Controlled ligand distortion and its consequences for structure, symmetry, conformation and spin-state preferences of iron(II) complexes†‡

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The ligand-field strength in metal complexes of polydentate ligands depends critically on how the ligand backbone places the donor atoms in three-dimensional space. Distortions from regular coordination geometries are often observed. In this work, we study the isolated effect of ligand-sphere distortion by means of two structurally related pentadentate ligands of identical donor set, in the solid state (X-ray diffraction, $^{57}$Fe-Mössbauer spectroscopy), in solution (NMR spectroscopy, UV/Vis spectroscopy, conductometry), and with quantum-chemical methods. Crystal structures of hexacoordinate iron(II) and nickel(II) complexes derived from the cyclic ligand L$^1$ (6-methyl-6-(pyridin-2-yl)-1,4-bis(pyridin-2-ylmethyl)-1,4-diazepane) and its open-chain congener L$^2$ (N$^3$-N$^3$,2-trimethyl-2-(pyridine-2-yl)-N$^3$-bis(pyridine-2-ylmethyl) propane-1,3-diamine) reveal distinctly different donor set distortions reflecting the differences in ligand topology. Distortion from regular octahedral geometry is minor for complexes of ligand L$^2$, but becomes significant in the complexes of the cyclic ligand L$^1$, where trans elongation of Fe–N bonds cannot be compensated by the rigid ligand backbone. This provokes trigonal twisting of the ligand field. This distortion causes the metal ion in complexes of L$^1$ to experience a significantly weaker ligand field than in the complexes of L$^2$, which are more regular. The reduced ligand-field strength in complexes of L$^1$ translates into a marked preference for the electronic high-spin state, the emergence of conformational isomers, and massively enhanced lability with respect to ligand exchange and oxidation of the central ion. Accordingly, o xoiron(IV) species derived from L$^2$ and L$^1$ differ in their spectroscopic properties and their chemical reactivity.

Introduction

In vitro modelling of the biological function of a metal ion requires both an understanding of the factors governing its reactivity, and their control. An important determinant, which is often difficult to study in isolation from other factors, is the distortion of the ligand sphere as imposed by the biological matrix (cf. the concept of the entatic state$^{1,2}$). Studies of entasis, both in vivo and in vitro,$^{3–7}$ are most numerous for copper-based redox catalytic systems. Here, catalytic activity is associated with the mismatch between actual coordination geometry and coordination chemical preference, which is tetrahedral for copper(ii) and square planar (pyramidal) for copper(i). We posit that redox processes involving metal centres other than copper are similarly controlled by ligand-field distortion and therefore synthetically addressable. In particular, the electronic nature and reactivity of ox oiron(IV) species deriving from catalytically active iron(II) complexes, both in vivo and in vitro,$^{8–17}$ are expected to be highly susceptible to ligand-field effects. For instance, variation of the ligand-field strength has been used by Que et al. to tune the spin-state energetics of o xoiron(IV) in a functional model of taurine dioxygenase (TauD) through variation of a donor atom (N vs. O).$^{18}$

In this work, we describe ligand-imposed distortion of the coordination environment as a powerful tool to tune the geometry, electronics and reactivity of a pair of iron(II) complexes. In two closely related N$_5$ ligands of identical donor atom set, distortion of the latter allows us to study the effects of changes
in ligand-sphere geometry and symmetry. This approach decouples the metal centre under study from first-order ligand-field strength effects, as induced by donor set variation, either in terms of donor element (e.g., N vs. O, vide supra) or in terms of hybridisation state within one class of donor atom (e.g., sp² N vs. sp³ N). Control of ligand-field strength via incremental distortion of the geometry necessitates control of intra-ligand strain and thus, synthesis of “tailor-made” polydentate ligands. In previous work, we have provided synthetic access to numerous polydentate nitrogen-dominated ligand systems and have reported on structures and reactivity of their transition-metal complexes (e.g., iron(II/III/V), cobalt(II/III), copper(II)).

For the study presented here, we have prepared the cyclic ligand L¹ (6-methyl-6-(pyridin-2-yl)-1,4-bis(pyridin-2-ylmethyl)-1,4-diazepane), and its open-chain congener L² (N¹,N³,2-trimethyl-2-(pyridine-2-yl)-N¹,N³-bis(pyridine-2-ylmethyl) propane-1,3-diamine). They both share the trisimine-bisamine donor set of the established pentadentate N₅ ligand Bn-TPEN, but differ in the connectivity and hence, structural flexibility of the central diamine unit (Scheme 1).

As is detailed here, structures and electronic properties of iron(n) complexes [FeLⁿ(X)] of these ligands reflect the differences in ligand topology and the inherent ligand-field strength of the co-ligand X. We have characterised the constitution, structure, and electronics of their iron(n) complexes in the solid state as well as in solution and by density-functional theory methods. Trigonal distortion of the coordination sphere, as a consequence of the angular constraint in L¹, is clearly shown to reduce the ligand-field strength significantly, thereby favouring electronic high-spin states of the iron(n) centres. Preliminary results indicate that ligand-imposed distortion also causes the related oxoiron(n) species to show distinctly different spectroscopic properties and reactivity.

Results and discussion
Ligand synthesis
Synthetic details for the 1,4-diazepane-based ligand L¹ have been given in a previous publication. The open-chain ligand L² was prepared from 2-methyl-2-(pyridine-2-yl)-propane-1,3-diamine in four steps with an overall yield of ca. 40%, (Scheme 2). Experimental details and analytical results are given in the Experimental section.

¹H-NMR spectra of the ligands in CDCl₃ are unexceptional. A 2 : 1 intensity pattern in the pyridine-based resonances indicates (time-averaged) Cₛ symmetry in solution in both cases. The spectra of both ligands are overall similar. This suggests
similar structural preferences in solution, \textit{i.e.}, the structural constraints of the diazepane ring in L\textsuperscript{1} (Scheme 1) do not restrict the conformational space of the picolyl donor groups to a significant extent.

**Coordination chemistry of L\textsuperscript{1} and L\textsuperscript{2}**

**Synthesis of metal complexes.** Synthesis and structures of iron(II) complexes of ligand L\textsuperscript{1} (≡ [1(X)]Y; with X = Cl, Br; Y = PF\textsubscript{6}) have been described in a previous publication.\textsuperscript{29} In the present work, we add two iron(II) complexes of ligand L\textsuperscript{1}, with X = Y = OTf and X = CH\textsubscript{3}CN, Y = (BPh\textsubscript{4})\textsubscript{2}, respectively. Complexation with Fe(OTf)\textsubscript{2} was performed in acetonitrile at room temperature. Single crystals of [1(OTf)](OTf) were grown by isothermal diffusion of diethyl ether into a solution of the resulting polycrystalline material (yellow powder) in dichloromethane. The acetonitrile complex [1(MeCN)](OTf)\textsuperscript{2} was synthesised from the perchlorato precursor [1(ClO\textsubscript{4})][ClO\textsubscript{4}] via ligand and anion metathesis. Dissolution of [1(ClO\textsubscript{4})][ClO\textsubscript{4}] in methanol and treatment with excess NaBPh\textsubscript{4} afforded a yellowish powder. Single crystals of [1(MeCN)][BPh\textsubscript{4})\textsubscript{2} were obtained by isothermal diffusion of diethyl ether into a solution of this powder in acetonitrile. Iron(II) complexes of ligand L\textsuperscript{2} (≡ [2(X)]Y; with X = Cl, OTf; Y = PF\textsubscript{6}, OTf) have been obtained by complexation of the open-chain ligand L\textsuperscript{2} with Fe(OTf)\textsubscript{2} or FeCl\textsubscript{2}.

Generation of single crystals was performed as described for ligand L\textsuperscript{1}.

**Crystal structures.** All compounds crystallise as racemic mixtures of two helically chiral enantiomeric complex units. Crystallographic data can be found in Table S1.\textsuperscript{‡} The molecular structures of the complex ions [1(X)]\textsuperscript{n+} and [2(X)]\textsuperscript{n+} are summarised in Fig. 1. Representative structural data of the complex ions are given in Table 1. X-ray structure analysis reveals the expected function of L\textsuperscript{1} and L\textsuperscript{2} as pentadentate ligands, with the sixth coordination site occupied either by a coordinated anion or a solvent molecule. For the sake of structural comparison, the nickel(II) complexes [NiL\textsuperscript{1}(ClO\textsubscript{4})][ClO\textsubscript{4}] and [NiL\textsuperscript{2}(OH\textsubscript{2})][ClO\textsubscript{4}] have been synthesised and their solid-state structures analysed by X-ray crystallography (Fig. 1; characteristic bond lengths and angles are given in Table S2‡).

The coordination polyhedron of the iron(II) complexes is a (slightly distorted) octahedron in the case of [2(X)]\textsuperscript{n+}, but fails to obey any regular geometry in the case of [1(X)]\textsuperscript{n+}. The much stronger distortion of the coordination sphere in [1(X)]\textsuperscript{n+} is obviously due to constraints imposed by its cyclic ligand backbone. In particular, it is the 1,4-diazepane ring that forces and fixes the \textit{cis} angle subtended by the amine-donor atoms at a value much smaller than the ideal value of 90°. As a consequence, the \textit{cis} angle distortion \(\Sigma\) (summed deviation of the 12
cis angles in the polyhedron from 90°) is substantially higher for [1(X)]‡ than in [2(X)]‡.

Iron–nitrogen bond lengths are in the range 210 pm < d(Fe–N) < 235 pm in all cases (see Table 1). This clearly indicates iron(ii) in its high-spin electronic configuration (hs, S = 2, t_2g^6 e_g^0) irrespective of both the nature of the N_3 ligand and the identity of the co-ligand. It is noted, however, that UV/Vis and ^1H-NMR data of [2(MeCN)]^+ in acetonitrile solution at low temperature and Mössbauer spectra of powder samples of [2(MeCN)]^+ reveal significant contributions of low-spin iron(ii) (ls, S = 0, t_2g^6 e_g^0) (vide infra). While XRD data of the acetonitrile complex of L^2 are as yet unavailable (single crystals could not be obtained), its behaviour in solution and in the solid state resembles the closely related N_3 ligand Bn-TPEN, whose iron(ii) complex with coordinated acetonitrile [Fe(Bn-TPEN)(CH3CN)]^+ shows low-spin characteristics in the solid state and in solution.

The Fe–N bonds trans to the co-ligands X, which involve one of the amine N atoms, are elongated in the solid-state structures (Fe1–N4 in Fig. 1 and Table 1) owing to the operation of a strong trans influence. This causes secondary structural effects, which are distinctly different between the two types of N_3 ligand.

Firstly, complexes of the ring-derived ligand L^1 show substantial scatter among the Fe–N bond lengths in the N_4 equatorial plane. In Fig. 2a, for both [1(X)]‡ and [2(X)]‡, the maximum variation in the bond lengths, Δd_eq, is illustrated by a plot against the (essentially invariant) average Fe–N bond lengths in the N_4 equatorial plane, d_eq. Secondly, there is massive distortion from planarity within this N_4 donor set only in the case of [1(MeCN)][OTf]_2 (torsion amounts to 50°; Fig. S1‡). In conclusion, angular distortion and bond-length scatter are correlated with each other. Both reflect the different degrees of structural feedback within the ligands.

This having been said, the distorted structure of [1(X)]‡ can be analysed as a blend of octahedral and trigonal-prismatic arrangements; i.e., the trigonal Bailar twist angle θ between co-facial donor triads (see Fig. S2‡) amounts to 27.5°, intermediate between an ideal octahedron (θ = 60°) and trigonal prism.
a regular trigonal prism ($\theta = 0^\circ$). Thus, the spatial arrangement of donor atoms in $L^1$ supplies the central atom with a ligand field poised between tetragonal and trigonal symmetry. This conclusion is supported by an analysis of continuous symmetry/shape measures $S(O_n)$ and $S(TP)_n$ which quantify the deviation from regular octahedral and trigonal-prismatic geometry, respectively.

In Fig. 2b, the $S(O_n)$ and $S(TP)$ values of the iron(II) complexes (from Table 1; DFT-derived data from Table S3) are given as a continuous shape map of the trigonal prism transition along the trigonal Bailar twist (line).38 Evidently, the complexes of either ligand are in distinctly separated regions of this map. The values for $S(O_{h})$, which is zero for an ideal octahedron, cluster around $S(O_{h}) = 6 \pm 1$, for complexes $[1(X)]^{n+}$ of the constrained ligand $L^1$, but are substantially smaller for complexes $[2(X)]^{n+}$ of the open-chain ligand $L^2$, $S(O_{h}) = 2.0 \pm 0.5$.

**Characterisation of $[1(X)]^{n+}$ and $[2(X)]^{n+}$ in solution**

Solutions of $[1(X)]^{n+}$ and $[2(X)]^{n+}$ in acetonitrile and dichloromethane have been characterised by $^1$H- and $^{19}$F-NMR spectroscopy, AC conductometry, and UV/Vis spectroscopy. The results are summarised in Table 2.

**Speciation.** The chemical reactivity of hexacoordinated complexes with pentadentate ligands necessarily reflects the lability of the co-ligand $X$ with respect to substitution.22 The speciation of the complexes under study was therefore expected to be solvent-dependent. Speciation of the iron(II) complexes $[1(OTf)]^2$ and $[2(OTf)]^2$ has been studied by means of $^{19}$F-NMR spectroscopy (Fig. S3; $[Fe] \approx 15$ mmol L$^{-1}$) and conductometric measurements ($[Fe] = 1.3$ mmol L$^{-1}$) in acetonitrile and dichloromethane solutions. The weakly coordinating triflate ligands, both in $[1(OTf)]^2$ and $[2(OTf)]^2$, are actually found to be exchanged for solvent in neat acetonitrile, but remain coordinated in neat dichloromethane.

Both types of experiment indicate the dissociation of coordinated triflate upon solution in acetonitrile. $^{19}$F-NMR spectra of both compounds in $(D)_2$-acetonitrile show a single resonance located at $\delta = -72.9$ ppm and $-79.0$ ppm for $[1(X)]^{n+}$ and $[2(X)]^{n+}$, respectively. The peak width (fwhm; full-width at half-maximum) is ca. 15 Hz in both cases. Spectral signature, chemical shifts and peak width are as expected for free triflate ion.39,40 A molar conductivity in the range 227 S mol$^{-1}$ cm$^{-2}$ $< \Lambda < 277$ S mol$^{-1}$ cm$^{-2}$ indicates the (dominant) presence of a 2:1 electrolyte, and thus the formation of di-cationic complexes upon dissolution of the triflate complexes in acetonitrile, most probably $[1(CH_3CN)]^{2+}$ and $[2(CH_3CN)]^{2+}$.

In $(D)_2$-dichloromethane solution, the $^{19}$F-NMR spectra of $[1(X)]^{n+}$ and $[2(X)]^{n+}$ consist of two signals of equal area, indicating two different chemical environments for triflate in solution in both cases. A resonance at $-76$ ppm with a $\text{fwhm} = 18$ Hz is characteristic of free triflate, whereas a significantly broadened singlet, shifted strongly downfield at $\delta = -2$ ppm, is attributable to coordinated triflate. Fully consistent with predominating mono-cationic complexes, most probably $[1(OTf)]^+$ and $[2(OTf)]^+$, a molar conductivity in the range 15 S mol$^{-1}$ cm$^{-2}$ $< \Lambda < 19$ S mol$^{-1}$ cm$^{-2}$ suggests the presence of a 1:1 electrolyte.41 The speciation of the complexes in solution is fully corroborated by $^{57}$Fe-Mössbauer spectroscopic studies of powder samples prepared from these solutions via rapid precipitation (vide infra).

**Spin state.** The visual appearance of the complex salts $[1(OTf)](OTf)$ and $[2(OTf)](OTf)$ is very similar in the solid state. Whereas the faint yellow colour of $[1(OTf)](OTf)$ is conserved in acetonitrile solution ($f_{\text{max}} = 370$ nm; $f_{\text{max}} = 1100$ cm$^{-1}$ L mol$^{-1}$), $[2(OTf)](OTf)$ shifts to an intensely red-orange colour upon contact with acetonitrile. UV/Vis spectra (UV/Vis data in Table 2; spectra in Fig. 3a) of the resulting dilute solutions of $[2(\text{MeCN})]^{2+}$ are dominated by an intense absorption at 400 nm ($f_{\text{max}} = 6700$ cm$^{-1}$ L mol$^{-1}$). This signature is strongly reminiscent of the solution spectra of the Is-

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**Table 2** Speciation and spectroscopic data for dissolved $[1(OTf)](OTf)$ and $[2(OTf)](OTf)$ at room temperature

| Solvent | $[1(OTf)](OTf)$ | $[2(OTf)](OTf)$ |
|---------|-----------------|-----------------|
| DCM     | $[1(\text{MeCN})]^{2+}$ | $[2(\text{MeCN})]^{2+}$ |
| $\delta_1$ (ppm) | $[-2; 115]$ | $[-7; 86]$ |
| $\delta_2$ (ppm/fwhm [Hz]) | $[-76.0/18]$ | $[-76.2/18]$ |
| Conductometry | $[\Lambda \text{S mol}^{-1} \text{cm}^2]$ | 18.5 | 228 |
| UV/Vis | $\lambda_{\text{max}}$ (nm) | 372 | 370 |
| $f_{\text{max}}$ (cm$^{-1}$ L mol$^{-1}$) | 1200 | 1100 |

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**Fig. 3** Variable-temperature UV/Vis spectra of $[2(\text{MeCN})](OTf)_2$ in acetonitrile ($c = 1.0 \times 10^{-3}$ mol L$^{-1}$; light path $d = 0.1$ cm) with (a) decreasing temperature, (b) rising temperature; (c) temperature dependence of the molar absorption coefficient at $\lambda = 400$ nm (lines: sigmoidal fits with 9000 $< f_{\text{vis}}$ [cm$^{-1}$ L mol$^{-1}$] $< 9600$ and $f_{\text{vis}} = 1100$ cm$^{-1}$ L mol$^{-1}$).
iron(n) complex [Fe(Bn-TPEN)(MeCN)]^{2+} (\lambda_{\text{max}} = 390 \text{ nm}; \epsilon_{\text{max}} = 8892 \text{ cm}^{-1} \text{ L mol}^{-1})^{26} and is accordingly interpreted as being due to an MLCT transition within a ls-iron(n) species.

In agreement with this assignment, the intensity of the band is affected by temperature: at low temperature (Fig. 3a), a further increase to \epsilon_{\text{max}} = 8400 \text{ cm}^{-1} \text{ L mol}^{-1} accompanies a slight red-shift to \lambda_{\text{max}} = 406 \text{ nm}, whereas at elevated temperature (Fig. 3b), the band is successively bleached and blue-shifted (\lambda_{\text{max}} = 388 \text{ nm} at T = 353 \text{ K}). This behaviour is typical of thermal spin-crossover (SCO) systems (eqn (1)).

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\text{ls-}[2\text{MeCN}]^{2+} \rightarrow \text{hs-}[2\text{MeCN}]^{2+}
\] (1)

In order to extract the thermodynamic parameters of the SCO-induced thermochromism of [2MeCN]^{2+}, UV/Vis absorption at \lambda = 400 \text{ nm} has been analysed at temperatures between 233 K and 353 K. Because of solvent-inherent limitation of the temperature range, the absorption coefficient of the ls-form was estimated through sigmoidal fitting of the data to a Boltzmann model (Fig. 3c; the array of curves denotes fits with \epsilon(\text{ls}) fixed to values between 9000 and 9600 \text{ cm}^{-1} \text{ L mol}^{-1}). Van’t Hoff analysis of the SCO equilibrium constants that derive from these data (Fig. S4) reflects the uncertainty in the absorption coefficients. Within the given range of \epsilon(\text{ls}), the enthalpy and entropy of SCO vary between \Delta_{\text{SCO}}H_m = 19.8–22.7 \text{ kJ mol}^{-1} and \Delta_{\text{SCO}}S_m = 64.8–72.8 \text{ J K}^{-1} \text{ mol}^{-1}, respectively, with a turnover temperature T_{1/2} = 310(5) \text{ K}.

Our interpretation of the thermochromism of [2MeCN]^{2+} in terms of an SCO equilibrium between hs and ls forms is corroborated by the temperature dependence of its \textsuperscript{1}H-NMR spectra in (D\textsubscript{6})-acetonitrile (Fig. S5). The proton resonances in the room-temperature spectrum are widely spread between 44 ppm > \delta > –1 ppm and substantially broadened (typically 300 Hz > \text{fwhm} > 70 Hz) with respect to the spectrum of the free ligand. These findings indicate the presence in solution of paramagnetic species. On decreasing the temperature, the spectral range of resonances becomes successively narrower, accompanied by narrowing of the individual resonance profiles. At T = 233 K, close to the freezing point of (D\textsubscript{6})-acetonitrile, sharp lines with partially resolved J_{\text{HH}} coupling patterns are recorded within the range of 10 ppm > \delta > 1 ppm; that is, the SCO equilibrium has shifted towards the diamagnetic Is form of [2MeCN]^{2+}.

By contrast, both the \textsuperscript{1}H-NMR and UV/Vis spectra (\lambda_{\text{max}} = 370 \text{ nm}; \epsilon_{\text{max}} = 1100 \text{ cm}^{-1} \text{ L mol}^{-1} at T = 233 K and 298 K) of [1(OTf)]OTf solutions in acetonitrile clearly indicate the resulting acetonitrile complex to be a high-spin species. This is a consequence of conformational constraints in L\textsuperscript{1} and is reproduced by computed electronic energies of the SCO (Table 3).

Optimisations with the B3LYP hybrid functional slightly favour the singlet over the quintet state for [2MeCN]^{2+} but provide a clear preference for the quintet in case of [1(OTf)]OTf (Table 3). As B3LYP SCO energies had been found previously to artificially favour the hs forms,\textsuperscript{42} we have also carried out single-point calculations with the modified B3LYP* functional with 15% rather than 20% Hartree-Fock exchange. This functional had been suggested previously to better describe SCO in Fe(n) complexes.\textsuperscript{42} At B3LYP* level, the singlet preference for [2MeCN]^{2+} is more pronounced, the quintet preference for [1MeCN]^{2+} much smaller (Table 3). Yet, the computed overall difference in the SCO energies of the two complexes remains almost constant around 27 kJ mol\textsuperscript{−1}. The weaker ligand field of the co-ligand OTf in [1(OTf)]\textsuperscript{+} and [2(OTf)]\textsuperscript{2−} translates into a clear energetic preference for the hs state in both complexes, while comparison of the absolute values signals a marked dependence on the input of the respective N\textsubscript{5} ligand.

With the array of electronic SCO energies in hand (Table 3), it was possible to isolate the incremental contributions ascribable to the N\textsubscript{5} ligand (\delta\Delta_{\text{SCO}}E_{\text{el}}(N\textsubscript{5})) and the co-ligand (\delta\Delta_{\text{SCO}}E_{\text{el}}(X)). Interestingly, both factors are found to contribute similarly to the SCO energies. The incremental contribution of the co-ligand \delta\Delta_{\text{SCO}}E_{\text{el}}(X) (vertical difference in Table 3) amounts to ca. 25–27 kJ mol\textsuperscript{−1}, whereas the distortion-related increment of the N\textsubscript{5} ligand \delta\Delta_{\text{SCO}}E_{\text{el}}(N\textsubscript{5}) (horizontal difference in Table 3) amounts to ca. 26–28 kJ mol\textsuperscript{−1}. The latter value is a good measure of the difference in d-orbital splitting between the ligand fields as supplied by L\textsuperscript{1} and L\textsuperscript{2}, in fair agreement with energy differences derived from UV/Vis spectroscopy (vide infra).

As single crystals of [2MeCN]([OTf])\textsubscript{2} could not be obtained, the spin state of this compound in the solid state has been studied by \textsuperscript{57}Fe-Mössbauer spectroscopy on polycrystalline (powder) samples. Powders of the triflate complex [2OTf]OTf were taken as a reference system with temperature-invariant hs character. Mössbauer spectra of [2OTf]OTf and [2MeCN]([OTf])\textsubscript{2} were recorded at T \approx 100 K (Fig. 4a and b) and analysed by least-squares fitting with doublets of Lorentzian lines. The results with focus on the main components of the Mössbauer spectrum are summarised in Table 4. The results corroborate our spin-state assignments from the solution studies and agree with the implications of the DFT-derived SCO energies.

The Mössbauer spectra of [2OTf]OTf were analysed by use of three sub-spectra (Fig. 4b), whereby the main signal (volume fraction >80%) with an isomer shift of \delta = 1.088 mm s\textsuperscript{−1} and quadrupole splitting of $\Delta Q = 2.123 \text{ mm s}^{-1}$ is clearly attributable to a hs iron(n) complex, which corroborates the results of the solution studies of spin state and speciation discussed above. Minor amounts of Is iron(n) (volume fraction
with isomer shift of $\delta = 0.342$ mm s$^{-1}$ and quadrupole splitting of $\Delta E_Q = 1.077$ mm s$^{-1}$ are assigned to a thermally trapped residual ls iron(II) form of $[2\text{OTf}]\text{OTf}$; a small amount of hs iron(II) (volume fraction $\approx 9\%$) is associated with an impurity, which has been introduced in the preparation process.

The material formulated as $[2\text{MeCN}]\text{OTf}_2$, as deduced from $^{19}$F-NMR spectra, thermochromism and elemental analysis, gives Mössbauer spectra typical of ls iron(II) complexes with only minor distortions from octahedral geometry (Fig. 4a). The major component of the spectrum (volume fraction $>80\%$) provides a doublet of small isomer shift of $\delta = 0.520$ mm s$^{-1}$ and quadrupole splitting of $\Delta E_Q = 0.353$ mm s$^{-1}$. The additional signals in the spectrum with larger splitting indicate minor amounts of two different residual hs iron(II) species. The signal with approx. 4% volume fraction ($\Delta E_Q = 3.452$ mm s$^{-1}$) is associated with an impurity, as described for $[2\text{OTf}]\text{OTf}$. The second hs signal with ca. 11% volume fraction ($\Delta E_Q = 2.659$ mm s$^{-1}$) may be assigned as either the thermally trapped hs form of $[2\text{MeCN}]\text{OTf}_2$, or as $[2\text{OTf}]\text{OTf}$ formed by thermal ligand exchange in the solid.

The latter process is undoubtedly active at elevated temperature, where it is very efficient: thermal treatment of $[2\text{MeCN}]\text{OTf}_2$ at $T = 350$ K for three days under reduced pressure ($p \approx 10$ mbar) leads to an almost complete loss of the spectral features of the ls complex (Fig. 4c). The main component (volume fraction $>80\%$) of the spectrum obtained at $T \approx 100$ K from the thermally-treated sample shows signatures typical of hs iron(II) complexes ($\delta = 1.097$ mm s$^{-1}$; $\Delta E_Q = 2.069$ mm s$^{-1}$). For comparison, a similarly obtained spectrum for the thermally treated sample of $[2\text{OTf}]\text{OTf}$ is shown in Fig. 4d. The spectral appearance and the fit parameters of both thermally treated samples are virtually indistinguishable from the data recorded for native $[2\text{OTf}]\text{OTf}$ (Fig. 4b). That is, the substitution of coordinated triflate by MeCN, operative in MeCN solutions of $[2\text{OTf}]\text{OTf}$, is reversed by thermal treatment of solid $[2\text{MeCN}]\text{OTf}_2$. We note that DFT-derived isomer shifts are in close agreement (data in square brackets in Table 4) with the experimental data.

In agreement with an irreversible spin state change attendant on ligand exchange in the lattice at elevated temperature, SQUID magnetometry between 4 K $< T < 390$ K (Fig. S6‡) identifies a thermally driven gradual increase of the effective magnetic moment $\mu_{\text{eff}}$ to $> 5.2$ $\mu_B$. As is typical for high-spin 3d$^6$ transition metal ions, the observed effective magnetic moment is slightly larger than the expected $S = 2$ spin-only value of $\mu_{\text{eff}} = 4.9$ $\mu_B$, due to spin-orbit interactions and contributions of low-lying orbital states. The turnover temperature $T_{1/2} \approx$
Table 4 Mössbauer parameters with focus on the main components of the experimental spectra measured at \( T = 100 \) K*  

| Complex | Volume fraction [%] | \( \delta^b \) [mm s\(^{-1}\)] | \( \Delta E_Q \) [mm s\(^{-1}\)] | \( \Gamma_{HWHM} \) [mm s\(^{-1}\)] |
|---------|---------------------|---------------------------------|-----------------------------|------------------------|
| \([1\text{MeCN}](\text{OTf})_2\) | (1) | 16.1 | 1.220(19) | 2.909(43) | 0.224(35) |
| | (2) | 79.5 | 1.066(5) | 2.112(11) | 0.254(9)  |
| mer-\([1\text{MeCN}]^2\) \((S = 2)\) | | | 1.000 | [3.56] | |
| fac-\([1\text{MeCN}]^2\) \((S = 2)\) | | | 0.999 | [2.66] | |
| \([1\text{OTf}]\) \((\text{OTf})\) | (1) | 58.7 | 1.098(6) | 3.110(18) | 0.199(12) |
| | (2) | 23.5 | 1.138(15) | 2.335(52) | 0.215(35) |
| mer-\([1\text{OTf}]\) \((S = 2)\) | | | 1.011 | [3.36] | |
| fac-\([1\text{OTf}]\) \((S = 2)\) | | | 1.02 | [2.71] | |
| \([2\text{MeCN}]^2; S = 0\) | | | 0.520(1) | 0.353(2) | 0.145(2) |
| | | | [0.61] | [0.46] | |
| \([2\text{OTf}]\) \((\text{OTf})\) | | | 1.088(3) | 2.123(7) | 0.176(5) |
| \([2\text{OTf}]\) \((S = 2)\) | | | 1.00 | [3.53] | |
| \([2\text{OTf}]\) \((S = 0)\) | | | 0.77 | [1.16] | |
| \([2\text{OTf}]\) \((\text{OTf})_2\) \(^d\) | | | 1.097(2) | 2.069(4) | 0.196(3) |
| \([2\text{OTf}]\) \((\text{OTf})\) \(^e\) | 72.2 | 1.076(3) | 2.033(6) | 0.158(4) |

*The complete set of Mössbauer parameters and the results of measurements obtained at supplementary temperatures are given in Table S4. 
\(^b\) Isomer shift \( \delta \) is specified relative to metallic iron at room temperature. 
\(^c\) Data in square brackets from DFT computation (B3LYP; see Computational Details) of the respective complex cations. 
\(^d\) After tempering \([2\text{MeCN}]\)(\text{OTf})\(_2\) at \( T = 350 \) K for three days under reduced pressure. 
\(^e\) After tempering \([2\text{OTf}]\)(\text{OTf}) at \( T = 350 \) K for four days under reduced pressure.

320 K is in fair agreement with the value of \( T_{1/2} \approx 310 \) K obtained by UV-Vis spectroscopy in solution. Notably, the spin-state change of \([2\text{MeCN}]\)\(^2\), which is reversible in MeCN solution, is found to be irreversible in the solid state.

**Competing ligand conformations.** As discussed above, the topologies of complexes \([1\text{X}]\)\(^{\text{Hs}}\) and \([2\text{X}]\)\(^{\text{Hs}}\) in the solid-state structures agree with the sketches in Scheme 1. They also agree with the structural characteristics reported for iron(II) complexes of the closely related ligand Bn-TPEN.\(^{30}\) That is, in all iron(II) complexes under study, the sixth coordination site is trans to one of the tertiary amine donors. The three pyridine donors are arranged in meridional fashion (mer-py\(_3\)). The same holds for the nickel(II) complex salt \([\text{NiL}^2\text{(OH}_2\text{)}]_2\text{(ClO}_4\text{)}_2\) of the open-chain ligand L\(^2\) (see Fig. 1), which was synthesised for structural comparison.

X-ray crystallography reveals, however, a different situation in the nickel(II) complex \([\text{NiL}^1\text{(ClO}_4\text{)}]_2\text{(ClO}_4\text{)}\) of the constrained ligand L\(^1\) (Fig. 1; Table S2\(^\dagger\)). Here, the ligand adopts a topology with all three pyridine donors in a facial arrangement (fac-py\(_3\)). This causes the sixth coordination site to be trans to one of the pyridine donors. Obviously, ligand L\(^1\) is flexible enough to realise two distinctly different arrangements of its donor atoms in the solid state.

This raises the question whether the preference of the iron(II) complexes for the mer conformation in the solid state is conserved for the isolated complex ions \([1\text{X}]\)\(^{\text{Hs}}\) and \([2\text{X}]\)\(^{\text{Hs}}\) in solution (Scheme 3). Although we have no definite experimental proof of a conformational equilibrium we will, in the following, discuss results from experiment and theory indicating conformational dynamics in the case of \([1\text{X}]\)\(^{\text{Hs}}\).

Stereocchemical dynamics of a compound, if compatible with the method’s timescale, may be studied with NMR techniques. As discussed above, both complexes, \([1\text{X}]\)\(^{\text{Hs}}\) and \([2\text{X}]\)\(^{\text{Hs}}\), give rise to paramagnetically shifted resonances at room temperature (Table 2). The number of individual resonances, pertinent to \([1\text{X}]\)\(^{\text{Hs}}\) and \([2\text{X}]\)\(^{\text{Hs}}\), however, is strikingly different (Fig. S5\(^\ddagger\)). Eighteen individual resonances (accounting for 28 of the total 29 protons) can be unambiguously resolved in the spectrum of \([2\text{OTf}]\)(\text{OTf})\(_2\) in dichloromethane at room temperature (similar observations apply to \([2\text{MeCN}]\)(\text{OTf})\(_2\) in MeCN), indicating that an asymmetric structure of the hs complexes persists in solution. Individual resonances of all of the aromatic protons are resolved in the low-temperature spectra of \([2\text{MeCN}]\)(\text{OTf})\(_2\) in MeCN and leave no doubt that asymmetry applies also to its diamagnetic ls form.

By contrast, only ten individual resonances can be detected for complexes of ligand L\(^1\). This finding is incommensurate with a (static) asymmetric structure of \([1\text{X}]\)\(^{\text{Hs}}\) in solution. We suggest that the apparent symmetry is due to fast stereocchemical dynamics within the ligand L\(^1\) of \([1\text{X}]\)\(^{\text{Hs}}\), giving rise to spectral averaging of different conformers of the complex (Scheme 3).

DFT computations of relevant complex ions containing L\(^1\) and L\(^2\) were performed to gain insight into the energetics of the anticipated conformational equilibrium (Table 5; cf. Table S3\(^\ddagger\) for structural data). In the case of ligand L\(^2\),
optimisation of the structures of \([2(X)]^{n+}\) (with \(X = \text{OTf}^-, \text{MeCN}\)) clearly points to a preference for the \textit{mer} conformation in solution. In contrast, energy differences \(\Delta E_{\text{conf}}\) between the isomers of \([1(X)]^{n+}\) remain below 5 kJ mol\(^{-1}\), which means that, for complexes of ligand \(L_1\), a conformational equilibrium in solution must be taken into account.

In order to test the hypothesis of competing ligand conformations, powder samples have been prepared from solutions of \([1(\text{OTf})](\text{OTf})\) in acetonitrile and dichloromethane by rapid precipitation. As shown above for the complexes of ligand \(L_2\), these samples mirror the constitution of the complex in solution; that is, precipitation occurs without significant ligand scrambling. It was thus assumed that rapid precipitation can also "freeze out" conformational dynamics, such that the solid samples will depict also the conformational equilibrium of the complexes \([1(X)]^{n+}\). If this was actually the case, each conformer must contribute to the Mössbauer spectra individually; that is, two or three components will be visible.

Powder samples of \([1(\text{MeCN})](\text{OTf})_2\) and \([1(\text{OTf})](\text{OTf})\) actually give Mössbauer spectra typical of its iron(II) complexes (spectra at \(T \approx 100\) K in Fig. 5; fit parameters of the main components in Table 4). Importantly, the spectra are clearly dominated by two close-lying \(\text{HS}\) doublets at all temperatures studied (minor impurity signals are observed). We assign this pattern to conformers of the complexes; an assignment of the spectral components to specific complex conformers, \textit{i.e.}, \textit{mer} vs. \textit{fac}, is not attempted.

The nature of the co-ligand, \(\text{MeCN}\) or \(\text{OTf}\), significantly affects the appearance of the spectra, with respect to quadrupole splitting and volume fraction. In particular, the quadrupole splitting \(\Delta E_Q\) of \([1(\text{OTf})](\text{OTf})\) is temperature-dependent. Between \(T = 20\) K and \(200\) K, the quadrupole splitting decreases by ca. 1 mm s\(^{-1}\) with increasing temperature, whereas the quadrupole splitting of \([1(\text{MeCN})](\text{OTf})_2\) is almost invariant with temperature (\textit{cf.}, Table S4\(^\dagger\)). In principle, several sources may contribute to the thermal effect on \(\Delta E_Q\), e.g. concerning the thermal population of the ligand-field multiplets, the presence of spin-orbit interactions, or molecule dynamics (e.g., rotation or vibration of the molecule or parts of it), which then (partially) average out the effective electric field gradient at the \(^{57}\text{Fe}\) nucleus site. In the latter case, hindered molecule dynamics disfavours the averaging process at lower temperature. In view of the observed significant crystallino-

### Table 5 Relative electronic energies (in kJ mol\(^{-1}\)) of \textit{mer} and \textit{fac} conformers of iron(II) precursors \([1X]^n\) and \([2X]^n\) (from DFT calculations)\(^a\)

|          | \textit{mer} | \textit{fac} |
|----------|--------------|--------------|
| \([1(\text{OTf})]^+\) | 0            | +10.1 (+4.4) |
| \([1(\text{MeCN})]^+\) | 0            | +4.5 (+4.0)  |
| \([2(\text{OTf})]^+\) | 0            | +26.2 (+21.6)|
| \([2(\text{MeCN})]^+\) | 0            | +22.6 (+22.9)|

\(^a\) Fully optimised structures at B3LYP-D3/def2-TZVP level. Quintet state (\(S = 2\)). In parentheses: with COSMO solvent model (MeCN).

The nature of the co-ligand, \(\text{MeCN}\) or \(\text{OTf}\), significantly affects the appearance of the spectra, with respect to quadrupole splitting and volume fraction. In particular, the quadrupole splitting \(\Delta E_Q\) of \([1(\text{OTf})](\text{OTf})\) is temperature-dependent. Between \(T = 20\) K and \(200\) K, the quadrupole splitting decreases by ca. 1 mm s\(^{-1}\) with increasing temperature, whereas the quadrupole splitting of \([1(\text{MeCN})](\text{OTf})_2\) is almost invariant with temperature (\textit{cf.}, Table S4\(^\dagger\)). In principle, several sources may contribute to the thermal effect on \(\Delta E_Q\), e.g. concerning the thermal population of the ligand-field multiplets, the presence of spin-orbit interactions, or molecule dynamics (e.g., rotation or vibration of the molecule or parts of it), which then (partially) average out the effective electric field gradient at the \(^{57}\text{Fe}\) nucleus site. In the latter case, hindered molecule dynamics disfavours the averaging process at lower temperature. In view of the observed significant crystallino-
Formation of oxoiron(IV) complexes of \( L_1 \) and \( L_2 \)

As a consequence of ligand-imposed distortion of the coordination sphere, the structures, coordination isomers, and spin states of the iron(II) complexes \([1\{X\}]^{2+}\) and \([2\{X\}]^{2+}\) differ distinctly. Our preliminary work presented here addresses the question whether these differences affect the formation and reactivity of oxoiron(IV) complexes derived from these precursors. We find that formation kinetics, spectroscopic signature and reactivity of oxoiron(IV) complexes thus obtained are strongly affected by the degree of distortion in the ligand fields as supplied by ligands \( L_1 \) and \( L_2 \).

\[
[\text{Fe}^{II}L_1\{\text{MeCN}\}]^{2+} + m\text{CPBA} \rightarrow [L_1\text{Fe}^{IV}=\text{O}]^{2+} + m\text{CBA} \quad \text{(2)}
\]

Oxoiron(IV) complexes of both ligands, \( L_1 \) and \( L_2 \), are accessible in moderate yields by reaction of their iron(II) precursors with equimolar amounts of meta-chloroperbenzoic acid (mCPBA) according to eqn (2). The assignment of the oxoiron(IV) complexes relies on \textit{in situ} UV/Vis spectroscopic methods and \textit{ex situ} mass spectrometric analysis, as the limited lifetimes of the metastable products interfered with their isolation and bulk chemical analysis.

Reactions of dilute solutions \((0.1 \text{ mmol L}^{-1} < [\text{Fe}] < 5 \text{ mmol L}^{-1})\) of the iron(II) precursors \([1\{OTf\}]^{2+}\) and \([2\{OTf\}]^{2+}\) in acetonitrile with equimolar amounts of mCPBA proceed with characteristic UV/Vis-spectroscopic response (Fig. 6; data in Table 6). In both cases, diagnostic absorption bands at \( \lambda = 810 \text{ nm} \) and \( \lambda = 730 \text{ nm} \) are recorded in the visible spectral region, for \([1\{O\}]^{2+}\) and \([2\{O\}]^{2+}\), respectively. It is noted that in the case of \([1\{O\}]^{2+}\) (Fig. 6, right panel) measurements had to be performed at \( T = 233 \text{ K} \) due to the high intrinsic reactivity of the oxoiron(IV) species at room temperature. While the peak positions of these absorption bands agree with values reported

![Fig. 6 UV/Vis spectra of iron(II) precursor solutions in acetonitrile before (grey) and after reaction with one equivalent of mCPBA (black); (a) \([2\{OTf\}]^{2+}\) and \([1\{OTf\}]^{2+}\) at \( T = 293 \text{ K} \); light path \( d = 1.0 \text{ cm} \) at \( t = 0 \text{ s} \); (b) \([2\{OTf\}]^{2+}\) at \( T = 233 \text{ K} \); light path \( d = 0.1 \text{ cm} \) at \( t = 0 \text{ s} \)],

\[\lambda_{\text{max}}/\text{nm} = \varepsilon/\text{cm}^{-1} \text{ L mol}^{-1} \]

\( T/K \quad \lambda_{\text{max}}/\text{nm} \quad \varepsilon/\text{cm}^{-1} \text{ L mol}^{-1} \quad \text{t}_{\text{form}}/\text{s} \quad \text{t}_{1/2}/\text{s} \)

\begin{tabular}{cccc}
\hline
\( [1\{O\}]^{2+} \) & 233 & 810 (>80) & <2 & \( >10^3 \) \\
\( [2\{O\}]^{2+} \) & 293 & 730 (>150) & \( \approx 10^3 \) & \( >10^3 \) \\
\hline
\end{tabular}

\( a \) Apparent molar absorption coefficient, normalised to iron content.
for other oxoiron(IV) species, the molar absorption coefficients are somewhat smaller than the majority of published values.\(^\text{10}\) Although we cannot rule out intrinsically small values, we assume sub-stoichiometric formation of the oxoiron(IV) species.

Further arguments in favour of our assignment derive from ESI mass-spectrometric (ESI-MS) analysis of acetonitrile solutions of \([\text{2}](\text{OTf})^2\) after reaction with iodosobenzene, PhIO. Formal addition of one oxygen atom to the complex fragment \([\text{FeL}^2]\) ([2]) is indicated by diagnostic signals in the mass spectra. Dominant signals (50\%) at \(m/z = 596.1226\) (calc. for \([\text{C}_{23}\text{H}_{29}\text{N}_5\text{FeO}_4\text{F}_3\text{S}]^{+}\): \(m/z = 596.1236\)) are assigned to \([[[2](\text{O})](\text{OTf})]^+\) (Fig. 7a and b). Weak signals at \(m/z = 223.5856\) (calc. for \([\text{C}_{23}\text{H}_{29}\text{N}_5\text{FeO}]^{2+}\): \(m/z = 223.5855\)) indicate small amounts of native \([[[2](\text{O})]^2]^+\). Experiments in the presence of \(\text{H}_2\text{O}^\text{18}\) gave strong signals (60\%) at \(m/z = 598.1268\) (calc. for \([\text{C}_{23}\text{H}_{29}\text{N}_5\text{FeO}^\text{18}\text{O}^\text{16}\text{O}_3\text{F}_3\text{S}]^{+}\): \(m/z = 598.1279\)) (Fig. 7c and d). Weak signals at \(m/z = 224.5875\) (calc. for \([\text{C}_{23}\text{H}_{29}\text{N}_5\text{Fe}^\text{18}\text{O}^\text{18}\text{O}]^{2+}\): \(m/z = 224.5877\)) are indicative of native \([[[2](\text{18O})]^2]^+\). The signals show that speciation is consistent, but they also highlight the presence of \(\text{18O}\) in the oxidation products of interest. This suggests isotope exchange between \(\text{18O}\text{H}_2\) and the product of the \(m\text{CPBA}\)-induced oxidation reaction, providing conclusive evidence for the formation of an oxoiron(IV) complex of ligand \(L^2\).\(^{46}\)

Mass-spectrometric analysis failed to provide direct evidence for the formation of the corresponding oxoiron(IV) complex of ligand \(L^1\). This failure is probably due to the complex’s high intrinsic reactivity: the UV/Vis spectra recorded directly after mixing the reactants at room temperature have no feature attributable to an oxoiron(IV) species; rather, they are assignable to the products of the latter’s rapid intramolecular decay. Current work seeks to clarify the decay pathway.

Differences in the long-wavelength absorption maxima of both oxoiron(IV) species reflect their diverging electronic properties. In particular, the oxoiron(IV) complex of the constrained ligand \(L^1\) exhibits a ligand-field strength significantly weaker than that of its less-strained congener. The difference of ca. 100 nm in the positions of their long-wavelength d → d absorption bands translates into a difference in the excitation energy of ca. 20 kJ mol\(^{-1}\). We note that this ligand-imposed energy difference ties in nicely with the DFT-derived ligand-imposed differences in ligand-field splitting (Table 3).

Differences between the complexes also extend to the formation kinetics. In the case of ligand \(L^1\), the growth of the characteristic long-wavelength band at 810 nm is limited by the mixing time of the substrates (\(t_\text{mix} \approx 2\) s). Growth is already complete by the time the first reaction spectrum is recorded. This behaviour is quite remarkable, as these experiments were performed at low temperature (\(T = 233\) K), pointing to a very labile iron(II) precursor. These indications of a labile ligand sphere and a weakened ligand field in the case of the oxoiron(IV) species of \(L^1\) are both in line with our “distortion hypothesis”. Accordingly, the less distorted iron(II) precursor, of ligand \(L^2\), forms the oxoiron(IV) species much more slowly, completing the reaction after ca. 15 minutes at ambient temperature.

**Conclusions**

In the present work, we have established incremental ligand-field distortion as a tool to tune the structural, conformational and spin-state preferences of iron(II) complexes, in ligand
fields set up by two pentadentate N₅ ligands. Within our pair of ligands (diazepane-based L¹; open chain L²), the donor-atom inherent strength of the donor set (diamine/trisiminine) is fully conserved. Accordingly, solely the consequences of ligand sphere distortion are recorded in complexes of the type [FeL²(X)]Y, in isolation from effects caused by a variation of the donor set.

The decisive structural distinction between the ligands is introduced as an angular constraint of the diamine unit, by forcing it into a diazepane ring in L¹; thereby enhancing the trans effect of the co-ligand X. The combination of both aspects translates into massive radial disorder and renders the coordination sphere intermediate between tetragonal and trigonal symmetry. Our combined experimental and quantum-chemical findings show that ligand-imposed differences are the root cause of the differences in properties observed for the iron(II) complexes of L¹ and L². Ligand-imposed distortion in L¹ reduces the ligand-field strength by ca. 20–30 kJ mol⁻¹ and, thus, places this factor on an equal footing with ligand-field effects due to variation in the co-ligand. Destabilisation of the ligand field translates into a marked preference of the resulting oxoiron(IV) complexes for high kinetic lability of the derived iron(II) complexes.

Preliminary results, obtained after reacting the iron(II) complexes [FeL¹(X)]Y with meta-chloroperoxybenzoic acid, indicate that the influence of ligand-imposed distortion of L¹ is traceable also in the properties of the resulting oxoiron(IV) complexes. Oxoiron(IV) species of L¹ and L² are identified through their diagnostic UV/Vis absorption spectra and by mass-spectrometric results (L¹). Significantly reduced ligand-field strength is accompanied by high intrinsic reactivity in the case of L¹. Current work addresses the question to what extent judiciously chosen substituents on L¹ and L² allow additional modulation of oxoiron(IV) reactivity.

**Experimental section**

**Materials and general procedure**

All reagents and solvents were purchased from commercial sources (Sigma-Aldrich, Acros). Reagents were used as received, and solvents dried according to published procedures.⁴⁷ The synthesis of the constrained ligand L¹ and of its complexes [FeL¹(Cl)][PF₆] (≡ [I(Cl)][PF₆]) and [FeL¹(Br)][PF₆] (≡ [I(Br)][PF₆]) has been described previously.²⁹

**UV/Vis spectroscopy**

UV/Vis spectra at ambient temperature were measured with a Varian Cary 50 spectrometer through quartz cells (light path length d = 1 cm). Sample concentration was in the range of 10⁻⁴ mol L⁻¹. For variable-temperature experiments, a UV/Vis quartz immersion probe (light path d = 1 mm, Hellma) with a home-built measuring cell came to use. Sample concentration was in the range of 10⁻³ mol L⁻¹ in this case. Temperature was controlled by an immersion thermometer.

**Mössbauer spectroscopy**

⁵⁷Fe-Mössbauer spectroscopic measurements have been performed on a conventional transmission spectrometer with sinusoidal velocity sweep. The activity of the Mössbauer source was about 40 mCi of ⁵⁷Co in a rhodium matrix kept at room temperature. The measurements were done with a CryoVac continuous flow cryostat with N₂ or Helium exchange gas. The temperature was measured with a calibrated Si diode located close to the sample container. The isomer shift δ is specified relative to metallic iron at room temperature and was not corrected for second order Doppler shift. The measurements on [I(OTf)](OTf) were carried out with a Janis closed-cycle cryostat with comparable specifications, geometry and sample environments as described above. The activity of the Mössbauer source used here was about 10 mCi of ⁵⁷Co in a rhodium matrix.

**SQUID magnetometry**

SQUID magnetometry measurements were performed on a Cryogenic Ltd. closed-cycle SQUID magnetometer. The sample was weighed in a gelatin capsule and then fixed in a polyethylene sample holder. The background signal of the empty gelatin capsule and the sample holder were experimentally determined and subtracted from the experimental raw data set. The correction of the diamagnetic susceptibility of the complex was done by use of tabulated Pascal parameters.

**X-ray data collection and refinement details**

Data were collected at 130.00(10) K using an “Oxford Diffraction Xcalibur S” diffractometer equipped with a goniometer in space group P₃₁₂₁. Two sets of X-ray data were measured (extended and limited), and the latter was used to determine the space group. These data sets were solved iteratively with Superflip⁵⁹ (for [I(OTf)], [2(Cl)][PF₆]·Et₂O, and [NiL⁴(H₂O)][ClO₄]·MeOH) or with SHELXS-97 using direct methods (for [I(ClO₄)](ClO₄)·MeOH and with SHELXL-97 using direct methods (for [I(OTf)](OTf), [2(OTf)][PF₆]) and refined with SHELXL-97). The atomic coordinates were used as input for the full-matrix least-squares refinement. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically.

All disordered parts of the crystal structures were modelled in two discrete positions using (tight) rigid-bond and isotropy restraints. For the triflato ligand in [I(OTf)](OTf), the occupancies refined to 0.51(2)/0.49(2). In [NiL⁴(ClO₄)][ClO₄]·MeOH, the perchlorate ion containing Cl² was modelled using additional same-distance restraints for the oxygen atoms; occupancies refined to 0.49(3)/0.51(3). In [2(OTf)](OTf), the triflato ligand is rotationally disordered about the O40–S43 axis.
Using additional same-distance restraints with standard weights for the whole ligand, occupancies refined to 0.52(3)/0.48(3). The unit cell of \( [\text{NiL}_2(H_2O)][\text{ClO}_4]_2 \cdot \text{MeOH} \) contains half a very strongly disordered diethyl-ether molecule that had to be treated as a diffuse contribution to the overall scattering without specific atom positions by Squeeze/Platon. In \([\text{NiL}_2(H_2O)][\text{ClO}_4]_2 \cdot \text{MeOH}\), the hydrogen atoms of the aqua ligand were located on a Fourier difference map and refined semi-freely. The perchlorate ion containing \( \text{Cl}_2 \) exhibits a significant contribution to the overall scattering weight below 30 °C. The combined organic phases are diluted with water and extracted with three portions of CHCl₃. After evaporation of all volatiles the residue is extracted with pentane (6 × 5 ml) and the volume of the combined pentane phases reduced to 10 ml. The pentane solution is extracted with a concentrated NaHCO₃ solution (3 × 10 ml). The combined aqueous phases are extracted with CHCl₃ (3 × 10 ml). After evaporation of the combined organic phases under reduced pressure, the secondary amine B is obtained as a yellow oil (yield: 1.18 g; 53%).

1H-NMR (200 MHz, CDCl₃, 25 °C): \( \delta \) [ppm] = 8.51 (ddd, 1H, \( J_{H,H} = 5.5 \) Hz, \( J_{H,H} = 2.0 \) Hz, \( J_{H,H} = 1.0 \) Hz, \( H^{10} \)), 7.56 (dt, 1H, \( J_{H,H} = 8.0 \) Hz, \( J_{H,H} = 5.5 \) Hz, \( J_{H,H} = 1.3 \) Hz, \( H^{11} \)), 7.03 (ddd, 1H, \( J_{H,H} = 8.0 \) Hz, \( J_{H,H} = 5.5 \) Hz, \( J_{H,H} = 1.5 \) Hz, \( H^{14} \)), 3.39 (d, 2H, \( H^{5,7} \)), 3.42–2.11 (brm, 6H, \( H^{2,6} \)), 2.18 (s, 3H, \( H^{14,15} \)), 1.26 (brs, 3H, \( H^{11} \)).

HR-MS (ESI): Calcd for C₁₂H₂₇N₅: \( [\text{M} + \text{H}]^+ 374.2339 \); found. \( [\text{M} + \text{H}]^+ 374.2336 \).

**Synthesis of ligand L³**

1,3,5-Tris-methyl-5-(2-pyridinyl)-hexahydropyrimidine (A).

A solution of 2-methyl-2-(2-pyridyl)-propane-1,3-diamin (L²).

\( \delta \) [ppm] = 166.2 (Cq, 1C, \( C^{2} \)), 192.4 (Cq, 2C, \( C^{11,21} \)), 148.8 (Cq, 2C, \( C^{13,23} \)), 148.3 (Cq, 1C, \( C^{6} \)), 136.3 (CH, 2C, \( C^{13,23} \)), 122.7 (CH, 2C, \( C^{16,26} \)), 7.63 (dt, 1H, \( J_{H,H} = 1.5 \) Hz, \( H^{5} \)), 7.35 (td, 1H, \( J_{H,H} = 1.3 \) Hz, \( H^{3} \)), 7.10 (ddd, 1H, \( J_{H,H} = 5.5 \) Hz, \( J_{H,H} = 5.5 \) Hz, \( J_{H,H} = 1.3 \) Hz, \( H^{3} \)).

The aminal A (2.35 g; 11.42 mmol) is dissolved in technical 1,2-ethanediol (70 ml). After addition of HCl (32%; 150 ml) the mixture is stirred for 8 days at 55 °C. From 25 ml aliquots of the cooled mixture (0 °C), the amine is deliberated by addition of 1,2-ethanediol (15 ml; exothermic reaction; temperature below 30 °C). The combined alkaline mixtures are diluted with water and extracted with three portions of CHCl₃. After evaporation of all volatiles the residue is extracted with pentane (6 × 5 ml) and the volume of the combined pentane phases reduced to 10 ml. The pentane solution is extracted with a concentrated NaHCO₃ solution (3 × 10 ml). The combined aqueous phases are extracted with CHCl₃ (3 × 10 ml). After evaporation of the combined organic phases under reduced pressure, the secondary amine B is obtained as a yellow oil (yield: 1.18 g; 53%). 1H-NMR (200 MHz, CDCl₃, 25 °C): \( \delta \) [ppm] = 8.51 (ddd, 1H, \( J_{H,H} = 5.5 \) Hz, \( J_{H,H} = 2.0 \) Hz, \( J_{H,H} = 1.0 \) Hz, \( H^{10} \)), 7.56 (dt, 1H, \( J_{H,H} = 8.0 \) Hz, \( J_{H,H} = 5.5 \) Hz, \( J_{H,H} = 1.3 \) Hz, \( H^{11} \)), 7.03 (ddd, 1H, \( J_{H,H} = 8.0 \) Hz, \( J_{H,H} = 5.5 \) Hz, \( J_{H,H} = 1.5 \) Hz, \( H^{14} \)), 3.39 (d, 2H, \( H^{5,7} \)), 3.42–2.11 (brm, 6H, \( H^{2,6} \)), 2.18 (s, 3H, \( H^{14,15} \)), 1.26 (brs, 3H, \( H^{11} \)).

HR-MS (ESI): Calcd for C₁₂H₁₇N₅: \( [\text{M} + \text{H}]^+ 206.1652 \); found. \( [\text{M} + \text{H}]^+ 206.1652 \).

A mixture of the secondary amine B (0.55 g; 2.8 mmol) with Na₂CO₃ (3.03 g; 28.6 mmol) and 2-picolylchloride-hydrochloride (0.94 g; 5.7 mmol) in acetonitrile is stirred at 55 °C for two days. After cooling to ambient temperature, the solvent is removed under reduced pressure. The red oil obtained is dissolved in toluene and the resulting solution extracted with water. Toluene is removed under reduced pressure and the residue is extracted several times with pentane. From the combined pentane extracts, ligand L² is obtained as a yellow oil after removing all volatiles in vacuo (yield: 0.67 g; 63%).

1H-NMR (200 MHz, CDCl₃, 25 °C): \( \delta \) [ppm] = 166.2 (Cq, 1C, \( C^{2} \)), 192.4 (Cq, 2C, \( C^{11,21} \)), 148.8 (Cq, 2C, \( C^{13,23} \)), 148.3 (Cq, 1C, \( C^{6} \)), 136.3 (CH, 2C, \( C^{13,23} \)), 122.7 (CH, 2C, \( C^{16,26} \)), 7.63 (dt, 1H, \( J_{H,H} = 1.5 \) Hz, \( H^{5} \)), 7.35 (td, 1H, \( J_{H,H} = 1.3 \) Hz, \( H^{3} \)), 7.10 (ddd, 1H, \( J_{H,H} = 5.5 \) Hz, \( J_{H,H} = 5.5 \) Hz, \( J_{H,H} = 1.3 \) Hz, \( H^{3} \)).

The aminal A (2.35 g; 11.42 mmol) is dissolved in technical 1,2-ethanediol (70 ml). After addition of HCl (32%; 150 ml) the mixture is stirred for 8 days at 55 °C. From 25 ml aliquots of the cooled mixture (0 °C), the amine is deliberated by addition of 1,2-ethanediol (15 ml; exothermic reaction; temperature below 30 °C). The combined alkaline mixtures are diluted with water and extracted with three portions of CHCl₃. After evaporation of all volatiles the residue is extracted with pentane (6 × 5 ml) and the volume of the combined pentane phases reduced to 10 ml. The pentane solution is extracted with a concentrated NaHCO₃ solution (3 × 10 ml). The combined aqueous phases are extracted with CHCl₃ (3 × 10 ml). After evaporation of the combined organic phases under reduced pressure, the secondary amine B is obtained as a yellow oil (yield: 1.18 g; 53%).
(CH, 1C, C3), 121.7 (CH, 2C, C14,24), 120.9 (CH, 1C, C5), 66.9 (CH2, 2C, C18,20), 66.1 (CH2, 2C, C18,20), 48.2 (Cq, C, C7), 45.0 (CH3, 3C, C17,27), 20.8 (CH2, 1C, C3). **Combustion analysis:**

Calcd (%): C23H29N5 (375.51): C 73.57, H 7.78, N 18.65; found: C 73.59, H 7.72, N 18.95. HR-MS (ESI): Calcd for 

**Synthesis of metal complexes**

**Iron(II) Triflato complexes: general procedure.** After addition of a solution of the ligand in acetonitrile (2 ml) to a suspension of Fe(OTf)2, in acetonitrile (2 ml), the reaction mixture is stirred for 1 day at room temperature. After removing acetonitrile under reduced pressure, dichloromethane was added. The solution was stirred for 1 h and then treated with diethyl ether (20 ml) to give a light yellow solid. This is collected by filtration, washed with diethyl ether, and dried in vacuo. Isothermal diffusion of diethyl ether into a solution in dichloromethane affords yellow single crystals within several days. Yield: 0.15 g (77%).

**Nickel(II) complexes: general procedure.** After adding a slight excess of ligand L1 as a methanolic solution to a solution of Ni(ClO4)2·6H2O in methanol, the resulting violet mixture is stirred for one day at ambient temperature. Isothermal diffusion of diethyl ether into the solution at ambient temperature affords violet crystalline material within one day. The crystals are separated by filtration, washed with diethyl ether and dried in vacuo. 1H-NMR (400 MHz, CD3CN, 23 °C): δ [ppm] = 114.1, 50.9, 39.8, 37.5, 34.8, 15.0, 10.3, 6.2, −6.2, −0.9.

**Samples of FeL2(X)Y for Mössbauer spectroscopy**

Amorphous powder samples of the complexes were obtained by treating solutions of [FeL2(OTf)](OTf) with an excess of cold diethyl ether. (i) Acetonitrile complexes of L1 and L2 with X = Y for Mössbauer spectroscopy.
TURBOMOLE6.4 package. The latter allows variation of the amount of exact exchange in global hybrid functionals. def2-TZVP basis sets were used throughout. The B3LYP functional was used with 20% exact exchange, but for spin-cross-over (SCO) energies, B3LYP* (15% exact exchange) has been used, which had been parameterised to better describe SCO in iron(III) complexes. The SCF energies were converged to 10^-8 Hartree in energy and a fine m5 grid was chosen. Dispersion contributions were evaluated using Grimme’s DFT-D3 atom-pairwise dispersion corrections. In several cases, solvent effects were taken into account at the polarisable continuum model level, using COSMO (Conductor-Like Screening Model) implemented in TURBOMOLE6.3, with permittivity ε = 35.688 for acetonitrile.

For the calculation of Mössbauer parameters, an uncontracted def2-QZVPP basis set was used for iron and def2-TZVP for all other atoms. The structures for the Mössbauer calculations were optimised at B3LYP-D3/def2-TZVP level. The in-house MAG program was used to calculate the electron density ρ at the iron nucleus and the quadrupole splitting. For the isomer shifts the linear equation used is $\delta \equiv \rho(\text{DFT}) - 11 \times 10^2$. This equation was fitted to the isomer-shift test of Neese.

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