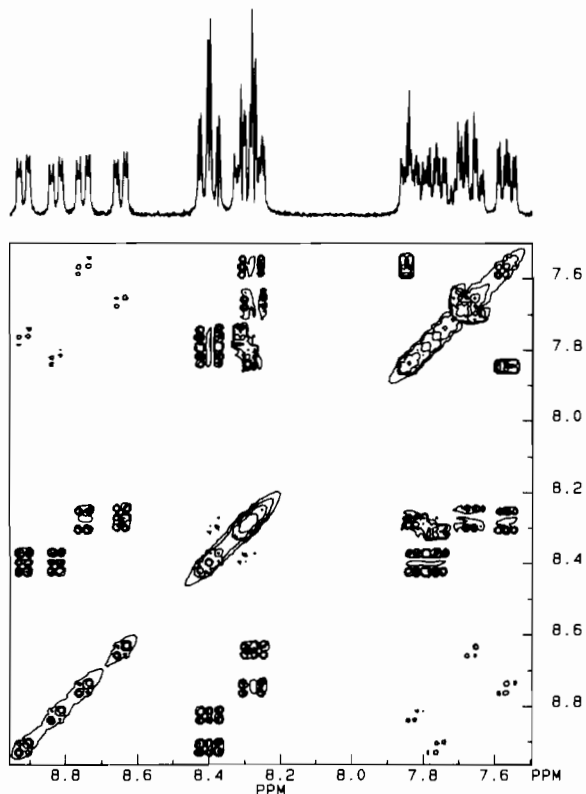


Fig. 2. COSY NMR spectrum of $[\text{Fe}(\text{dmpt})_3]^{2+}$, measured in d^6 -acetone.

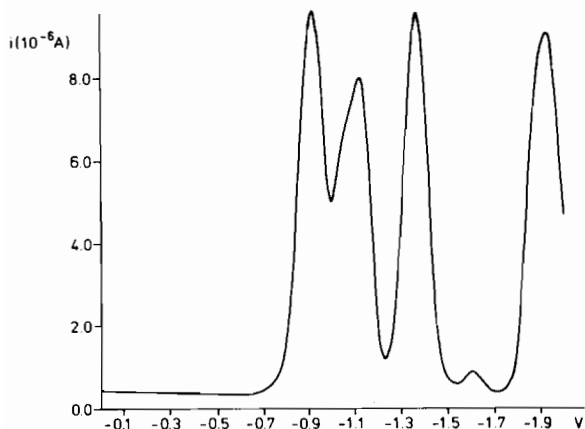


Fig. 3. Differential pulse polarogram of the reduction of $[\text{Fe}(\text{dmpt})_3]^{2+}$, measured in CH_3CN with 0.1 M TBAP, values vs. SCE.

The NMR spectrum of $[\text{Fe}(\text{tpt})_3]^{2+}$ is indeed very simple. As can be seen in Table 1, the iron compound with tpt has been isolated and identified as the *fac* isomer, while the compounds with the other ligands contain both *fac* and *mer* isomers. The yield of $[\text{Fe}(\text{tpt})_3](\text{PF}_6)_2$ was 86%, therefore at least 86% of this compound has been formed as *fac* isomer. It is expected that those stable low-spin iron(II) complexes do not easily give rise to fast ligand-exchange

reactions. It is surprising that mainly *fac*- $[\text{Fe}(\text{tpt})_3](\text{PF}_6)_2$ has been formed, because in the *fac* isomer more steric hindrance between the bulky pyridine groups is present. Also previous studies on tris(2-methyl-1,10-phenanthroline) iron(II) tetraphenylborate proved that only the *meridional* isomer was isolated [5].

The compounds with dmpt and dppt have been isolated as mixtures with a ratio of *fac*:*mer* of about 1:3, which is the statistical ratio. In the *fac*-isomer the three ligands point to one site (AAA), but for the *mer*-isomer three non-equivalent possibilities are now present to point one of the three ligands to the other site (AAB, ABA and BAA) [2].

Previously, we have shown that the differences in spectroscopic properties between the *facial* and *meridional* isomers of a number of related ruthenium compounds are small or not present [14, 18]. Therefore, no efforts were made to try to separate fractions with pure isomers. As is clear from Fig. 1, the ligands might coordinate in two ways: via N1 of the triazine ring and the nitrogen atom of the pyridine ring or via N4 of the triazine ring and the nitrogen atom of the pyridine ring. If coordination takes place via N1, then it would be expected that the steric hindrance between the R groups (methyl, phenyl or pyridyl) and an adjacent ligand would be small. If, on the other hand, the ligand is bound via N4 of the triazine ring, then the distance between the R group and a neighbouring pyridyltriazine ligand is expected to be short and a significant shift in the NMR spectrum would be expected. Inspection of the NMR data of the free ligands and of the coordinated ligands, revealed that the chemical shifts of the protons of the various R groups, do not change upon coordination on the metal ion; the changes are in all cases about 0.2 ppm. These small shifts prove that in all cases the ligands must be coordinated via N1 of the triazine group. Molecular models also indicate that this coordination mode is the most likely one, because in that case the R groups do not have any steric interaction with each other in these complexes.

Electrochemical Properties and Electronic Spectra

The electrochemical measurements revealed that the oxidation potentials of $[\text{Fe}(\text{dppt})_3]^{2+}$ and $[\text{Fe}(\text{dmpt})_3]^{2+}$ are about 200 mV lower than those of the analogous ruthenium complexes [18]. The main difference between iron and ruthenium is that the ligand-field splitting of iron(II) is smaller than that of ruthenium(II), because of a destabilisation of the filled d-orbitals. Therefore a lower oxidation potential for the iron complexes is observed.

The ligand-based reduction of $[\text{Fe}(\text{dppt})_3]^{2+}$ and $[\text{Fe}(\text{dmpt})_3]^{2+}$ are observed at approximately the same values as those of the analogous ruthenium compounds [18], i.e. at -0.91 and -1.15 V respectively (see Fig. 3).

The oxidation potentials of the iron complexes with the various pyridyltriazine ligands are higher than the oxidation potential of $[\text{Fe}(\text{bpy})_3]^{2+}$ (1.04 V versus SCE) (see Fig. 4), while the reduction potentials

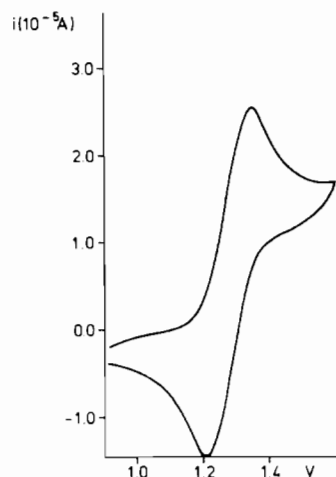


Fig. 4. Cyclic voltammogram of the oxidation of $[\text{Fe}(\text{dppt})_3]^{2+}$, measured in CH_3CN with 0.1 M TBAP, values vs. SCE.

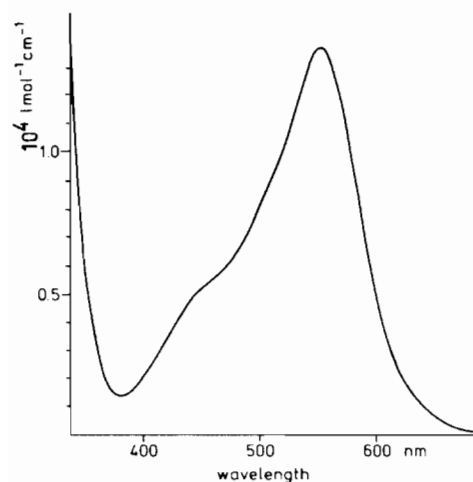


Fig. 5. MLCT absorption spectrum of $[\text{Fe}(\text{dppt})_3]^{2+}$, obtained in ethanol.

are less negative than those of $[\text{Fe}(\text{bpy})_3]^{2+}$ (-1.35 V versus SCE). Oxidation is removal of an electron from the highest occupied molecular orbital (HOMO), while in a reduction process, an electron is put into the lowest unoccupied molecular orbital (LUMO) of the complex. The observed electrochemical potentials indicate therefore that the HOMO (highest occupied molecular orbital) levels of the iron-pyridyltriazine complexes are stabilised compared to $[\text{Fe}(\text{bpy})_3]^{2+}$. Furthermore the LUMOs (lowest unoccupied molecular orbital) are relatively low and therefore the complexes are easily reduced.

The low-spin iron(II) complexes show very intense absorption bands in the visible region (Table 2; Fig. 5). By comparison with $[\text{Fe}(\text{bpy})_3]^{2+}$ (bpy = 2,2-bipyridine) and $[\text{Fe}(\text{phen})_3]^{2+}$ (phen = 1,10-phenanthroline) it has been concluded that these strong absorptions can be assigned to metal-to-ligand charge transfer bands (MLCT) [7]. Compared to $[\text{Fe}(\text{bpy})_3]^{2+}$, which has a MLCT band at 520 nm [7], the MLCT bands of $[\text{Fe}(\text{dppt})_3]^{2+}$ and $[\text{Fe}(\text{tpt})_3]^{2+}$ are shifted to lower energy, while the MLCT band of $[\text{Fe}(\text{dmpt})_3]^{2+}$ is at approximately the same energy as $[\text{Fe}(\text{bpy})_3]^{2+}$. A similar phenomenon has been observed for the analogous ruthenium complexes [18] and from the various measurements on the complexes it has been concluded that dppt and tpt have a much lower LUMO (lowest unoccupied molecular orbital) than bpy. Apart from these bands, clear shoulders at about 460 nm for most complexes were also observed. It is likely that these shoulders originate from d-d ($t_{2g} \rightarrow e_g$) transitions as previously observed for other low-spin iron(II) complexes [7].

Conclusions

The various 1,2,4-triazine ligands yield low-spin complexes of formula $[\text{Fe}(\text{LL})_3](\text{PF}_6)_2$. The structure of the complexes has been elucidated using NMR spectroscopy: for the octahedrally coordinated iron(II) complexes, two geometrical isomers have been detected for the compounds with methyl and phenyl substituted pyridyltriazine ligands. The electronic

TABLE 2. Electronic and electrochemical properties of the iron(II) compounds, referred to $[\text{Fe}(\text{bpy})_3]^{2+}$

	Absorption ^a		Oxidation potential ^b	Reduction potential ^b		
	λ_{max} (nm)	$(\epsilon \times 10^4 \text{ (l mol}^{-1} \text{ cm}^{-1}))$				
$[\text{Fe}(\text{dppt})_3]^{2+}$	551 (2.11)	465(sh)	1.29	-0.91	-1.12	-1.36
$[\text{Fe}(\text{tpt})_3]^{2+}$	556 (1.37)	461(sh)	1.40	-0.74	-0.98	-1.23
$[\text{Fe}(\text{dmpt})_3]^{2+}$	522 (1.83)	463(sh)	1.18	-1.11	-1.28	-1.53
$[\text{Fe}(\text{bpy})_3]^{2+}$	520 (0.62)	480(sh)	1.04	-1.35	-1.53	

^aMeasured in ethanol.

^bMeasured in CH_3CN with 0.1 M TBAP; values in V vs. SCE.

spectra and electrochemical measurements confirmed that the triazine ligands have low-lying empty orbitals. The ligands are strong π^* -acceptors resulting in a large ligand-field splitting.

Until now, only a few ligands have been used to prepare iron and ruthenium compounds, however a large number of similar substituted triazines can easily be prepared and it is therefore anticipated that the 1,2,4-triazine ligands will be used in future to prepare and study a large number of metal complexes.

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