fac-Specific syntheses of homochiral $[Fe(NN')_3]^{2+}$ complexes (NN′ = pyridine keto-hydrazone); origins of the stereoselectivity†

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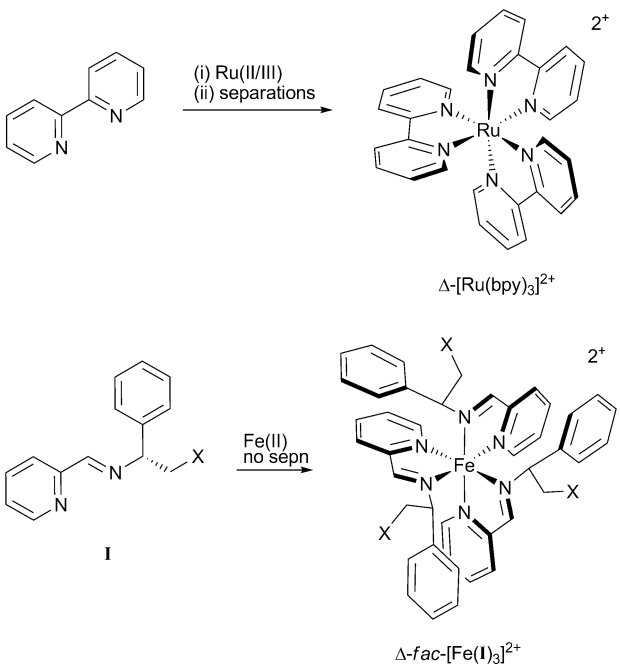
The 2-pyridinehydrazones (from condensation of pyridine-2-carbaldehyde and hydrazines) have previously been noted to have poor ligating ability as a result of a sterically demanding planar conformation. Destabilisation of this conformation is achieved through simple use of the ketohydrazones, and as a result the diamagnetic chiral tris-bidentate diimine complexes *fac*-$[FeL_3]^{2+}$ are readily isolated. In the solid state, inter-ligand π–π stacking and complex/counter-ion H-bonding are apparent, and these features persist in solution according to dynamic NMR spectra, which also indicate extremely high stereoselectivity for the *fac* isomers (>200 : 1). The compounds crystallise as conglomerates, and time-resolved CD spectra of non-racemic samples indicate a high degree of persistence of chirality (racemisation $t_{1/2}$ *ca* 77 min). Variations of solvent and counter-ion indicate that H-bonding is unimportant in determining the structure of the cation. The *fac*-selectivity arises in the induction of a chiral conformation in the coordinated ligand, and the fact that such non-planar ligands can only be accommodated about the Fe(II) centre if they all have the same absolute configuration. Adding a hydrazine *N*-methyl group increases the steric demand further, while retaining the novel non-planar conformation, and as a result paramagnetic chiral bis-bidentate complexes such as $[FeL^7{}_2(CH_3CN)_2]^{2+}$ are readily available.

Introduction

Stereochemically pure tris-chelate compounds are of great current interest, not least because of the potential for applications in supramolecular chemistry,[1-4] molecular sensors,[5,6] anion recognition,[7,8] DNA targeting[9-12] and protein probes.[13] Synthesis of such compounds is however very challenging principally because of the number of possible isomers present.

In a standard synthesis of a tris-chelate $M(a\text{-}b)_3$ complex, the number of possible orientations leads to an expected *mer* : *fac* ratio of 3 : 1. In addition, the *mer* and *fac* isomers are chiral with respect to the configuration at the metal (Δ/Λ). Separation of the four possible isomers has been achieved for inert systems such as Ru(II) by crystallisation, chromatography and other techniques,[14-17] but this is laborious, inherently low yielding, subject to racemisation and leads to uncertainty in optical purity.[18] For labile metal systems there exists the possibility of thermodynamic diastereoselection, and we recently showed that simple diimine ligands **I** derived from 2-iminopyridine and *e.g.* phenylglycinol gave optically and stereochemically pure *fac* tris complexes $[Fe(\mathbf{I})_3]^{2+}$ (X = H, OH, OMe, OCH_2Ph, OCH_2Py, $OCH_2C{\equiv}CH$) with dr >200 : 1.[19] The origins of this unprecedented stereoselectivity are evident from (i) molecular models of the unobserved isomers which show unfavourable steric interactions and (ii) the molecular structure determinations which show favourable arene π–π stacking.



Numerous coordination compounds of pyridinylhydrazones **II** have been reported.[20-27] We asked the question: might phenylhydrazones **IIa**—notionally derived from substituting the stereogenic CH in **I** with "N:"—give exclusively the racemic *fac* series $[M(\mathbf{IIa})_3]^{2+}$ for the same reasons? This would be particularly interesting because of the possibility that such complexes could be formed enantioselectively in the presence of chiral non-racemic anions, and thereby act as chiral sensors reporting in the visible (charge transfer) region. In an early insightful

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study of the coordination chemistry of hydrazones **II**[28] Busch prepared a range of complexes, and while no structural data or NMR studies were possible, it was convincingly concluded from synthetic observations, IR and UV data that the anomalously poor coordinating ability of **IIb** was due to there being a substantial contribution from the polar resonance form shown in Fig. 1(a). This would be prevalent on coordination to a positively charged metal. The resulting planarisation of the alkylated N atom would project a methyl group towards the metal centre causing untenable steric compression in the target complexes. Busch also asserted that the inability of phenylhydrazone **IIa** to form tris complexes resulted from similar steric effects. We fully agree (*vide infra*) but nevertheless report here that as a result of some readily implemented ligand design, tris complexes of phenylhydrazones with Fe(II) are accessible. These complexes show extraordinary stereoselectivity for the *fac* structures, are isolated in non-racemic form, and are unusually inert to inversion of stereochemistry at Fe(II). The origins of the stereoselectivity are investigated using X-ray crystallography, NMR, circular dichroism and synthetic studies.

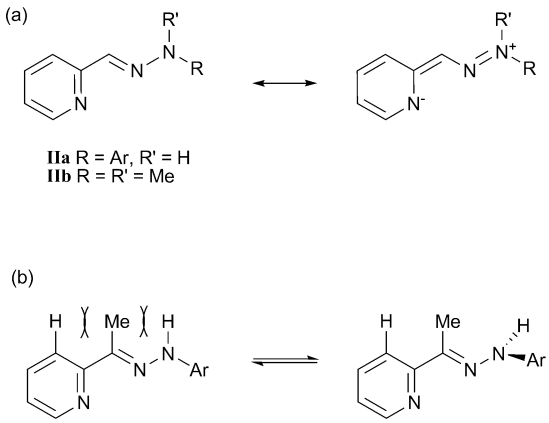
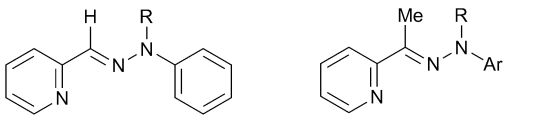


Fig. 1 Resonance and conformational issues in pyridinylhydrazone proligands.

Results and discussion

Synthesis and characterisation of ligands

The pyridinylarylhydrazone ligands used in this study $\mathbf{L}^{1-7}$ were synthesised using slight modifications of literature procedures.[27-36] NMR spectra of samples in d_3-acetonitrile and other data are nevertheless reported herein for comparison with the subsequent complexes.



$\mathbf{L}^1$ (R = H)
$\mathbf{L}^2$ (R = Me)

$\mathbf{L}^3$ (R = H, Ar = Ph)
$\mathbf{L}^4$ (R = H, Ar = *p*-$C_6H_4NO_2$)
$\mathbf{L}^5$ (R = H, Ar = *p*-C_6H_4OMe)
$\mathbf{L}^6$ (R = H, Ar = 2-pyridyl)
$\mathbf{L}^7$ (R = Me, Ar = Ph)

Robinson and Busch[28] mentioned an impure brown paramagnetic bis complex $[Fe\mathbf{L}^1{}_2]I_2$. In our hands treatment of ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ with Fe(II) perchlorate in acetonitrile also gave brown solutions and solids. Attempted crystallisation of products *via e.g.* addition of *anti*-solvents (diethyl ether, ethyl acetate) to the solution gave no precipitation but led instead to formation of paler yellow solutions. An examination of simple molecular models confirms Busch's assertion that there is some difficulty in arranging three such ligands around a first row metal. We proposed however that for the ketohydrazone series $\mathbf{L}^{3-7}$ since there would be substantial intra-ligand steric compression in the planar conformation [see Fig. 1(b)], a non-planar structure would be favoured. We were thus pleased to find that the reaction of $Fe(ClO_4)_2{\cdot}6H_2O$ with three molar equivalents each of 2-acetylpyridine and phenylhydrazine in acetonitrile gave an intense purple solution, and the purple diamagnetic solid $[Fe\mathbf{L}^3{}_3][ClO_4]_2$ was isolated in good yield on addition of ethyl acetate. Large single crystals were obtained in another experiment by adding a small amount of ethyl acetate to the reaction mixture and leaving to stand overnight. The tetrafluoroborate salt $[Fe\mathbf{L}^3{}_3][BF_4]_2$ was prepared and crystallised in a similar manner. We were not able to isolate the analogous Zn(II) complexes.

The crystal of $[Fe\mathbf{L}^3{}_3][ClO_4]_2$ selected for X-ray diffraction had the chiral space group $P6_3$ and contained the *fac*-Λ isomer only, *i.e.* the compound crystallises as a conglomerate. The molecular structure is shown in Fig. 2 along with key bond lengths and angles. The asymmetric unit contains one pyridyl hydrazone ligand, one third of an Fe atom, one third of a ClO_4 unit, and a further ClO_4 refined at a one third occupancy to balance the charge on Fe and to give it meaningful thermal parameters. The Fe sits on a three-fold axis as do Cl(1) and O(2) of the perchlorate. In the unit cell there are two complexes, two perchlorates on the three-fold axis,

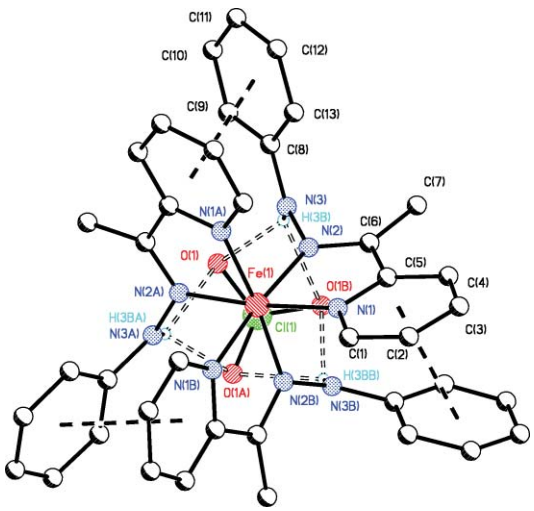


Fig. 2 Molecular structure of *fac*-Λ-$[Fe\mathbf{L}^3{}_3][ClO_4]_2$ viewed approximately down the C_3 axis, showing tripodal arrangement of the hydrazone NH units, attendant bifurcated hydrogen bonds with ClO_4 ion, and inter-ligand π-stacking. Hydrogen atoms not involved in H-bonding have been removed for clarity. Selected bond length (Å) and angles (°): Fe(1)-N(2) 1.946(3), Fe(1)-N(1) 1.978(3), N(2)-N(3) 1.409(4), N(2)-Fe(1)-N(2B) 95.38(12), N(2)-Fe(1)-N(1) 80.36(11), N(2B)-Fe(1)-N(1) 89.06(11), N(2A)-Fe(1)-N(1) 174.14(10), N(1)-Fe(1)-N(1A) 95.47(12). Hydrogen bond lengths (Å) (DH···A) and angles (°) (<DHA): N(3)-H(3)···O(1) 2.19, N(3)-H(3)···(O1A) 2.41, N(3)-H(3)-O(1) 143.3, N(3)-H(3)-O(1A) 139.5.

and six perchlorates at a third occupancy, hence two complexes and four perchlorates in total.

The molecular structure for this pyridine hydrazone system is analogous to that observed for the optically and diastereomerically pure α-methylbenzylimine series *e.g.* $[Fe(\mathbf{I})_3]^{2+}$ with *fac* coordination of the bidentate ligand,[19] but is nevertheless unusual since reported structures of $M(a\text{-}b)_3$ complexes are dominated by the presence of *mer* isomers.

Three inter-related features are apparent from examination of these structures: (i) as for $[Fe(\mathbf{I})_3]^{2+}$, π–π interactions are present between each of the three phenyl groups and the pyridine ring of an adjacent ligand.[19] The closest interatomic contact C(5)-C(8) is *ca* 3.25 Å and the angle between mean pyridine and phenyl planes involved in the π-stacking is *ca* 19°. The centroid - centroid distance is *ca* 3.83 Å; (ii) the mean plane of this π-stacked hydrazone phenyl ring is also nearly orthogonal to that of the pyridine ring in the same ligand [inter-plane angle *ca* 79°]. This minimises the steric interactions with acetylpyridine hydrazone methyl group C(7) as shown in Fig. 1(b); (iii) the three fold arrangement of hydrazone NH units at N(3) present a complimentary H-bonding arrangement to the three oxygen atoms on one face of the perchlorate tetrahedron. Each of these oxygen atoms is held in a bifurcated arrangement with two H atoms of the NH triad, consisting of one close contact and one slightly longer interaction with a neighbouring NH. In addition, the oxygen O(2) of the perchlorate ion has a three point interaction with the α pyridyl CH of the chelated pyridines from a neighbouring complex in the crystal [C–H···O(2) 2.513 Å]. An infinite chain is thus formed of alternating perchlorate and complex ions along the three fold axis (Fig. 3).

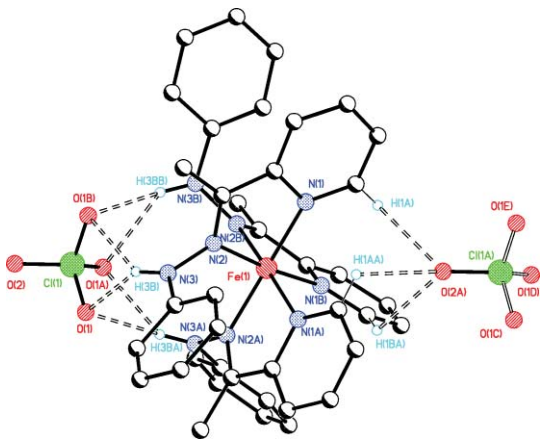


Fig. 3 Catenation of ions in the crystal structure of *fac*-Λ-$[Fe\mathbf{L}^3{}_3][ClO_4]_2$. Bifurcated N(3)-H···O(1) and C(1)-H···O(2) hydrogen bonding motifs indicated.

The crystal structure of $[Fe\mathbf{L}^3{}_3][BF_4]_2$ (Fig. 4) is isomorphic with that of $[Fe\mathbf{L}^3{}_3][ClO_4]_2$, and the crystal selected also contained the complex in Λ configuration. The hydrogen bonding motifs were also analogous.

We were readily able to isolate optically pure crystals of *fac*-$[Fe\mathbf{L}^3{}_3][BF_4]_2$ from the racemic mixture. The circular dichroism (CD) spectra of one such sample *fac*-Δ_{Fe}-$[Fe\mathbf{L}^3{}_3][BF_4]_2$ in acetonitrile are shown in Fig. 5 along with that of authentic *fac*-Δ_{Fe}-S_C-$[Fe(\mathbf{I})_3][ClO_4]_2$ (X = H).[19] The spectra have very similar features

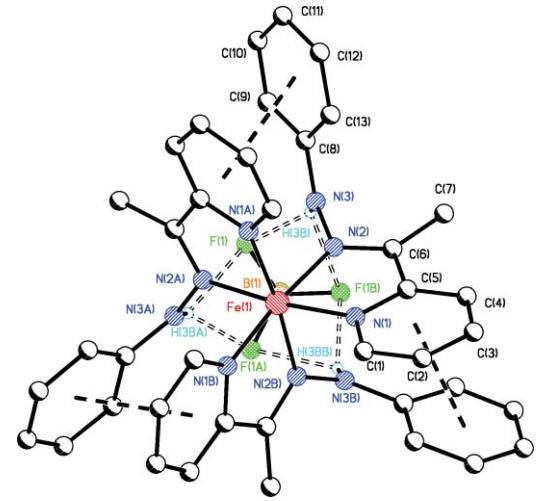


Fig. 4 Molecular structure of *fac*-Λ-$[Fe\mathbf{L}^3{}_3][BF_4]_2$ viewed approximately down the C_3 axis. See also Fig. 2 and 3 of isomorphic *fac*-Λ-$[Fe\mathbf{L}^3{}_3][ClO_4]_2$. Selected bond length (Å) and angles (°): Fe(1)-N(2) 1.957(3), Fe(1)-N(1) 1.967(3), N(2)-N(3) 1.409(4), N(2)-Fe(1)-N(2B) 94.13(14), N(2)-Fe(1)-N(1) 80.97(13), N(2B)-Fe(1)-N(1) 89.77(13), N(2A)-Fe(1)-N(1) 173.96(13), N(1)-Fe(1)-N(1A) 95.40(14). Hydrogen bond lengths (Å) (DH···A) and angles (°) (<DHA): N(3)-H(3)···F(1) 2.14, N(3)-H(3)···F(1A) 2.38, N(3)-H(3)-F(1) 145.9, N(3)-H(3)-F(1A) 139.4.

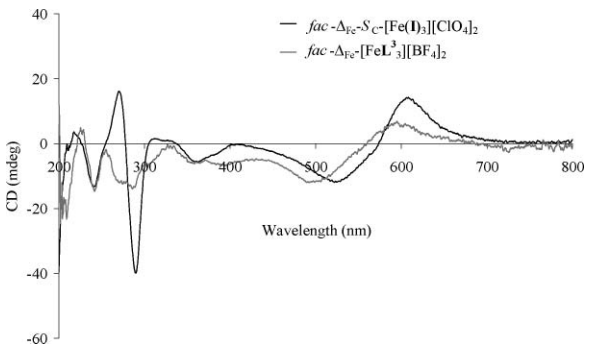


Fig. 5 CD spectra of *fac*-Δ_{Fe}-S_C-$[Fe(\mathbf{I})_3][ClO_4]_2$ (X = H) and *fac*-Δ_{Fe}-$[Fe\mathbf{L}^3{}_3][BF_4]_2$.

in all regions, consistent with the solutions structures being, as expected, very similar. The decay in the CD signal of *fac*-Δ_{Fe}-$[Fe\mathbf{L}^3{}_3][ClO_4]_2$ was monitored for the full spectrum as shown in Fig. 6, and also by acquiring spectra over 5 h in the 500 nm region. The data were analysed following Brunner.[37] The log plot shown in Fig. 6 is consistent with the expected unimolecular kinetics for isomerisation of the complex, with an observed rate constant $k_{obs} = 2.82\ (\pm 0.07)\times10^{-4}\ s^{-1}$. This corresponds to $t_{1/2}$ for the decay of 77 (± 2) min.

The ^1H and ^{13}C NMR spectra of $[Fe\mathbf{L}^3{}_3][ClO_4]_2$ and $[Fe\mathbf{L}^3{}_3][BF_4]_2$ in dry acetonitrile were essentially superimposable, with the exception of the hydrazinimino NH signals which were observed at 7.89 (ClO_4^- salt) and 7.77 ppm (BF_4^- salt) compared to the free ligand at 8.26 ppm. Most importantly, only one set of coordinated ligand peaks were observed. We noticed however that in the spectra at *ca* 298 K there was significant broadening of resonances. VT NMR studies were carried out in the accessible range 233-343 K (Fig. 7). At 343 K all signals were sharp, and on

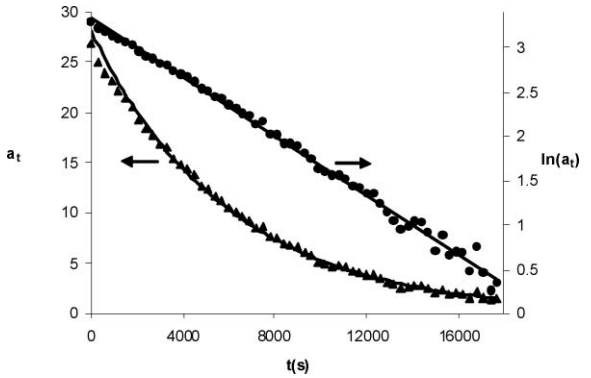


Fig. 6 Racemisation of *fac*-Λ_{Fe}-[Fe$\mathbf{L}^3{}_3$][ClO_4]$_2$ in acetonitrile at 298 K.

lowering the temperature some broadening occurred throughout but much more so for those resonances assigned to the phenyl *meta* and *ortho* substituents $H^{a/a'}$ and $H^{b/b'}$. The signal for H^c was relatively unaffected. At 233 K, the lower limit imposed by the melting point of the solvent, the signals for H^a and H^b broadened into the baseline and very broad new peaks are detectable for $H^a/H^{a'}$ (*ca* 7.2 and 6.55 ppm) and $H^b/H^{b'}$ (*ca* 7.2 & 5.2 ppm). The CD studies above show that coordination isomerisation (*e.g.* *fac*/*mer*-Δ/Λ exchange) processes are occurring several orders of magnitude slower than the NMR chemical shift timescale, and are thus excluded as a mechanism here. Restricted NH–C_{Ph} bond rotation is thus responsible for averaging the magnetic environments of $H^a/H^{a'}$ and $H^b/H^{b'}$. The origins of this behaviour are apparent from the structural studies above; π–π coordination, the steric effect of the acetyl methyl group and the inter-ion H-bonding. The *fac* structure observed in the solid state also thus persists in solution, and indeed there is an unusually high thermodynamic preference for this structure, with a *fac* : *mer* ratio >200 : 1.

Probing the importance of H-Bonding. In order to probe the importance of H-bonding on the observed stereoselectivity we have further varied the counter-ion, examined the effects of solvents and attempted some electronic variation of the hydrazone unit.

On mixing three equivalents of $\mathbf{L}^3$ in d_3-acetonitrile with [Fe(CH_3CN)$_6$][BPh_4]$_2$,‡ containing the more weakly coordinating tetraphenylborate anion, the complex *fac*-[Fe$\mathbf{L}^3{}_3$][BPh_4]$_2$ was formed exclusively. The ^{1}H-NMR spectra obtained were almost identical to those above. The NH resonance was observed at 7.75 ppm. Unfortunately, we were unable to crystallise this complex.

NMR spectra of these compounds obtained in a range of solvents also showed similar signals pattern, although in the case of protic systems there was the expected competitive solvolysis. For example, a sample of pure [Fe$\mathbf{L}^3{}_3$][ClO_4]$_2$ was dissolved in dry d_4-methanol to give a purple solution. The ^{1}H NMR spectrum acquired after a few minutes showed a mixture of the complex and free ligand (as compared with an authentic sample). After a few hours the complex had fully decomposed. Nevertheless, the NMR spectra of the complex did not show the presence of *mer* isomers.

‡ Similar compounds have previously been mentioned.[41-43] [Fe($MeCN$)$_6$][BPh_4]$_2$ was synthesised analogously to [Fe($MeCN$)$_6$][B{$C_6H_3(CF_3)_2$}$_4$]$_2$ (see experimental section).[41]

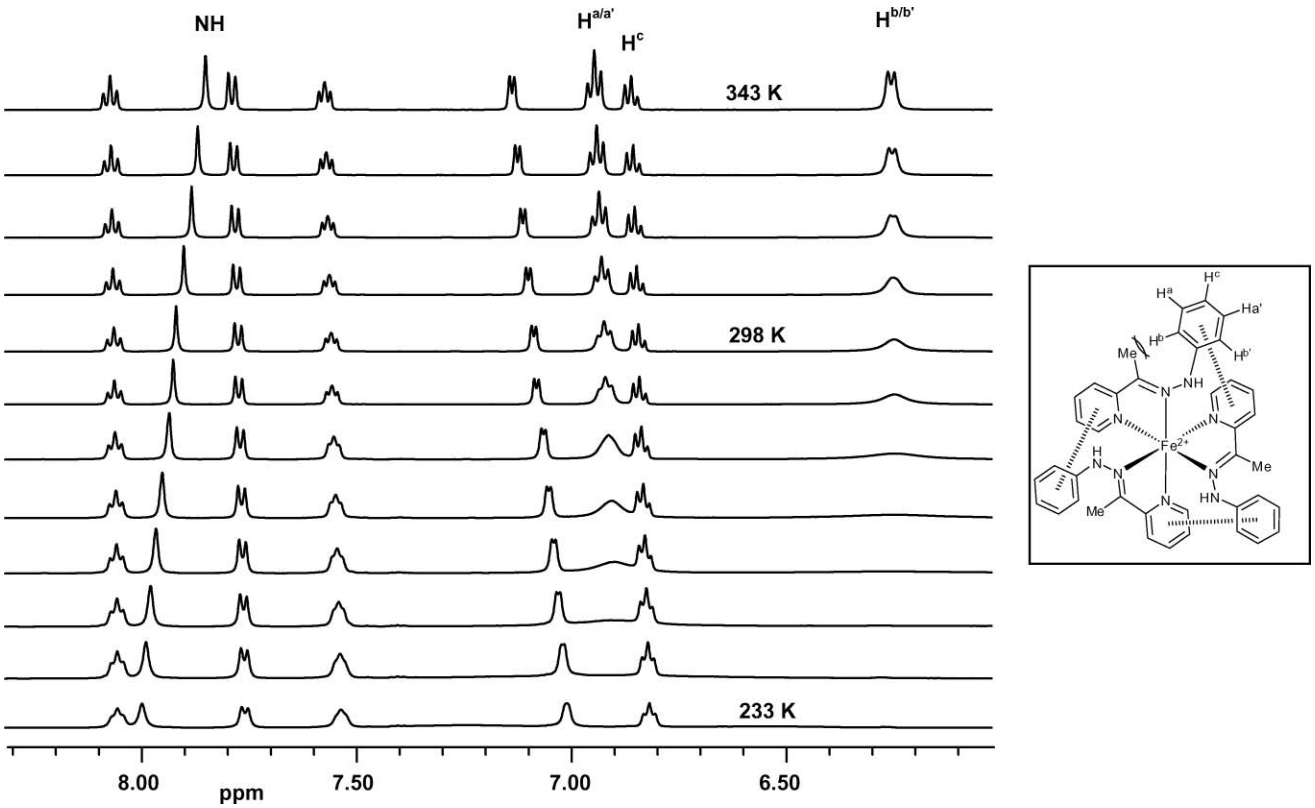


Fig. 7 NH/aromatic region of VT ^{1}H NMR spectra of [Fe$\mathbf{L}^3{}_3$][ClO_4]$_2$, in d_3-acetonitrile (inset—structure of [Fe$\mathbf{L}^3{}_3$]$^{2+}$).

The *p*-nitro compound $\mathbf{L}^4$ was synthesised successfully, but on treatment with Fe(II) salts deposited an insoluble yellow solid. The *p*-methoxy compound $\mathbf{L}^5$ has previously been described,[38] but in our hands (and using the published method) the orange salt $[\mathbf{HL}^5]Cl{\cdot}H_2O$ was obtained, according to microanalysis. The ^{1}H-NMR spectrum in d_6-DMSO was the same as that previously assigned to $\mathbf{L}^5$.[38] Attempts to synthesise Fe(II) complexes of this ligand under suitably basic conditions were unsuccessful.

Further ligand modifications. In confirmation of a previous report,[39] treatment of Fe(II) with $\mathbf{L}^6$ led to diamagnetic red bis tridentate complexes $[Fe\mathbf{L}^6{}_2][ClO_4]_2$ and $[Fe\mathbf{L}^6{}_2][BF_4]_2$ regardless of the stoichiometry. The yellow Zn(II) compounds $[Zn\mathbf{L}^6{}_2][ClO_4]_2$ and $[Zn\mathbf{L}^6{}_2][BF_4]_2$ were also isolated here.

In contrast with the unpromising behaviour of $\mathbf{L}^2$, treatment of $Fe(ClO_4)_2$ in acetonitrile with ketohydrazone $\mathbf{L}^7$ forms a red/purple solution from which racemic crystals of the octahedral C_2-symmetric bis complex $[Fe\mathbf{L}^7{}_2(NCMe)_2][ClO_4]_2[MeCN]_2$ are readily isolated. The molecular structure of this compound is shown in Fig. 8. The Fe atom lies on a two-fold axis. The *cis* angles for acetonitrile [N(4)-Fe–N(4A)] and hydrazone [N(2)-Fe–N(2A)] ligands are 89.66(12) and 95.29(12)° respectively, with the *trans* pyridine angle [N(1)-Fe–N(1A)] of 177.11(13)°. In a similar manner to the structures of $\mathbf{L}^3$ complexes above, the hydrazone unit is non-planar with torsion angle C(6)-N(2)-N(3)-C(8) of *ca* 82.4°. As a result, the non-bonded p-orbital of N(3) cannot be considered to be in conjugation with the imine and this atom is correspondingly pyramidalised (sum of angles 349°). Again, as for the tris structures, there is reciprocal inter-ligand π-stacking between phenyl groups and adjacent pyridines. The closest atomic contact N(1)-C(9A) is *ca* 3.05 Å.

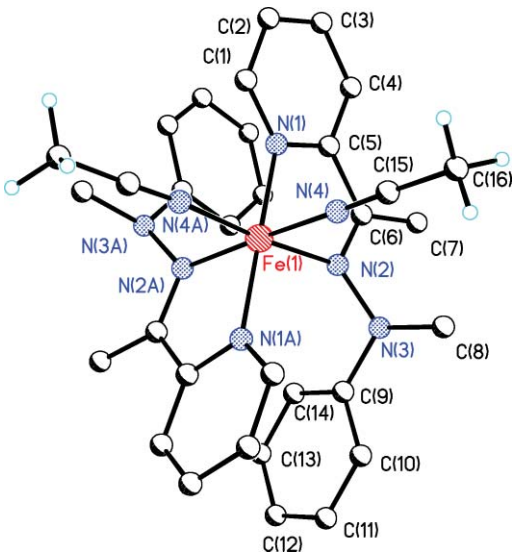


Fig. 8 Structure of the cationic unit of $[Fe\mathbf{L}^7{}_2(NCMe)_2][ClO_4]_2{\cdot}2(CH_3CN)$. Hydrogen atoms have been removed for clarity. Selected bond length (Å) and angles (°):N(4)1-Fe(1)-N(4A) 89.66(12), N(4A)1-Fe(1)-N(1A) 87.35(8), N(4)-Fe(1)-N(1A) 94.70(8), N(4A)-Fe(1)-N(1) 94.70(8), N(4)-Fe(1)-N(1) 87.35(8), N(1A)-Fe(1)-N(1) 177.11(13), N(4A)-Fe(1)-N(2) 175.28(8), N(4)-Fe(1)-N(2) 87.65(8), N(1A)-Fe(1)-N(2) 96.73(8), N(1)-Fe(1)-N(2) 81.30(8), N(4A)-Fe(1)-N(2A) 87.65(8), N(4)-Fe(1)-N(2A) 175.28(8), N(1A)-Fe(1)-N(2A) 81.30(8), N(1)-Fe(1)-N(2A) 96.73(8), N(2)-Fe(1)-N(2A) 95.29(12).

Conclusions

The poor ligating ability of hydrazones $\mathbf{L}^1$ and $\mathbf{L}^2$, previously proposed to result from the high steric demand of their planar conformation [Fig. 1(a)], is confirmed here. Destabilisation of this conformation as shown in Fig. 1(b) is achieved through use of ketohydrazones such as $\mathbf{L}^{3\text{-}7}$ and this in turn allows the ready isolation of chiral tris complexes *fac*-$[Fe\mathbf{L}^3{}_3]^{2+}$. The solid state structures from X-ray crystallography indicate three related features; inter-ligand π–π stacking, the steric effect of acetyl hydrazone methyl group and complex/counter-ion H-bonding. These features persist in solution, and there is very high stereoselectivity for the *fac* isomers (as indicated by dynamic NMR behaviour). The degree of persistence of chirality for these compounds (as demonstrated by a measured racemisation $t_{1/2}$ of *ca.* 77 min) is also striking for a labile Fe(II) centre. Given that the stereoselectivity persists in methanol and is the same for the BPh_4^- salt, it would seem that H-bonding is unimportant in determining the structure. The origin of the *fac*-selectivity is thus primarily steric; the presence of the hydrazone *C*-methyl group induces an element of chirality in the coordinated ligand (the conformation is chiral) and the only sterically tenable combination of three such ligands around the metal is homochiral. In other words, $\mathbf{L}^3$ behaves like a prochiral version of optically pure **I**.[19]

The stability of the octahedral tris complexes is nevertheless finely balanced: Zn(II) complexes, for which there would be no OSPE, are not isolated, despite the existence of related $[Zn(\mathbf{I})_3]^{2+}$,[19] and electron withdrawing (NO_2) substituents in the hydrazone are not tolerated. The presence of ligating atoms in the hydrazone unit of $\mathbf{L}^6$ leads in contrast to stable, diamagnetic octahedral bis complexes of both Fe(II)[39] and Zn(II).

Finally, the more sterically-demanding *N*-methyl system $\mathbf{L}^7$ gives a fascinating paramagnetic chiral complex $[Fe\mathbf{L}^7{}_2(CH_3CN)_2]^{2+}$. There is also a fine balance here in terms of the magnetic properties of the bis(diimine) systems, with $[Fe\mathbf{L}^7{}_2(CH_3CN)_2]^{2+}$ and the previously reported $[Fe(\mathbf{I})_2]^{2+}$ (X = OH) being paramagnetic while $[Fe\mathbf{L}^6{}_2]^{2+}$ is diamagnetic. It may be possible to exploit this in the synthesis of chiral spin-crossover materials.

Experimental section

Starting materials for ligand syntheses were purchased from Sigma Aldrich and Acros Organics and used without further purification. Schlenck techniques were applied in handling the air sensitive compounds. 2-Acetylpyridine phenylhydrazone ($\mathbf{L}^3$) was synthesised as previously reported.[23,27,30]

NMR spectra were recorded at 298 K on a Bruker DPX300 and Bruker DPX400 spectrometers. VT NMR spectra were obtained by Dr Adam J. Clarke on Bruker DRX500. Proton and carbon NMR assignments were routinely confirmed by ^{1}H-^{13}C (HMQC) and COSY experiments. Elemental analyses were performed by Warwick Analytical Services, Coventry, UK and Medac Limited, Surrey, UK. Mass Spectra were recorded on Bruker Esquire2000 and micrOTOF by the Department of Chemistry Mass Spectrometry Service, University of Warwick. IR data were recorded on Perkin Elmer Spectrum 100. CD spectra were recorded at 298 K on Jasco J-815 circular dichroism spectropolarimeter and UV spectra were obtained on Jacso V-550 UV-visible absorption spectrometer.

Crystallography

[FeL$^3_3$][ClO$_4$]$_2$. $C_{39}H_{39}N_9Cl_2O_8Fe$, M = 888.54, purple block 0.32 × 0.10 × 0.10 mm, hexagonal, space group P6$_3$, $a = b$ = 15.8761(4) Å, c = 10.5809(3) Å, V = 2309.63(10) Å^3, Z = 2, D_c = 1.278 g cm^{-3}, T = 100(2) K, with MoKa (0.71073), 11159 reflections collected, 2842 unique (R_{int} = 0.0568), R1 [$I > 2s(I)$] = 0.0778, wR2 (F, all data) = 0.1520, GoF = 0.947, Flack 0.03(3). CCDC 761423.

[FeL$^3_3$][BF$_4$]$_2$. $C_{39}H_{39}N_9B_2F_8Fe$, M = 863.26, purple block 0.20 × 0.08 × 0.05 mm, hexagonal, space group P6$_3$, $a = b$ = 15.8761(4) Å, c = 10.5809(3) Å, V = 2309.63(10) Å^3, Z = 2, D_c = 1.241 g cm^{-3}, T = 100(2) K, with MoKa (0.71073), 8792 reflections collected, 2578 unique (R_{int} = 0.0599), R1 [$I > 2s(I)$] = 0.0812, wR2 (F, all data) = 0.1535, GoF = 0.960, Flack 0.03(3). CCDC 761424.

[FeL$^7_2$(NCMe)$_2$][ClO$_4$]$_2$.2(CH$_3$CN). $C_{36}H_{42}N_{10}O_8Cl_2Fe$, M = 869.55, orange plate 0.08 × 0.05 × 0.01 mm, monoclinic, space group $C2/c$, a = 12.0681(6) Å, b = 16.8580(12) Å, c = 19.7972(9) Å, β = 104.057(5)°, V = 3907.0(4) Å^3, Z = 2, D_c = 1.478 g cm^{-3}, T = 100(2) K, with MoKa (0.71073), 23664 reflections collected, 2763 unique (R_{int} = 0.0400), R1 [$I > 2s(I)$] = 0.0564, wR2 (F, all data) = 0.0966, GoF = 0.901. CCDC 761425.

The crystals were mounted on a glass fibre using an inert oil prior to transfer to a cold nitrogen gas stream from an Oxford Cryosystems Cobra on a Oxford Diffraction Gemini four-circle diffractometer system with a Ruby CCD area detector using Mo-Kα radiation (= 0.71073 Å). Diffractometer control and data collection were with CrysAlis CCD (Oxford Diffraction 2008). Data were collected with 1° frame exposures using phi and omega scans with data reduction by CrysAlis RED (Oxford Diffraction, 2008). Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections with ABSPACK (CrysAlis, Oxford Diffraction, 2008). The structures were solved by direct methods (SHELXS) with additional light atoms found by Fourier methods. All non-hydrogen atoms were refined anisotropically. H atoms were placed at calculated positions and constrained with a riding model. U(H) was set at 1.2 (1.5 for methyl hydrogen atoms as applicable) times U_{eq} for parent atom. SHELXTL was used for structure solution, refinement, and molecular graphics.

Syntheses

2-Pyridinecarboxaldehyde phenylhydrazone[28] (L^1). A pale yellow solution of phenylhydrazine (2.10 g, 19.0 mmol) in absolute ethanol (5 mL) was added to a pale yellow solution of 2-pyridine carboxaldehyde (2.00 g, 19.0 mmol) in absolute ethanol (5 mL) at ambient temperature, resulting in a bright yellow solution and yellow precipitate. Stirring was continued for 24 h at reflux. After cooling, the yellow solid, **L**^{1}, was obtained by vacuum filtration and dried *in vacuo* at 30 °C (2.91 g, 74%). M.p. 189–190 °C. Anal. Found (Calcd. for $C_{12}H_{11}N_3$)% C 72.88 (73.07), H 5.60 (5.62), N 21.30 (21.30). ^{1}H NMR (300 MHz, 298 K, Acetone-d_6) δ 6.84 (tt, J = 7, 1.5 Hz, 1H, Py), 7.24 (m, 5H, Ph), 7.76 (td, J = 6, 1.5 Hz, 1H, Py), 7.91 (s, 1H, CH), 8.03 (d, J = 8 Hz, 1H, Py), 8.52 (dt, J = 1.5, 4.5 Hz, 1H, Py), 9.85 (br s, 1H, NH). ^{13}C{^{1}H} NMR (75 MHz, 298 K, Acetone-d_6) δ 113.4 (Ph), 119.6 (Py), 120.7 (*p*-Ph), 123.2 (Py), 130.1 (Ph), 136.9 (CH), 138.2 (Py), 146.1 (C_q), 150.1 (Py), 156.5 (C_q). IR (neat) ν cm^{-1} 3181 (NH), 1597 (C=N), 1565 (pyridine ring), 996 (N–N). MS (ESI$^+$): m/z 198.00 [$C_{12}H_{11}N_3$+H]$^+$.

2-Pyridinecarboxaldehyde-*N*-methyl-*N*-phenylhydrazone[29] (L^2). The *N*-methyl-*N*-phenylhydrazine (1.20 g, 10.0 mmol) was dissolved in absolute ethanol (5 mL), giving a pale yellow solution. The addition of the pale yellow solution of 2-pyridinecarboxaldehyde (1.00 g, 10.0 mmol) in absolute ethanol (5 mL) to the *N*-methyl-*N*-phenylhydrazine solution caused the colour to change to bright yellow. The solution was stirred overnight at reflux. All the solvent was removed completely under reduced pressure and a yellow solid was obtained, **L**^{2}. The yellow solid was then collected and dried overnight *in vacuo* at 30 °C (1.83 g, 88%). M.p. 76–78 °C. Anal. Found (Calcd. for $C_{13}H_{13}N_3$)% C 73.92 (73.91), H 6.18 (6.20), N 19.89 (19.89). ^{1}H NMR (300 MHz, 298 K, Acetone-d_6) δ 3.55 (s, 3H, CH_3), 6.95 (td, J = 7.5, 2 Hz, 1H, *p*-Ph), 7.19 (ddd, J = 1, 5, 7.5 Hz,1H, Py), 7.34 (m, 2H, *m*-Ph), 7.49 (d, J = 8 Hz, 2H, *o*-Ph), 7.64 (s, 1H, N=CH), 7.75 (td, J = 8, 2.5 Hz, 1H, Py), 8.02 (d, J = 8 Hz, 1H, Py), 8.53 (d, J = 5 Hz, 1H, Py). ^{13}C{^{1}H} NMR (75 MHz, 298 K, Acetone-d_6) δ 33.3 (CH_3), 116.2 (*o*-Ph), 119.4 (Py), 121.8 (*p*-Ph), 122.8 (Py), 129.8 (*m*-Ph), 133.7 (Py), 136.9 (Py), 150.0 (Py). IR (neat) ν cm^{-1} 1599 (C=N), 1560 (pyridine ring), 994 (N–N). MS (ESI$^+$): m/z 212.00 [$C_{13}H_{13}N_3$+H]$^+$.

2-Acetylpyridine-4-nitrophenylhydrazone (L^4). A brown suspension of 4-nitrophenylhydrazine (1.86 g, 12.16 mmol) in absolute ethanol (25 mL) was added to 2-acetylpyridine (1.47 g, 12.16 mmol) at ambient temperature. Two drops of acetic acid was added. The solution was stirred at reflux overnight and then filtered. Distilled water was added to the yellow filtrate. The crystallised yellow solid, **L**^{4}, was collected and dried *in vacuo* (0.90 g, 29%). M.p. 262-263 °C. Anal. Found (Calcd. for $C_{13}H_{12}N_4O_2$)% C 60.74 (60.93), H 4.58 (4.72), N 21.13 (21.86). ^{1}H NMR (400 MHz, 298 K, Acetone-d_6) δ 2.47 (s, 3H, CH_3), 7.34 (dd, J = 1 Hz, 1H, Py), 7.48 (d, J = 9 Hz, 2H, Ph), 7.82 (t, J = 7.5 Hz, 1H, Py), 8.18 (d, J = 9 Hz, 2H, Ph), 8.27 (d, J = 8 Hz, 1H, Py), 8.59 (d, J = 4.5 Hz, 1H, Py), 9.70 (br s, 1H, NH). ^{13}C NMR (400 MHz, 298 K, Acetone-d_6) δ 10.9 (CH_3), 113.3 (Ph), 120.8 (Py), 123.9 (Py), 126.6 (Ph), 137.0 (Py), 147.7 (C_q), 149.5 (Py), 151.8 (C_q), 156.7 (C_q). IR (neat) ν cm^{-1} 3323 (NH), 1601 (C=N), 1575 (pyridine ring). MS (ESI$^+$): m/z 257.0 [$C_{13}H_{12}N_4O_2$+H]$^+$.

2-Acetylpyridine-4-methoxyphenylhydrazone hydrochloride mono hydrate, [HL^5]Cl·H$_2$O. A purple suspension of 4-methoxyphenylhydrazine mono hydrochloride (0.5 g, 2.86 mmol) in absolute ethanol (25 mL) was added to 2-acetylpyridine (0.35 g, 2.86 mmol) in absolute ethanol (10 mL) ambient temperature, followed by glacial acetic acid (2 drops). The resultant orange solution was stirred at reflux for 3 h before cooling to ambient temperature. The solvent was reduced to one third of the original volume. The crystallised orange solid was collected and dried *in vacuo*. The orange solid, **L**^{5}, was recrystallised from hot ethanol (0.45 g, 65%). M.p. 218-220 °C. Anal. Found (Calcd. for $C_{14}H_{18}N_3ClO_2$)% C 56.47 (56.85), H 6.09 (6.13), N 14.08 (14.21). ^{1}H NMR (400 MHz, 298 K, DMSO-d_6) δ 2.38 (s, 3H, CH_3), 3.73 (s, 3H, CH_3), 6.90 (d, J = 9 Hz, 2H, Ph), 7.55 (d, J = 9 Hz, 2H, Ph), 7.71 (br t, J = 6.5 Hz, 1H, Py), 8.22 (d, J = 8.5 Hz,

1H, Py), 8.39 (br t, $J = 7.5$ Hz, 1H, Py), 8.67 (d, $J = 4.5$ Hz, 1H, Py), 10.34 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, DMSO-d_6) δ 11.6 (CH_3), 55.2 (CH_3), 114.3 (Ph), 115.5 (Ph), 122.5 (Py), 123.2 (Py), 142.3 (Py), 143.9 (br Py). IR (neat) ν cm^{-1} 3383 (NH), 1606 (C=N), 1552 (pyridine ring). MS (ESI^+): m/z 242.0 $[C_{14}H_{15}N_3O+H]^+$.

2-Acetylpyridine-2-pyridylhydrazone (L^6). The pale yellow solution of hydrazinopyridine (1.00 g, 9.17 mmol) in ethanol (15 mL) was added to the colourless solution of 2-acetylpyridine (1.11 g, 9.17 mmol) and stirred at reflux for 24 h. The solvent was reduced to ~ 1/3 before adding distilled water dropwise to an ice cold solution. A yellow solid precipitated and was collected by filtration. The yellow crystals, $\mathbf{L}^6$, were then collected and dried *in vacuo* (1.39 g, 71%). M.p.: *ca* 58 °C. Anal. found (Calcd. for $C_{12}H_{12}N_4$)% C 66.94 (67.90), H 5.74 (5.70), N 25.69 (26.40). ^1H NMR (400 MHz, 298 K, Acetonitrile-d_3) δ 2.37 (s, 3H, CH_3), 6.83 (dd, $J = 7$, 5 Hz, 1H, Py), 7.25 (dd, $J = 3.5$, 1 Hz, 1H, Py), 7.40 (d, $J = 8.5$ Hz, 1H, Py), 7.66 (t, $J = 8.5$ Hz, 1H, Py), 7.73 (t, $J = 5$ Hz, 1H, Py), 8.17 (dd, $J = 11$, 4.5 Hz, 2H, Py), 8.53 (d, $J = 4.5$ Hz, 1H, Py), 8.55 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, Acetonitrile-d_3) δ 9.9 (CH_3), 107.2 (Py), 116.1 (Py), 119.6 (Py), 122.7 (Py), 136.1 (Py), 138.1 (Py), 147.7 (Py), 148.4 (Py). IR (neat) ν cm^{-1} 3234 (NH), 1602 (C=N), 1572, 1514 (pyridine ring). MS (ESI^+): m/z 213.00 $[C_{12}H_{12}N_4+H]^+$. λ_{max} nm (ε_{max} $M^{-1}cm^{-1}$): 322 (22105), 469 (988).

2-Acetylpyridine-*N*-methyl-*N*-phenylhydrazone [40] (L^7). The solution of N-methyl-*N*-phenylhydrazine (1.11 g, 9.09 mmol) was treated with HCl (37%, 2 drops) in EtOH (10 mL), stirred at reflux for 20 mins. A solution of 2-acetylpyridine (0.86 g, 7.10 mmol) in ethanol (10 mL) was added dropwise. The colour changed from pale yellow to bright red-brown and the solution was refluxed for a further 3 h. The solvent was removed completely and left a brown oil. The brown oil was extracted into chloroform and washed with distilled water (5 × 50 mL). The organic portion was dried over sodium sulfate overnight. The solution was filtered and the solvent was removed *in vacuo*. The resulting product, $\mathbf{L}^7$, was purified *via* column chromatography with eluent petroleum ether: diethyl ether (7 : 3 v/v) and was obtained as an orange oil (1.00 g, 63%). Anal. Found (Calcd. for $C_{14}H_{15}N_3$)% C 74.40 (74.64), H 6.77 (6.71), N 18.26 (18.65). ^1H NMR (400 MHz, 298 K, Acetone-d_6) δ 2.44 (s, 3H, CH_3), 3.23 (s, 3H, CH_3), 6.89 (t, $J = 7.5$ Hz, 1H, *p*-Ph), 7.07 (d, $J = 8$ Hz, 2H, *o*-Ph), 7.27 (t, $J = 7$ Hz, 2H, *m*-Ph), 7.36 (td, $J = 5$, 1 Hz, 1H, Py), 7.79 (td, $J = 7.5$, 2 Hz, 1H, Py), 8.24 (d, $J = 8$ Hz, 1H, Py), 8.61 (d, $J = 4$ Hz, 1H, Py). $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, Acetone-d_6) δ 16.0 (CH_3), 43.3 (CH_3), 116.6 (*o*-Ph), 121.0 (Py), 121.5 (*p*-Ph), 124.9 (Py), 129.6 (*m*-Ph), 136.9 (Py), 149.6 (Py), 152.4 (C_q), 157.6 (C_q), 163.9 (C_q). IR (neat) ν cm^{-1} 1598 (C=N), 1573 (pyridine ring), 987 (N–N). MS (ESI^+): m/z 226.00 $[C_{14}H_{15}N_3+H]^+$.

$[Fe(CH_3CN)_6][BPh_4]$. In the dark, a mixture of $AgBPh_4$ (1.00 g, 2.35 mmol) and $FeBr_2$ (0.25 g, 1.17 mmol) in dry acetonitrile (15 mL) was stirred overnight at ambient temperature. The excess $AgBPh_4$ and AgBr were filtered off and the solution left to settle before re-filtering. The solvent was reduced slowly to ~5 mL. A beige crystalline solid began to precipitate and the solution was cooled to -40 °C (cooling bath of acetonitrile and dry ice) for 4 h. The solid was collected by filtration *via* cannulae and dried *in vacuo* (0.15 g, 14%). Anal. Found (Calcd. for $C_{60}H_{58}N_6B_2Fe$)% C 75.58 (76.61), H 6.88 (6.21), N 9.22 (8.93). ^1H NMR (400 MHz, 298 K, Acetonitrile-d_3) δ 6.69 (t, $J = 6$ Hz, 1H, *p*-Ph), 6.83 (t, $J = 7$ Hz, 2H, *m*-Ph), 7.12 (br d, 2H, *o*-Ph). $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, Acetonitrile-d_3) δ 120.9 (*p*-Ph), 124.7 (*m*-Ph), 134.8 (*o*-Ph), 162.6 (C_q).

***fac*-$[FeL^3_3][ClO_4]_2$.** Under an atmosphere of dinitrogen, a colourless solution of 2-acetylpyridine (0.20 g, 1.80 mmol) and phenylhydrazine (0.18 g, 1.80 mmol) in MeCN (10 mL) was treated with a solution of $Fe(ClO_4)_2\cdot 6H_2O$ (0.20 g, 0.60 mmol) in MeCN (5 mL) at ambient temperature with stirring. The resultant purple solution was stirred overnight and the solvent was evaporated to approximately 1/3 volume. The dropwise addition of ethyl acetate caused a purple solid to precipitate which was filtered, collected and dried *in vacuo* (0.39 g, 79%). Suitable crystals for X-ray crystallography were obtained by slow evaporation of the supernatant. M.p. 186–188 °C. Anal. Found (Calcd. for $C_{39}H_{39}N_9FeCl_2O_8$)% C 51.87 (52.72), H 4.17 (4.42), N 13.82 (14.19). ^1H NMR (300 MHz, 298 K, Acetonitrile-d_3) δ 2.09, (9H, s, CH_3), 6.23 (br, 6H, *o*-Ph), 6.85 (t, $J = 7$ Hz, 3H, *p*-Ph), 6.91 (br t, 6H, *m*-Ph), 7.05 (d, $J = 5$ Hz, 3H, Py), 7.53 (t, $J = 6$ Hz, 3H, Py), 7.74 (d, $J = 8$ Hz, 3H, Py), 7.89 (s, 3H, NH), 8.03 (t, $J = 7.5$ Hz, 3H, Py). $^{13}C\{^1H\}$ NMR (75 MHz, 298 K, Acetonitrile-d_3) δ 15.4 (CH_3), 114.4 (*o*-Ph), 122.4 (*p*-Ph), 127.8 (Py), 128.3 (Py), 129.1 (*m*-Ph), 138.3 (Py), 143.2 (C_q), 154.1 (Py), 158.3 (C_q), 178.8 (C_q). IR (neat) ν cm^{-1} 3319 (NH), 1600 (C=N), 1563 (pyridine ring), 1081 (N–N). MS (ESI^+): m/z 688.26 $[FeL^3_3-H]^+$, 577.00 $[(FeL^3_2)(ClO_4)]^+$, 477.15 $[FeL^3_2-H]^+$. UV/vis λ_{max} nm (ε_{max} $M^{-1}cm^{-1}$): 335 (9113), 524 (5503).

***fac*-$[FeL^3_3][BF_4]_2$.** A colourless solution of the $Fe(BF_4)_2\cdot 6H_2O$ (0.53 g, 1.57 mmol) in acetonitrile (5 mL) was added to solution of 2-acetylpyridine phenylhydrazone (L^3) (1.00 g, 4.73 mmol) in acetonitrile (60 mL) at ambient temperature. The resulting purple solution was stirred for 24 h at ambient temperature. The solvent was concentrated under reduced pressure to around 15 ml and diethyl ether was added. The precipitated solid was collected and dried *in vacuo* (1.18 g, 87%) at 30 °C. M.p. 190–193 °C. Anal. found (Calcd. for $C_{39},H_{39}N_9FeB_2F_8$)% C 52.91 (54.26), H 4.38 (4.55), N 14.17 (14.60). ^1H NMR (300 MHz, 298 K, Acetonitrile-d_3) δ 2.10, (9H, s, CH_3), 6.21 (br s, 6H, Ph), 6.81 (t, $J = 7$ Hz, 3H, Ph) 6.88 (m, 6H, Ph), 7.03 (d, $J = 5$ Hz, 3H, Py), 7.52 (t, $J = 6.5$ Hz, 3H, Py), 7.74 (d, $J = 8$ Hz, 3H, Py), 7.91 (s, 3H, NH), 8.03 (t, $J = 7.5$ Hz, 3H, Py). $^{13}C\{^1H\}$ NMR (75 MHz, 298 K, Acetonitrile-d_3) δ 15.4 (CH_3), 114.4 (*o*-Ph), 122.3 (*p*-Ph), 127.8 (Py), 128.3 (Py), 129.1 (*m*-Ph), 138.3 (Py), 143.2 (C_q), 154.1 (Py), 158.3 (C_q), 178.8 (C_q). IR (neat) ν cm^{-1} 3339 (NH), 1601 (C=N), 1564 (pyridine ring), 1058 (N–N). MS (ESI^+): m/z 477.10 $[FeL^3_2-H]^+$, 343.60 $[FeL^3_3-H]^{2+}$. λ_{max} nm (ε_{max} $M^{-1}cm^{-1}$): 335 (6664), 270 (3247).

$[ZnL^6_2][ClO_4]_2$. A yellow solution of $\mathbf{L}^6$ (0.10 g, 0.48 mmol) in acetonitrile (10 mL) was added to a colourless solution of $Zn(ClO_4)_2\cdot 6H_2O$ (0.009 g, 0.24 mmol) in acetonitrile (15 mL) at ambient temperature. The resulting bright yellow solution was stirred at reflux for 24 h. The solvent was reduced to a third of the original volume and the addition of diethyl ether resulted in a yellow precipitate, which was collected and dried *in vacuo* (0.11 g, 67%). Anal. Found (Calcd. for $C_{24}H_{24}Cl_2ZnN_8O_8$)% C 41.35 (41.85), H 3.42 (3.51), N 15.98 (16.27). ^1H NMR (400 MHz,

298 K, Acetonitrile-d_3) δ 2.69 (s, 6H, CH_3), 6.87 (t, $J = 6.5$ Hz, 2H, Py), 7.23 (d, $J = 8.5$ Hz, 2H, Py), 7.39 (t, $J = 6.5$ Hz, 2H, Py), 7.67 (d, $J = 5$ Hz, 2H, Py), 7.82 (t, $J = 8.5$ Hz, 2H, Py), 8.16 (m, 6H, Py), 10.34 (s, 2H, NH). $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, Acetonitrile-d_3) δ 12.2 (CH_3), 110.6 (Py), 118.1 (Py), 122.9 (Py), 126.1 (Py), 140.8 (Py), 141.6 (Py), 144.7 (C_q), 147.9 (Py), 151.4 (C_q). IR (neat) ν cm^{-1} 3300 (NH), 1618 (C=N), 1599 (pyridine ring), 1086 (N–N). MS (ESI^+): m/z 244.0 $[ZnL^6{}_2]^{2+}$. λ_{max} nm (ε_{max} $M^{-1}cm^{-1}$): 336 (43779), 475 (26266).

$[FeL^7{}_2(MeCN)_2][ClO_4]_2$. The solution of L^7 (0.20 g, 0.89 mmol) was added with the solution of $Fe(ClO_4)_2{\cdot}6H_2O$ (0.17 g, 0.47 mmol) in acetonitrile (10 ml) at ambient temperature to give a red/purple solution. The mixture was stirred overnight and solvent was reduced by half under reduced pressure. Addition of diethyl ether gave purple solid which was isolated and dried over vacuo at 30 °C, leading to loss of solvent of crystallisation (0.34 g, 84%). Anal. Found (Calcd. for $C_{32}H_{36}Cl_2FeN_8O_8$)% C 48.32 (48.81), H 4.52 (4.61), N 15.06 (14.23). IR (neat) ν cm^{-1} 1596 (C=N), 1084 (N–N). MS (ESI^+): m/z 253.1 $[FeL^7{}_2]^{2+}$.

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