Consequences of Incremental Steric Crowding at the $Fe^{II}N_6$ ($S = 2$) Co-ordination Sphere. Synthesis, Spectra and Electrochemistry

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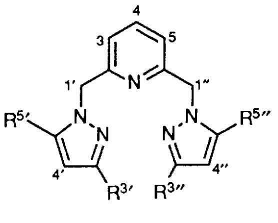
The effect of methyl substituents adjacent to donor atoms on the complexing properties of a novel family of tridentate (N_3) heterocyclic ligands has been explored. In the course of this investigation a new group of high-spin iron(II) complexes has been synthesised. The characterization in solution of $Fe^{II}N_6$ co-ordination has been done on the basis of paramagnetically shifted ^1H NMR spectroscopy. Increased steric crowding progressively decreases the values of 10 *Dq* for these ligands with iron(II) and nickel(II) in the grossly octahedral complexes. The iron(II) complexes also display metal-to-ligand charge-transfer (m.l.c.t.) transitions at *ca.* 360 nm. Cyclic voltammetric studies (MeCN solutions) reveal reversible one-electron Fe^{III}–Fe^{II} redox couples at high potentials [1.06–1.22 V *vs.* saturated calomel electrode (SCE)]. The electrochemical experiments further corroborate the fact that in the present system steric effects due to 3-Me substituent(s) predominate over the electronic contributions of the 5-Me substituent.

Nitrogen-containing heterocycles in general and imidazole, pyrazole and pyridine in particular have been used extensively in the construction of ligands.[1–10] Derivatization of the heterocycles is a crucial factor in designing and controlling subtle electronic and steric effects on the properties and reactivity of the resulting complexes while keeping the rest of the molecule fixed. Imidazole and pyrazole are good candidates[7–10] in this regard to be incorporated into chelating ligands. Pyridine is incorporated into chelates using either vinylpyridine or 2,6-bis(chloromethyl)pyridine, precursors which however unfortunately offer limited possibilities for derivatizing the heterocycle.

This work originates from an attempt to explore the effect of substituents near the donor site on the metal-centred redox potentials in closely related transition-metal complexes. Specifically, we are interested in the ligating properties of a new family of ligands, L^{1-3}, having two pyrazole groups attached to a pyridine ring at the 2,6 positions.



$L^1 : R^{3'} = R^{3''} = R^{5'} = R^{5''} = H$
$L^2 : R^{3'} = R^{5'} = H; R^{3''} = R^{5''} = Me$
$L^3 : R^{3'} = R^{3''} = R^{5'} = R^{5''} = Me$

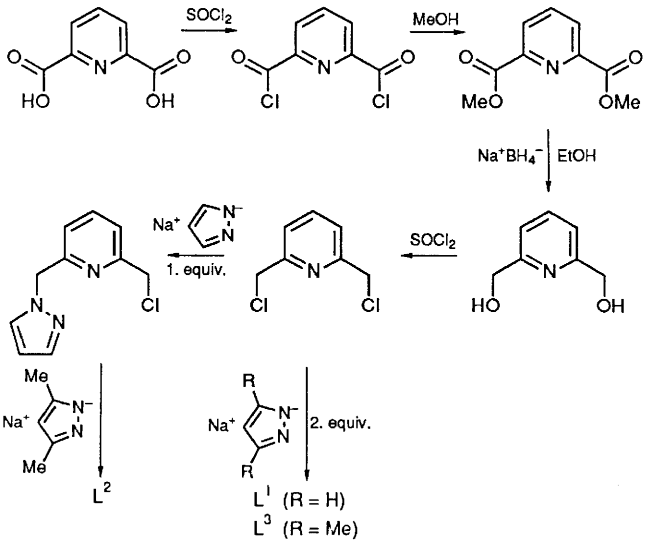
The reasons for choosing the ligands L^{1-3} are threefold. First, to examine whether or not incremental incorporation of ligand steric crowding still gives rise to bis-chelates as is known[11] for unsubstituted ligand L^1. Secondly, the number of high-spin iron(II) complexes having an FeN_6 co-ordination sphere is limited.[12,13] Additionally, Lever[14] has recently pointed out that high-spin Fe^{III}–Fe^{II} redox potential data with non-porphyrin nitrogen-containing ligands are rather restricted so giving an impetus to the present study. Thirdly, in the ligands L^1–L^3 there are methylene groups between the non-ligating pyrazole nitrogens and the pyridine ring. Our objective is to squeeze the pyrazole nitrogen atoms into the metal co-ordination sphere and increase the substituent-induced steric effect at the donor sites. In this paper we report the syntheses and properties of high-spin iron(II) bis-chelates using the ligands L^{1-3}. Proton NMR spectroscopy has been utilized to elucidate the metal co-ordination geometry while UV/VIS spectroscopic and voltammetric studies reveal the relative importance of electronic and steric effects.

Experimental

Chemicals and Starting Materials.—Solvents and reagents were obtained from commercial sources and used without further purification unless otherwise stated. Acetonitrile was dried by distillation over CaH_2. For electrochemical experiments (see below) further purification was achieved by treatment with $KMnO_4$–Li_2CO_3[15] followed by distillation over P_4O_{10}. Ethanol and methanol were distilled from $Mg(OEt)_2$ and $Mg(OMe)_2$ respectively. Diethyl ether was dried first with fused $CaCl_2$ and then refluxed with and stored over Na. Benzene was first stirred with concentrated sulphuric acid until it was free from thiophene. To remove acid it was then shaken twice with water, once with 10% Na_2CO_3 solution, again with water, and finally dried over fused $CaCl_2$ and stored over Na. 2,6-Bis(hydroxymethyl)pyridine[16] and 2,6-bis(chloromethyl)pyridine hydrochloride[17] were prepared according to the literature procedures. Tetrabutylammonium perchlorate was prepared as before.[18]

2-*Chloromethyl*-6-(*pyrazol*-1-*ylmethyl*)*pyridine*.—This was prepared as described,[11] except that in this work (on a preparative scale) the product was purified by column chromatography on silica gel by use of a 40% Et_2O–60% hexane mixture as eluent. Yield: 28%. ^1H NMR: δ 7.6 (m, 3 H, H^4, $H^{3'}$ and $H^{5'}$), 7.4 (d, 1 H, H^3), 6.8 (d, 1 H, H^5), 6.3 (t, 1 H, $H^{4'}$), 5.5 (s, 2 H, NCH_2) and 4.7 (s, 2 H, CH_2Cl).

2-(3,5-Dimethylpyrazol-1-ylmethyl)-6-(pyrazol-1-ylmethyl)-pyridine L^2 and 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine L^3 were prepared following the procedure reported[11] for 2,6-bis(pyrazol-1-ylmethyl)pyridine L^1. Proton NMR: L^2, δ 7.5 (m, 3 H, H^4, H^3 and $H^{5'}$), 6.7 (t, 2 H, H^3 and H^5), 6.3 (t, 1 H, $H^{4'}$), 5.8 (s, 1 H, $H^{4''}$), 5.4 [s, 2 H, CH_2 ($H^{1'}$)], 5.2 [s, 2 H,



Scheme 1

Table 1 Microanalytical, molar conductance and magnetic moment data for the complexes

	Analysis[a] (%)				
Compound	C	H	N	$\Lambda_M{}^b/\Omega^{-1}$ cm^2 mol^{-1}	$\mu_{eff}{}^c$
[Fe(L^1)$_2$][ClO$_4$]$_2$·H$_2$O	41.4	3.70	18.65	284	5.40
	(41.6)	(3.75)	(18.65)		(4.90)[d]
[Fe(L^2)$_2$][ClO$_4$]$_2$·2H$_2$O	43.4	4.55	16.95	281	5.43
	(43.6)	(4.60)	(16.95)		
[Fe(L^3)$_2$][ClO$_4$]$_2$·2H$_2$O	46.8	4.95	15.65	294	5.44
	(46.3)	(5.20)	(15.90)		(5.11)[d]
[Ni(L^1)$_2$][ClO$_4$]$_2$	42.7	3.50	19.00	282	*e*
	(42.4)	(3.55)	(19.05)		
[Ni(L^2)$_2$][ClO$_4$]$_2$	45.7	4.25	17.75	275	*e*
	(45.5)	(4.30)	(17.70)		
[Ni(L^3)$_2$][ClO$_4$]$_2$	48.3	5.00	16.60	281	*e*
	(48.1)	(4.95)	(16.50)		

[a] Required values in parentheses. [b] Expected 1:2 electrolyte range 220–300 Ω^{-1} cm^2 mol^{-1}. [c] Measured in MeCN solution (298 K) using Evans method.[20] [d] Room-temperature solid-state values in parentheses. [e] Not measured.

Table 2 Proton NMR chemical shifts relative to SiMe$_4$ for high-spin pseudo-octahedral iron(II) complexes

Compound			
[Fe(L^1)$_2$][ClO$_4$]$_2$·H$_2$O	[Fe(L^3)$_2$][ClO$_4$]$_2$·2H$_2$O	Intensity	Assignment
44.0	50.0	4	H^3, H^5
39.0	47.5	4	H$^{4'}$
27.0	39.5	4, 12	H or CH$_3$ (3′)
22.0	21.5	4, 12	H or CH$_3$ (5′)
10.0	9.0	2	H^4
−18.0	−25.0	4	CH$_2$
−48.0	−68.0	4	CH$_2$

CH$_2$ (H$^{1''}$)], 2.2 [s, 3 H, CH$_3$ (H$^{5''}$)] and 2.1 [s, 3 H, CH$_3$ (H$^{3''}$)]; L^3, δ 7.4 (m, 1 H, H^4), 6.6 (d, 2 H, H^3 and H^5), 5.9 (s, 2 H, H$^{4'}$), 5.3 (s, 4 H, CH$_2$), 2.3 (s, 6 H, CH$_3$) and 2.2 (s, 6 H, CH$_3$).

Preparation of the Complexes.—The iron(II) and nickel(II) bis-chelates of the ligands L$^{1-3}$ were prepared according to the reported procedure[11] for L^1.

CAUTION: All of the above complexes have perchlorate as the counter ion. While we have worked on these complexes without incident, perchlorate salts of metal complexes with organic ligands are potentially explosive.[19] Care should be exercised in their handling.

Measurements.—The IR spectra were recorded in KBr disks with a Perkin-Elmer M-580 spectrophotometer. Electronic spectra were measured with a Perkin-Elmer Lambda-2 spectrophotometer. Solution magnetic susceptibility measurements were made by the usual NMR method[20] with a PMX-60 JEOL (60 MHz) or Brüker WP-80 spectrometer and made use of the paramagnetic shift of the methyl protons of MeCN and the SiMe$_4$ reference as the measured NMR parameter. Solvent susceptibility[21a] and diamagnetic corrections[21b] were taken from literature tabulations. Magnetic susceptibility measurements in the solid state were performed using a Cahn–Faraday electromagnetic balance. The ^{1}H NMR spectra were measured in CDCl$_3$ or CD$_3$CN on either a Brüker WP-80 (80 MHz) or a Brüker WM-400 (400 MHz) spectrometer. The 400 MHz NMR spectra were obtained by the Analytical Facilities, Regional Sophisticated Instrumentation Centre, Lucknow, India. Chemical shifts are reported as positive values downfield from an internal standard of SiMe$_4$. Solution electrical conductivity measurements were made with an Elico (Hyderabad, India) type CM-82 conductivity bridge. Cyclic voltammetric measurements were performed using the PAR model 370-4 electrochemistry system incorporating the following: model 174A polarographic analyser; model 175 universal programmer; model RE 0074 *x–y* recorder. All experiments were done under a nitrogen atmosphere and at 298 K. Potentials are referenced to an aqueous saturated calomel electrode (SCE) and are uncorrected for junction potentials. The solutions were ≈1.00 × 10^{-3} mol dm^{-3} in complex and 0.2 mol dm^{-3} in supporting electrolyte, NBu$_4$ClO$_4$. In MeCN solution at a scan rate of 50 mV s^{-1} and using platinum electrodes the above conditions were found to give optimum performance for the [Fe(η-C$_5$H$_5$)$_2$]$^+$–[Fe(η-C$_5$H$_5$)$_2$] couple with E_f and peak-to-peak separation (ΔE_p) values of 0.40 V and 80 mV.

The platinum-inlay planar working electrode (Beckman model 39273) was cleaned by immersion in 6 mol dm^{-3} HNO$_3$, rinsing with water and then with acetone, and drying. The details of the cell configuration are the same as described before.[18]

Results and Discussion

Syntheses of Ligands and their Iron(II) *Complexes.*—The tridentate ligands were prepared (Scheme 1) by phase-transfer catalysed reactions of 2,6-bis(chloromethyl)pyridine with pyrazole and its derivatives. The purity of the ligands was checked by their ^{1}H NMR spectra.

The bis-ligand complexes were readily obtained when methanolic solutions of the ligands and aqueous solutions of iron(II) perchlorate were mixed. An interesting observation is that the colour of the complexes varies from light green, [Fe(L^1)$_2$]$^{2+}$ to yellowish brown, [Fe(L^2)$_2$]$^{2+}$ to yellow [Fe(L^3)$_2$]$^{2+}$.

While the presence of methyl substituents in the 3- and 5-positions of the pyrazole rings in the ligands L$^{1-3}$ has a profound effect (see below) on the properties of the complexes derived from these ligands, the co-ordinating ability of these ligands with selected transition-metal ions such as iron(II), nickel(II) or ruthenium(II) is dominated by the formation of bis-ligand[11] complexes.

Measurements of magnetic susceptibilities on MeCN solutions (Evans method[20]) of the iron complexes [FeL$_2$][ClO$_4$]$_2$ (L = L$^{1-3}$) gave effective magnetic moments, μ_{eff} ≈5.40 and solid-state values of 4.90–5.11 (Table 1). This is in excellent agreement with the solid-state values of other high-spin iron(II)

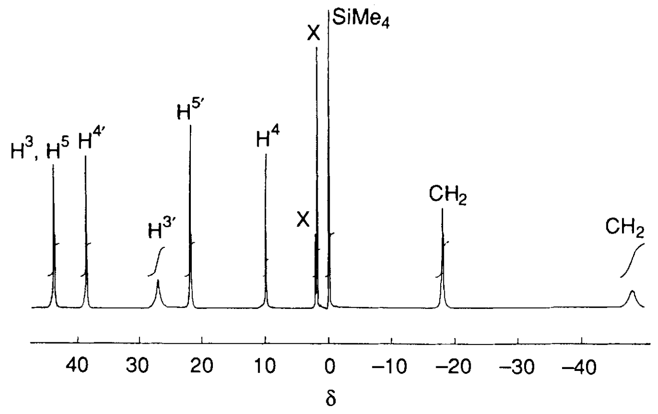


Fig. 1 400 MHz ^1H NMR spectrum of $[Fe(L^1)_2][ClO_4]_2{\cdot}H_2O$ in CD_3CN at *ca.* 298 K (solvent and water peaks marked by X)

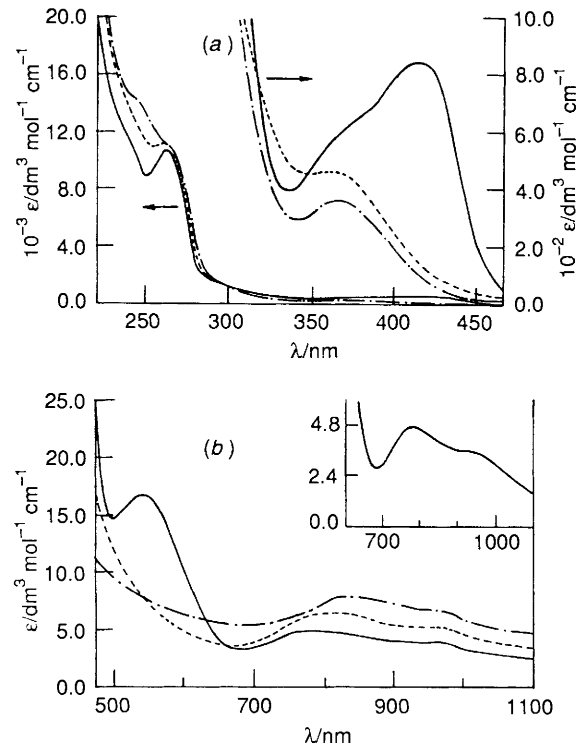


Fig. 2 Electronic spectra of $[Fe(L^1)_2][ClO_4]_2{\cdot}H_2O$ (——), $[Fe(L^2)_2][ClO_4]_2{\cdot}2H_2O$ (– – –), and $[Fe(L^3)_2][ClO_4]_2{\cdot}2H_2O$ (– · – · –) in acetonitrile solution. (*a*) High-energy region and (*b*) low-energy region, inset shows expansion for $[Fe(L^1)_2]^{2+}$ in the region 600–1100 nm

Table 3 Electronic spectra and cyclic voltammetric data[a] of the complexes at 298 K in acetonitrile

Complex	λ/nm (ε/dm³ mol⁻¹ cm⁻¹)	Fe^{III}–Fe^{II} couple E_f/V	ΔE_p/mV
$[Fe(L^1)_2][ClO_4]_2{\cdot}H_2O$	931 (4), 781 (5), 543 (17), 415 (840), 368 (sh) (600), 304 (sh) (1200), 262 (10 750)	1.06	80
$[Fe(L^1)_2][ClO_4]_2{\cdot}2H_2O$	955 (6), 813 (7), 360 (460), 262 (11 150)	1.16	80
$[Fe(L^1)_2][ClO_4]_2{\cdot}2H_2O$	962 (7), 852 (8), 365 (340), 265 (sh) (10 700), 245 (sh) (14 100)	1.22	80
$[Ni(L^1)_2][ClO_4]_2$	868 (9), 538 (11), 272 (sh) (7 050), 265 (9 400), 224 (13 950)	*b*	
$[Ni(L^2)_2][ClO_4]_2$	903 (10), 556 (sh) (25), 378 (sh) (268), 266 (10 100), 218 (24 250)	*b*	
$[Ni(L^3)_2][ClO_4]_2$	932 (11), 583 (15), 370 (sh) (33), 265 (9 900), 223 (24 950)	*b*	

[a] Supporting electrolyte NBu_4ClO_4 (0.1 mol dm⁻³); all potentials are referenced to SCE; $E_f = 0.5\ (E_{pc} + E_{pa})$; E_{pc} and E_{pa} are the cathodic and anodic peak potentials respectively; scan rate, 50 mV s⁻¹ at a platinum electrode. [b] Not measured.

complexes.[12b,e,13b] These magnetic data clearly establish[22] the high-spin electronic configuration ($S = 2$). The iron(II) complexes display ν(OH) bands at ≈3400 cm⁻¹ and $\nu(ClO_4^-)$ absorptions at ≈1100 cm⁻¹ in their IR spectra. The complexes are highly soluble in polar organic solvents and MeCN solutions show the expected[23] 1:2 electrolytic behaviour (Table 1).

Properties of the High-spin $Fe^{II}N_6$ *Co-ordination Sphere.*—As we have so far been unsuccessful in growing single crystals of these bis-ligand iron(II) complexes, we have used spectroscopic techniques to throw light on the geometry of the $Fe^{II}N_6$ co-ordination sphere. We have undertaken a ^1H NMR study on $[Fe(L^1)_2][ClO_4]_2{\cdot}H_2O$ and $[Fe(L^3)_2][ClO_4]_2{\cdot}2H_2O$ focusing on paramagnetically shifted[24,25] resonances. In this work we have assigned resonances (Fig. 1, Table 2) by a combination of the expected behaviour for paramagnetically shifted resonances[24,25] and integrated area ratios.

The resonances at δ *ca.* 10 are consistent with their assignments as the *para* protons (H^4) of the pyridine rings. A comparative analysis of the spectra of $[Fe(L^1)_2]^{2+}$ and $[Fe(L^3)_2]^{2+}$ clearly establishes the resonances at δ *ca.* 20 as due to protons (methyl groups) $H^{5'}$ of the pyrazole rings. Comparatively broad resonances at δ *ca.* 27 for $[Fe(L^1)_2]^{2+}$ and *ca.* 40 for $[Fe(L^3)_2]^{2+}$ with a relative intensity ratio of 1:3 are assignable as protons (methyl groups) $H^{3'}$ of the pyrazole rings. The two upfield broad resonances of relative intensity 1:1 are assigned to the methylene protons. There are two remaining resonances at δ *ca.* 39 and *ca.* 44 for $[Fe(L^1)_2]^{2+}$ and δ *ca.* 48 and 50 for $[Fe(L^3)_2]^{2+}$ respectively. It is expected that the pyridine-ring protons H^3 and H^5 and pyrazole ring proton $H^{4'}$ would experience similar effects since they are almost the same distance from the iron centre. We tentatively assign the most downfield resonances in each complex to the equivalent pyridine protons H^3 and H^5 and the other resonance to the pyrazole proton $H^{4'}$.

An octahedral high-spin Fe^{II} centre generally give rise to both contact and dipolar contributions to isotropic shifts[24] (*i.e.* the observed chemical shift minus a reference diamagnetic shift). At this level of available experimental results we cannot elucidate the relative contributions of σ- and π-spin delocalization mechanisms in these complexes. From the above analysis however we are inclined to believe that the geometry around the iron(II) centre in the present complexes is fairly distorted octahedral.

Absorption Spectra.—The spectra of the iron(II) complexes in MeCN solution show two weak broad bands in the near-IR region assignable as d–d transitions (Fig. 2, Table 3). These split bands are due to[26,27] a combination of a dynamic Jahn–Teller effect in the electronic excited states and a lowering of metal site symmetry. The energy of these bands lies in the order $[Fe(L^1)_2]^{2+} > [Fe(L^2)_2]^{2+} > [Fe(L^3)_2]^{2+}$. This clearly demonstrates a monotonous decrease in the strength of the ligand field as the number of methyl groups near the donor atom increases. The complex $[Fe(L^1)_2]^{2+}$ exhibits an additional observable ligand-field band at *ca.* 540 nm.

The nickel(II) complexes $[Ni(L^1)_2]^{2+}$, $[Ni(L^2)_2]^{2+}$ and $[Ni(L^3)_2]^{2+}$ were also studied for a better evaluation of the

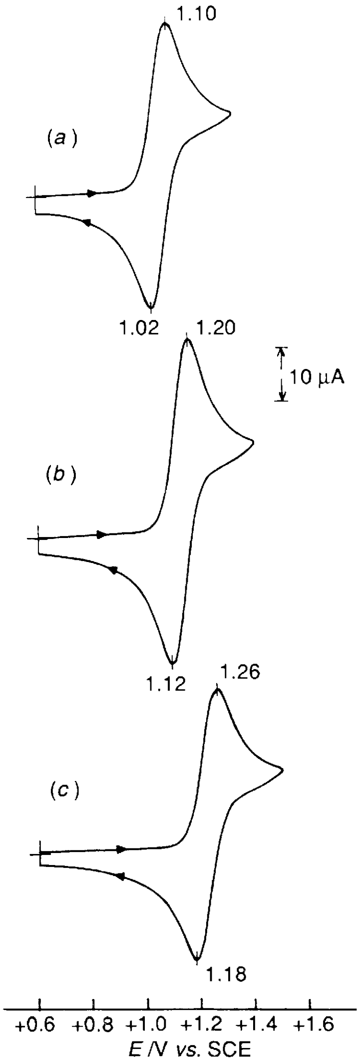


Fig. 3 Cyclic voltammograms of (*a*) $[\mathrm{Fe(L^1)_2}][\mathrm{ClO_4}]_2\cdot\mathrm{H_2O}$, (*b*) $[\mathrm{Fe(L^2)_2}][\mathrm{ClO_4}]_2\cdot 2\mathrm{H_2O}$ and (*c*) $[\mathrm{Fe(L^3)_2}][\mathrm{ClO_4}]_2\cdot 2\mathrm{H_2O}$ in acetonitrile (0.2 mol $\mathrm{dm^{-3}}$ $\mathrm{NBu_4ClO_4}$) at a platinum electrode; scan rate 50 mV $\mathrm{s^{-1}}$. The solute concentrations are 1.00×10^{-3} mol $\mathrm{dm^{-3}}$

ligand-field splitting parameter 10*Dq* noting that the X-ray crystal structure[11] of $[\mathrm{Ni(L^1)_2}]^+$ is symmetrically octahedral. The spectra of the nickel(II) complexes consist of two principal crystal-field bands[27] (Table 3). From the energies of the $^3A_{2g} \longrightarrow {}^3T_{2g}$ transitions the values for *Dq* (for $\mathrm{Ni^{2+}}$) are estimated as 1152, 1107 and 1073 $\mathrm{cm^{-1}}$ for ligands $\mathrm{L^1}$, $\mathrm{L^2}$ and $\mathrm{L^3}$ respectively. The iron complexes give rise to a similar trend (see above). Such an effect is clearly not explainable on the basis of electronic effects, and is best attributed to the steric effect of methyl groups adjacent to the donor atom. This behaviour has been noted previously[12b] for other nickel(II) complexes having a $\mathrm{NiN_6}$ co-ordination sphere. Examination of molecular models provides some support for a steric interpretation (interligand repulsion) that would cause an increase in the metal–pyrazole bond distance with an accompanying decrease in ligand-field strength.

The iron(II) complexes exhibit metal-to-ligand charge-transfer (m.l.c.t.) transitions at *ca.* 360 nm (Fig. 2, Table 3). The molar absorption coefficient values decrease with an increase in the number of methyl groups in the ligands owing to poorer metal–ligand orbital overlap. Apparently the overlap between $\mathrm{Fe^{II}}$ (donor) and pyrazole/pyridine (acceptor) orbitals is relatively small to allow appreciable intensity for the m.l.c.t. transition in the absence of mixing with available low-energy $\pi \longrightarrow \pi^*$ transitions. Interestingly, the complex $[\mathrm{Fe(L^1)_2}]^{2+}$ exhibits an additional m.l.c.t. transition at 415 nm. Intraligand transitions are also observed at still higher energies.

Electrochemistry.—Cyclic voltammetry was used to investigate the effect on the $\mathrm{Fe^{III}}$–$\mathrm{Fe^{II}}$ redox potential upon incorporating methyl substituents into the two pyrazole rings of ligand $\mathrm{L^1}$. In acetonitrile solution all the complexes undergo reversible electron-transfer reactions [equation (1)] at high

$$[\mathrm{Fe^{III}L_2}]^{3+} + e^- \rightleftharpoons [\mathrm{Fe^{II}L_2}]^{2+} \tag{1}$$

potentials (Fig. 3, Table 3). The formal potentials E_f are taken as the average of the cathodic (E_{pc}) and anodic peak potentials (E_{pa}). The peak-to-peak separations (ΔE_p) are characteristic of reversible one electron transfer in equation (1) (Table 3).

The formal potentials of the complexes $[\mathrm{Fe(L^2)_2}]^{2+}$ and $[\mathrm{Fe(L^3)_2}]^{2+}$ are completely unexpected as one would predict less positive values for the methyl substituted complexes compared with the unsubstituted complex $[\mathrm{Fe(L^1)_2}]^{2+}$ based on the electron-releasing properties of methyl substituents. The present effect clearly demonstrates the predominance of steric crowding at the 3 position(s) over the electronic contribution prevailing at the 5 position(s) in the ligands $\mathrm{L^2}$ and $\mathrm{L^3}$.

Electrochemical studies have been made[28] on sterically hindered $\mathrm{CuN_4}$ complexes of tripodal ligands and similar unusual electrochemical results obtained were rationalized as a result of pronounced environmental effects. However, whereas geometrical factors are regarded as being of importance in $\mathrm{Cu^{II}}$–$\mathrm{Cu^{I}}$ chemistry,[29] such an influence has not been regarded as being so crucial in $\mathrm{Fe^{III}}$–$\mathrm{Fe^{II}}$ redox behaviour. Thus the unusual electrochemical behaviour of our complexes demands special attention.

The paucity of $\mathrm{Fe^{III}}$–$\mathrm{Fe^{II}}$ redox potentials for high-spin iron(II) complexes having an $\mathrm{Fe^{II}N_6}$ co-ordination sphere limits comparison of our E_f values with other systems. The iron(II) oxidation state in $[\mathrm{Fe(L^1)_2}]^{2+}$ is stabilized by more than 100 mV[12c] compared to $[\mathrm{Fe(L^4)}]^{2+}$ {$\mathrm{L^4}$ = tris[4-(2-pyridyl]-3-aza-but-3-enyl]amine} and by ≈200 mv[13b] compared to $[\mathrm{Fe(L^5)_2}]$ [$\mathrm{L^5}$ = hydridotris(3-phenylpyrazol-1-yl)borate] which has an identical co-ordination sphere and spin state.

Conclusion

This research has resulted in the recognition and characterization of a new class of tridentate $\mathrm{N_3}$ ligands $\mathrm{L^{1-3}}$ and the influence of methyl substitution near the donor site of their iron(II) complexes. The high-spin iron(II) complexes display paramagnetically shifted ^{1}H NMR resonances and distorted octahedral $\mathrm{Fe^{II}N_6}$ co-ordination. Steric crowding near the donor site for complexes with ligands $\mathrm{L^2}$ and $\mathrm{L^3}$ reduces the ligand-field strength (10 *Dq*) relative to $\mathrm{L^1}$. By observation of the $\mathrm{Fe^{III}}$–$\mathrm{Fe^{II}}$ redox couples it has been nicely demonstrated that in the present system steric effects due to 3-Me substituents predominate over the electronic effect of 5-Me substituents. We are not aware of any previous high-spin $\mathrm{Fe^{II}N_6}$ system in which systematic spectral and electrochemical studies have been performed to investigate the controlled effect of methyl substituents adjacent to donor sites. Careful choice of ligand design has allowed us to achieve this goal. A proper manipulation of the size of the central metal ion can also give rise to an opposite effect in which electronic effects predominate over steric factors. Such studies are in progress.[30]

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