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Deciphering the Influence of Meridional vs Facial Isomers in Spin Crossover Complexes.

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Abstract

Chelate coordination of non-symmetrical didentate pyrazine-benzimidazole (L1) or pyridine-benzimidazole (L2) N-donor ligands around divalent iron in acetonitrile produces stable homoleptic triple-helical spin crossover [Fe(Lk)$_3$]$^{2+}$ complexes existing as mixtures of meridional ($C_1$-symmetry) and facial ($C_3$-symmetry) isomers in slow exchange on the NMR time scale. The speciation deviates from the expected statistical ratio $mer/fac = 3:1$, a trend assigned to the thermodynamic trans-influence combined with solvation effects. Consequently, the observed spin state Fe$^{II}_{\text{low-spin}} \leftrightarrow Fe^{II}_{\text{high-spin}}$ equilibria occurring in [Fe(Lk)$_3$]$^{2+}$ refer to mixtures of complexes in solution, an issue usually not considered in this field, but which limits rational structure-properties correlations. Taking advantage of the selective and quantitative formation of isostructural facial isomers in non-constrained related spin crossover d-f helicates (HHH)-[LnFe(Lk)$_3$]$^{5+}$ (Ln is a trivalent lanthanide, Lk = L5, L6), we propose a novel strategy for assigning pertinent thermodynamic driving forces to each spin crossover triple-helical isomer. The different enthalpic contributions to the spin state equilibrium found in $mer$-[Fe(Lk)$_3$]$^{2+}$ and $fac$-[Fe(Lk)$_3$]$^{2+}$ reflect the Fe-N bond strengths dictated by the trans-influence, while a concomitant solvent-based entropic contribution reinforces the latter effect and results in systematic shifts of the spin crossover transitions toward higher temperature in the facial isomers.

Introduction

Almost nine decades after the discovery of the spin state equilibrium phenomenon,[1] a plethora of d$^4$-d$^7$ complexes has been identified for their spin crossover properties, which can be induced by thermal, pressure, optical or pH stimuli.[2] Among them, the d$^6$ pseudo-octahedral six-coordinate [Fe$^{II}$N$_6$] chromophore[3] found in [FeL$_3$] (L is a didentate N-donor ligand) and in [Fe(L')$_2$] (L' is a tridentate N-donor ligand) plays a central role.[4] Taking pure octahedral symmetry ($O_h$) as a guide for [FeN$_6$] entities, the electronic ground state of the Fe$^{II}$ center ‘hesitates’ between low-spin (ls) and high-spin (hs) configurations depending on the balance between the magnitude of the ligand-field strength $\Delta_{\text{oct}}$ and that of the electron spin pairing energy $P$ (Scheme 1).
Scheme 1. The thermodynamic origin of Fe$^{II}$ spin state equilibria in octahedral symmetry ($P$ is the electron spin pairing energy).

Since both the spectrophotometric series (which controls $\Delta_{oct}$)\cite{5} and the nephelauxetic series (which controls $P$ via the Racah parameters $B$ and $C$)\cite{6} depend on the strength and on the nature of the metal-ligand interactions, it is not so surprising that, for [FeN$_6$] units, the coordination sphere of which is systematically made up of six heterocyclic nitrogen donor, some simple metric parameters were found to be valuable reporters for predicting the emergence of either pure low-spin state ($E_{ls}^{O_h} - E_{ls}^{O_h} = 2P - 12/5 \Delta_{oct}$), pure high-spin state ($E_{hs}^{O_h} - E_{hs}^{O_h} = -2/5 \Delta_{oct}$) or spin state equilibria ($E_{hs}^{O_h} - E_{ls}^{O_h} = 2(\Delta_{oct} - P)$).

In the famous family of homoleptic tris-diimine complexes [FeL$_3$]$^{2+}$, the interatomic distance $d$(N···N) between the two N-donor atoms in the non-coordinated didentate diimine ligands proved to be the searched indicator for predicting spin crossover (SCO) behaviors.\cite{7} Values of $d$(N···N) larger than 2.91 Å, as found in non-constrained didentate ligands made up of connected five-membered ring/five-membered ring (for instance 2,2'-biimidazole), produce loose Fe-N bonding and high-spin ground states. On the contrary, $d$(N···N) distances smaller than 2.75 Å as found in 2,2'-bipyridine, the archetype of two connected six-membered ring/six-membered ring, strongly stabilize low-spin configurations. Spin crossover behaviors match the intermediate regime ($2.75 \leq d$(N···N) $\leq 2.91$ Å).
provided by non-symmetrical didentate ligands made up of connected five-membered ring/six-membered ring as found in 2,2’-pyridine-imidazole or derivatives of it.[7] Taking now for granted that favorable metric parameters are in hand, some further tuning of the thermodynamic SCO parameters (Eq. (1)) results from the modulation of specific \( \sigma \)-donating (mainly affecting \( \Delta_{\text{oct}} \) and/or \( \pi \)-accepting characteristics (mainly affecting the spin pairing energy \( P \) via the Racah parameter \( B \)) encoded in the bound heterocyclic rings. Reminiscent of Tanabe-Sugano diagrams,[8] the trivial thermodynamic analysis summarized in Scheme 1 implies that the spin crossover properties in Fe\( ^{\text{II}} \) complexes depend on the \( \Delta_{\text{oct}}/B \) ratio where (i) large values favor low-spin configurations, (ii) small values stabilize high-spin states and (iii) intermediate values induce SCO behaviors. A precise and rational correlation between molecular ligand structures and thermodynamic \( \Delta H_{\text{SCO}}, \Delta S_{\text{SCO}} \) parameters (especially the equilibrium temperature \( T_{1/2} = \Delta H_{\text{SCO}}/\Delta S_{\text{SCO}} \)) thus goes through the \( \Delta_{\text{oct}}/B \) ratio, a crucial strategy for the rational programming of accessible spin state transitions, which can be implemented in magnetic[9] and/or optical[10] (nano)molecular switches for practical applications. With this goal in mind, major efforts were focused on the systematic synthesis of large collections of didentate and tridentate polyimine binding units with variable coordinating properties for tuning the SCO transition temperatures and thermodynamic cooperativities in \([\text{FeL}_3]^{2+}\) and \([\text{Fe(L')}_2]^{2+}\) complexes.[2]-[4],[9],[10]

Although unsymmetrical didentate ligands have been often reacted with Fe\( ^{\text{II}} \) to give triple-helical homoleptic \([\text{FeL}_3]^{2+}\) complexes, the influence of standard meridional and facial isomerization on the spin state equilibrium mainly escaped attention and interest (Figure 1). Only a few salts containing a single isomer could be isolated in the solid state (meridional or facial as certified by their X-ray crystal structures),[11] but the associated SCO parameters did not give any clear evidences or trends, probably because intermolecular packing interactions responsible for the stabilization of the crystal structures largely dominate minor molecular effects. To the best of our knowledge, no attempt was made to address the meridional/facial challenge in solution where the limited solvation effects offer the opportunity to establish direct links between molecular geometries and SCO properties.
Figure 1. a) Perspective view along the helical axis for the meridional→facial isomerization processes (flip of the yellow ligand) operating in homoleptic [M(L2a)3]2⁺ complex where L2a is the archetype of a non-symmetrical didentate ligand (see Scheme 2) and M is a pseudo-octahedral six-coordinate metal center. b) Schematic views of the two enantiomeric pairs of mer/fac geometrical isomers.

Pioneer attempts to address this challenge aim at connecting three unsymmetrical didentate units to a short hydrocarbon-containing tripod, thus producing sexidentate ligands L”, which force the formation of the facial isomer fac-[FeL”]2⁺ as the unique complex in solution.[4d],[7],[12] However, this strategy induces drastic intramolecular thermodynamic constraints during the formation of the [FeN₆] chromophore, an effect which can be quantified with the help of the concept of effective molarity.[13] Applied to related podands bound to more flexible trivalent lanthanides, free-energy penalties as large as 70-80 kJ/mol are common for the preorganization of three unsymmetrical binding units by short to medium-size tripods. Compared with a total binding energy of 110-120 kJ/mol accounting for pure intermolecular processes, this facial organization in a single tripodal ligand corresponds to c.a. 60% reduction of the affinity for the entering metal.[14] One therefore understands why such constrained
tripodal complexes were not further considered as fair models for extracting the SCO properties of analogous, but unconstrained fac-[FeL₃]²⁺ isomers. However, some recent progresses made in the understanding of the thermodynamic trans-influence occurring in simple mononuclear mer/fac-[Zn(Lₖ)₃]²⁺ isomers (Lₖ = L₁, L₂; Scheme 2 top)¹⁵ combined with the design of flexible non-covalent tripods displaying minor intramolecular cost (≤ 20 kJ/mol) in HHH-[ZnLn(Lₖ)₃]⁵⁺ helicates (Lₖ = L₅, L₆; Scheme 2 bottom),¹⁶ reactivate the search for a rational treatment of the influence of molecular mer-[FeL₃]²⁺ ↔ fac-[FeL₃]²⁺ isomerization on the SCO properties of these complexes in solution. We report here on the discovery that the meridional and facial isomers, due to their structural differences indeed display synergestic enthalpic and entropic contributions, which may shift the spin crossover transition temperature $T_{1/2}$ by up to 60 degrees. A thermodynamic analysis assigns this effect to trans-influence and to changes in (dipole-based) solvation energies accompanying the change in volume produced by the SCO reaction.

Scheme 2. Chemical structures of ligands L₁-L₇ considered in this work.
**Experimental section**

Chemicals were purchased from Sigma-Aldrich and Acros and used without further purification unless otherwise stated. The didentate ligands $L_1$, $L_2$, $L_3$ and segmental ligands $L_5$, $L_6$ and $L_7$ were prepared according to literature procedures. Dichloromethane, diethyl ether and $N,N$-dimethylformamide were dried through an alumina cartridge. Silica-gel plates (Merck, 60 F$_{254}$) were used for thin-layer chromatography, SiliaFlash® silica gel P60 (0.04-0.063 mm) and Acros silica gel 60 (0.035-0.07 mm) were used for preparative column chromatography.

**Preparation of $N$-methyl-2-nitroaniline (1).** 1-chloro-2-nitrobenzene (31.75 g, 201.5 mmol, 1.0 eq) and methylamine (198 mL, 40% wt in H$_2$O, 2295.6 mmol, 11.4 eq) were introduced into a Carius tube equipped with a magnetic stirrer, and heated at 120 °C for 48 h. Excess of methylamine was rotatory evaporated and the residual brown oil was partitioned between CH$_2$Cl$_2$ (300 mL) and half sat. aq. NH$_4$Cl (300 mL). The organic layer was separated and the aq. phase was further extracted with CH$_2$Cl$_2$ (3 x 150 mL). The combined organic extracts were dried over anhydrous Na$_2$SO$_4$, filtered and the solvent evaporated to dryness. The resulting red oil was purified by column chromatography (silica, CH$_2$Cl$_2$) to give 28.99 g of $N$-methyl-2-nitroaniline (1, 190.5 mmol, yield 94.5 %) as a deep red orange oil, which slowly crystallized within hours. $^1$H NMR (CDCl$_3$, 400 MHz, 298 K) δ ppm : 8.13 (1H, dd, $^3J = 8.8$ Hz, $^4J = 1.6$ Hz), 8.00 (1H, bs), 7.43 (1H, ddd, $^3J = 8.8$ Hz, $^3J = 7.2$ Hz, $^4J = 1.6$ Hz), 6.81 (1H, dd, $^3J = 8.6$ Hz, $^4J = 1.0$ Hz), 6.62 (1H, ddd, $^3J = 8.4$ Hz, $^3J = 7.2$ Hz, $^4J = 1.2$ Hz), 2.99 (3H, s).

**Preparation of 3-methyl-picolinic acid (2).** 3-methyl-picolinonitrile (1.53 g, 13.0 mmol, 1.0 eq) in aq. 5M NaOH (5 mL) were refluxed for 4 h. After cooling, the mixture was neutralized (pH = 2.0) with concentrated hydrochloric acid (12 M) and evaporated to dryness. The residual solid was suspended in ethyl acetate (250 mL), refluxed for 3 h and filtered when hot through a Büchner funnel. The filtrate was evaporated to dryness to give 1.61 g of 3-methyl-picolinic acid (2, 11.7 mmol, yield 91 %) as a white powder. $^1$H NMR (CDCl$_3$, 400 MHz, 298 K) δ ppm: 9.97 (1H, bs), 8.46 (1H, dd, $^3J = 4.8$ Hz, $^4J = 0.8$ Hz), 7.72 (1H, dd, $^3J = 7.8$ Hz, $^4J = 0.6$ Hz), 7.48 (1H, dd, $^3J = 7.8$ Hz, $^3J = 4.6$ Hz), 2.78 (3H, s). RMN $^1$H ((CD$_3$)$_2$SO, 400 MHz, 298 K) δ ppm: 13.07 (1H, s), 8.46 (1H, dd, $^3J =
4.6 Hz, $^4J = 1.0$ Hz), 7.77 (1H, d, $^3J = 8.0$ Hz), 7.47 (1H, dd, $^3J = 7.8$ Hz, $^3J = 4.6$ Hz), 2.46 (3H, s).

$^{13}$C NMR (CDCl$_3$, 100 MHz, 298 K) δ ppm: 164.40 (C$_q$), 145.32 (CH), 143.39 (C$_q$), 141.80 (CH), 137.67 (C$_q$), 129.79 (CH), 20.30 (CH$_3$).

**Preparation of N,N,N-trimethyl-N-(2-nitrophenyl)picolinamide (3).** Thionyl chloride (4.8 mL, 66.1 mmol, 6.0 eq) were dropwise added to a mixture of 3-methyl-picolinic acid (2, 1.51 g, 11.0 mmol, 1.0 eq) and $N,N$-dimethylformamide (200 µl) in dry 1,2-dichloroethane (10 mL). The solution was refluxed for 4 h under an inert atmosphere, then cooled and evaporated to dryness. The residue was dissolved in dry CH$_2$Cl$_2$ (15 mL) and a solution of $N$-methyl-2-nitroaniline (1, 4.41 g, 27.2 mmol, 2.5 eq) in dry CH$_2$Cl$_2$ (10 mL) was added dropwise. The final mixture was refluxed for 14 h during which two portions of (iPr)$_2$NEt (3 mL, 17.2 mmol, 1.6 eq) were added after 20 min and 12 h, respectively. Evaporation to dryness provided a solid, which was partitioned between CH$_2$Cl$_2$ (200 mL) and half sat. aq. NH$_4$Cl (200 mL). The organic layer was separated and the aq. phase was further extracted with CH$_2$Cl$_2$ (3 x 120 mL). The combined organic extracts were dried over anhydrous Na$_2$SO$_4$, filtered and the solvent evaporated to dryness to give 2.38 g of N,N,N-trimethyl-N-(2-nitrophenyl)picolinamide (3, 8.8 mmol, yield 80 %) as a brownish solid. $^1$H NMR (CDCl$_3$, 400 MHz, 298 K) δ ppm: mixture of rotamers A (2/3) et B (1/3): 8.50-7.50 (4H, m), 7.48-6.95 (3H, m), 3.56 (3H, s, A), 3.28 (3H, s, B), 2.44 (3H, s, B), 2.38 (3H, s, A). ESI-MS (soft positive mode, $m/z$): [3+H]$^+$: 272.1 (exp.), 272.3 (calc.); [(3)$_2$+H]$^+$: 543.8 (exp.), 543.6 (calc.).

**Preparation of ligand L4.** N,N,N-trimethyl-N-(2-nitrophenyl)picolinamide (3, 2.38 g, 8.8 mmol, 1.0 eq) and activated powdered iron (9.77 g, 174.9 mmol, 19.9 eq) were refluxed for 24 h in a mixture of ethanol (400 mL), water (115 mL) and concentrated hydrochloric acid (37 % in H$_2$O, 25 mL, 294.3 mmol, 33.5 eq). Excess iron was removed with a magnet and ethanol was evaporated. Water (50 mL) and EDTA disodium dihydrate (65.3 g, 175.4 mmol, 20.0 eq) in water (250 mL) were successively added to the solution and its pH was adjusted to 9.5 with concentrated aq. ammonia. CH$_2$Cl$_2$ (300 mL) was finally added together with concentrated hydrogen peroxide (30 % in H$_2$O, 5 mL, 44.1 mmol, 5.0 eq) in small portions under vigorous stirring. The organic layer was separated and the aq.
phase was further extracted with CH₂Cl₂ (3 x 300 mL). The combined organic extracts were dried over anhydrous Na₂SO₄, filtered and the solvent evaporated to dryness. The solid residue was purified by column chromatography (silica, CH₂Cl₂/MeOH 98:2) to give 1.45 g of L₄ (6.5 mmol, yield 74 %) as a cream powder.¹H NMR (CDCl₃, 400 MHz, 298 K) δ ppm: 8.58 (1H, dd, ³J = 4.6 Hz, ⁴J = 0.6 Hz), 7.85-7.83 (1H, m), 7.70 (1H, d, ³J = 7.6 Hz), 7.45-7.43 (1H, m), 7.38-7.29 (3H, m), 3.88 (3H, s), 2.56 (3H, s).¹³C NMR (CDCl₃, 100 MHz, 298 K) δ ppm: 150.94 (Cq), 148.69 (Cq), 146.52 (CH), 142.62 (Cq), 139.02 (CH), 135.83 (Cq), 135.04 (Cq), 123.79 (CH), 123.03 (CH), 122.24 (CH), 120.11 (CH), 109.69 (CH), 31.39 (CH₃), 19.58 (CH₃). ESI-MS (soft positive mode, m/z) : [L₄+H]^+: 224.4 (exp.), 224.3 (calc.). Elemental analysis: calcd: %C 75.31, %H 5.87, %N 18.82 ; found: %C 75.16, %H 5.83, %N 19.02.

**Preparation of mononuclear Fe**⁺⁺** complexes with L1-L4.** In a typical synthesis, 1.47 mmol of ligand Lₖ (3.0 eq) in CH₂Cl₂ (8 mL) were added to 0.49 mmol (1.0 eq) of Fe(CF₃SO₃)₂ or Fe(BF₄)₂·6H₂O in acetonitrile (48 mL). The resulting mixture was stirred for 12 h under argon, then evaporated to dryness. The solid residue was dissolved in acetonitrile (4 mL) and diethylether was slowly diffused until the formation of microcrystalline powders or monocrystals suitable for X-ray diffraction studies. Filtration followed by washing with diethyl ether gave 62-85 % of [Fe(Lₖ)₃](CF₃SO₃)₂·xSolvent or [Fe(Lₖ)₃](BF₄)₂·xSolvent. For the hexafluorofluorophosphate salt, the same procedure was repeated in presence of (ⁿBu)₄NPF₆ (25 eq) to yield 59-82% of [Fe(Lₖ)₃](PF₆)₂·xSolvent. All complexes were characterized by elemental analyses (Table S1 Supporting Information) and X-ray crystal structures could be solved for [Fe(L₂a)₃](PF₆)₂ (4) and [Fe(L₄)₃](ClO₄)₂·CH₃CN (5). The latter complex was crystallized in presence of a large excess of (ⁿBu)₄NCIO₄.

Caution! Dry perchlorates may explode and should be handled in small quantities and with the necessary precautions.²⁰

**Preparation of dinuclear Ln**⁺⁺⁺Fe⁺⁺ and Ln⁺⁺⁺Zn⁺⁺ complexes with L₅-L₇. In a typical synthesis, 27.6 μmol of Ln(CF₃SO₃)₃ (1.0 eq; Ln = La or Eu) and 27.6 μmol of M(CF₃SO₃)₂ (1.0 eq; M = Fe or Zn)
in acetonitrile/water (99:1, 1.38 mL) were added to 82.8 μmol of ligand \( Lk \) (3 eq) in dichloromethane (700 μl) and the resulting clear solution was stirred for 4 h under an inert atmosphere. The solvent were removed and the solid residue was dissolved in acetonitrile (2 mL). Diethylether was slowly diffused until the formation of microcrystalline powders or monocrystals suitable for X-ray diffraction studies. Filtration followed by washing with diethyl ether gave 68-93 % of [LnFe(\( Lk \))\( _3 \)](CF\(_3\)SO\(_3\))\(_5\)·xSolvent or [LnZn(\( Lk \))\( _3 \)](CF\(_3\)SO\(_3\))\(_5\)·xSolvent. For the hexafluorofluorophosphate, the same procedure was repeated in presence of (\( \text{^nBu} \))\(_4\)NPF\(_6\) (25 eq) to yield 69-87% of [LnFe(\( Lk \))\( _3 \)](PF\(_6\))\(_5\)·xSolvent. All complexes were characterized by elemental analyses (Table S2 Supporting Information). Single crystal X-ray crystal structures could be solved for [LaFe(\( L5 \))\( _3 \)](ClO\(_4\))\(_5\)·5CH\(_3\)CN (6), [EuFe(\( L5 \))\( _3 \)](ClO\(_4\))\(_5\)·6CH\(_3\)CN (7), [EuFe(\( L6 \))\( _3 \)](CF\(_3\)SO\(_3\))\(_5\)·2.5CH\(_3\)CN·(CH\(_3\))\(_3\)C(OCH\(_3\)) (8), {[LaFe(\( L7 \))\( _3 \)](ClO\(_4\))\(_5\)·2·6CH\(_3\)CN·1.5H\(_2\)O (9), {[EuFe(\( L7 \))\( _3 \)](CF\(_3\)SO\(_3\))\(_5\)·2·4CH\(_3\)CN·3(CH\(_3\))\(_3\)C(OCH\(_3\)) (10) and [LuFe(\( L7 \))\( _3 \)](CF\(_3\)SO\(_3\))\(_5\)·2CH\(_3\)CN (11). The perchlorate complexes were crystallized in presence of a large excess of (\( \text{^nBu} \))\(_4\)NCIO\(_4\).

**Spectroscopic and analytical measurements**

1\(^H\) and 13\(^C\) NMR spectra were recorded at 293 K on a Bruker Avance 400 MHz spectrometer. Chemical shifts are given in ppm with respect to TMS. Spectrophotometric titrations were performed with a J&M diode array spectrometer (Tidas series) connected to an external computer. In a typical experiment, 25 cm\(^3\) of ligand in acetonitrile (2·10\(^{-4}\) M) were titrated at 298 K with a solution of Fe(CF\(_3\)SO\(_3\))\(_2\) (2·10\(^{-3}\) M) in acetonitrile under an inert atmosphere. After each addition of 75 μL, the absorbance was recorded using Hellma optrodes (optical path length 0.1 cm) immersed in the thermostated titration vessel and connected to the spectrometer. Mathematical treatment of the spectrophotometric titrations was performed with factor analysis\(^{[21]}\) and with ReactLab™ Equilibria (previously Specfit/32).\(^{[22]}\) Pneumatically-assisted electrospray (ESI-MS) mass spectra were recorded from 10\(^{-4}\) M (ligands) and 10\(^{-3}\) M (complexes) solutions on an Applied Biosystems API 150EX LC/MS System equipped with a Turbo Ionspray source. Elemental analyses were performed by K. L. Buchwalder from the Microchemical Laboratory of the University of Geneva. Electronic spectra in
the UV-Vis region were recorded at 293 K from solutions in CH$_3$CN with a Perkin-Elmer Lambda 1050 using quartz cells of 0.1 or 1.0 mm path length. Solid-state magnetic data were recorded on a MPMS 3 or MPMS 5 QUANTUM DESIGN magnetometers using magnetic fields of 1000-5000 Oe and at 2 K/min rates within the 2-400 K range. The magnetic susceptibilities were corrected for the magnetic response of the sample holder and for the diamagnetism of the compounds.$^{[23]}$ Magnetic data for samples in acetonitrile were obtained by the Evans method$^{[24]}$ using methanol for temperature calibration.$^{[25]}$ The method was modified for application with a superconducting magnet.$^{[26]}$ Specific problems associated with the ‘solvent correction term’$^{[27]}$ were overcome by determining the diamagnetic contribution under the same experimental conditions.$^{[28]}$ Measurements were carried out on degassed CD$_3$CN solutions containing 1% (v/v) and using tert-butanol as an internal reference. All the data were corrected for changes in solvent density with temperature.$^{[29]}$

**X-ray crystallography**

Single crystals. Summary of crystal data, intensity measurements and structure refinements for compounds (4) to (11) were collected in Tables S3-S10. The crystals were mounted on MiTeGen kapton cryoloops with protection oil. X-ray data collections were performed with an Agilent SuperNova Dual diffractometer equipped with a CCD Atlas detector (Cu[Kα] radiation). The structures were solved by using direct methods.$^{[30]}$ Full-matrix least-square refinements on $F^2$ were performed with SHELX2014.$^{[31]}$ CCDC 1862027-1862034 contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/.

Powder crystals. Variable temperature X-ray powder diffraction experiments were performed on an Empyrean (PANalytical) diffractometer in capillary mode, with a focusing X-ray mirror for Cu[Kα] radiation and a PIXcel3D area detector. Variable temperatures were achieved with a nitrogen cryostreamer (Oxford cryosystem). Temperature cooling ramps from 340 K to 140 K were performed at 3 K·min$^{-1}$ and data collections were performed at fixed temperature plateau (2theta range from 7 to 30° with continuous scan total time 26 min/diagram)
Results and Discussions


The didentate ligands L1-L2\[15\] and L3\[17\] were previously obtained according to standard Phillips-modified strategies similar to that used for the novel ligand L4 (Scheme 3). 3-methyl-picolinic acid (2) was in situ activated as its acid chloride, which was further reacted with N-methyl-2-nitroaniline (1) to give the ortho-nitroamide (3) in good yield. Final reductive cyclization provided the target constrained ligand L4.


Stoichiometric reactions of L1-L4 (3.0 eq) with Fe(CF₃SO₃)₂ or Fe(BF₄)₂ (1.0 eq) in dichloromethane/acetonitrile mixtures followed by slow diffusion of volatile ether provided fair yields (62-85%) of microcrystalline [Fe(Lk)₃](CF₃SO₃)₂ and [Fe(L4)₃](BF₄)₂ complexes with various amounts of co-crystallized solvent molecules (Table S1 in the Supporting Information). Subsequent metathesis of the triflate anions with the help of ("Bu)₄NPF₆ in acetonitrile/ether mixtures additionally yielded [Fe(Lk)₃](PF₆)₂ (Lk = L1a, L2a, L4, Table S1). Intense efforts for producing mono-crystals of sufficient quality for X-ray diffraction studies were only successful for [Fe(L2a)₃](PF₆)₂ (4) and [Fe(L4)₃](ClO₄)₂·CH₃CN (5, after metathesis with ("Bu)₄NCIO₄, Figure 2 top, Tables S3-S4 and Figures S1-S2 in the Supporting Information). The six-coordinate homoleptic tris-diimine [Fe(L2a)₃]²⁺ and [Fe(L4)₃]²⁺ cations in 4 and 5 adopt meridional arrangements, in which the [FeN₆]
chromophores only slightly deviate from perfect octahedrons according to SHAPE’s scores (Table 1, entries 5-6).\cite{32} The Fe-N bond lengths measured at 180 K are typical for a low-spin electronic configuration in \textit{mer}-[Fe(\textbf{L}2a)\textsubscript{3}]\textsuperscript{2+} (1.96-2.03 Å), whereas the 10% expansion found in \textit{mer}-[Fe(\textbf{L}4)\textsubscript{3}]\textsuperscript{2+} (2.14-2.26 Å, Table 1) is diagnostic for alternative high-spin configuration in the latter complex.\cite{2}-\cite{4}

\textbf{Figure 2.} Molecular structures of the Fe\textsuperscript{II}-containing cations in the crystal structures of [Fe(\textbf{L}2a)\textsubscript{3}](PF\textsubscript{6})\textsubscript{2} (4), [Fe(\textbf{L}4)\textsubscript{3}](ClO\textsubscript{4})\textsubscript{2}-CH\textsubscript{3}CN (5) [LaFe(\textbf{L}5)\textsubscript{3}](ClO\textsubscript{4})\textsubscript{5}-5CH\textsubscript{3}CN (6), [EuFe(\textbf{L}5)\textsubscript{3}](ClO\textsubscript{4})\textsubscript{5}-6CH\textsubscript{3}CN (7), [EuFe(\textbf{L}6)\textsubscript{3}](CF\textsubscript{3}SO\textsubscript{3})\textsubscript{5}-2.5CH\textsubscript{3}CN-(CH\textsubscript{3})\textsubscript{3}C(OCH\textsubscript{3}) (8), {[LaFe(\textbf{L}7)\textsubscript{3}](ClO\textsubscript{4})\textsubscript{5}}\textsubscript{2}-6CH\textsubscript{3}CN-1.5H\textsubscript{2}O (9), {[EuFe(\textbf{L}7)\textsubscript{3}](CF\textsubscript{3}SO\textsubscript{3})\textsubscript{5}}\textsubscript{2}4CH\textsubscript{3}CN-3(CH\textsubscript{3})\textsubscript{3}C(OCH\textsubscript{3}) (10) and [LuFe(\textbf{L}7)\textsubscript{3}](CF\textsubscript{3}SO\textsubscript{3})\textsubscript{5}-2CH\textsubscript{3}CN (11)
Table 1. Structural data for the six-coordinate metallic (M = FeII or ZnII) centers in complexes 4-11 in the solid state at 180 K.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>[Zn(L2a)3]2⁺</th>
<th>[Fe(L2a)3]2⁺</th>
<th>[Fe(L4)3]2⁺</th>
<th>[EuZn(L5)3]5⁺</th>
<th>[LaFe(L5)3]5⁺</th>
<th>[EuFe(L5)3]5⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>d_{M-N(bz)} /Å [a]</td>
<td>2.11(2)</td>
<td>1.96(1)</td>
<td>2.14(2)</td>
<td>2.09(3)</td>
<td>1.979(8)</td>
<td>1.973(9)</td>
</tr>
<tr>
<td>d_{M-N(py/pz)} /Å [a]</td>
<td>2.24(4)</td>
<td>2.04(3)</td>
<td>2.26(5)</td>
<td>2.26(7)</td>
<td>1.98(1)</td>
<td>1.970(8)</td>
</tr>
<tr>
<td>α /° [b]</td>
<td>12(9)</td>
<td>11(3)</td>
<td>41.1(2)</td>
<td>17(7)</td>
<td>9(6)</td>
<td>8(2)</td>
</tr>
<tr>
<td>β /° [c]</td>
<td>87(2)</td>
<td>88.3(4)</td>
<td>76(5)</td>
<td>88(1)</td>
<td>85.5(5)</td>
<td>87(2)</td>
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<tr>
<td>Octahedron [d]</td>
<td>1.66</td>
<td>0.829</td>
<td>1.957</td>
<td>1.61</td>
<td>0.71</td>
<td>0.68</td>
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<tr>
<td>d_{M-Ln} /Å [e]</td>
<td>-</td>
<td>-</td>
<td>8.92</td>
<td>9.19</td>
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<tr>
<td>d_{M-N(bz)} /Å [a]</td>
<td>2.05(6)</td>
<td>1.95(3)</td>
<td>1.968(5)</td>
<td>2.14(3)</td>
<td>2.13(2)</td>
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<tr>
<td>d_{M-N(py)} /Å [a]</td>
<td>2.3(2)</td>
<td>2.00(4)</td>
<td>1.988(4)</td>
<td>2.33(7)</td>
<td>2.34(7)</td>
<td>2.33(7)</td>
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<tr>
<td>α /° [b]</td>
<td>23(16)</td>
<td>9(4)</td>
<td>10.2</td>
<td>30(4)</td>
<td>23(11)</td>
<td>19(15)</td>
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<tr>
<td>β /° [c]</td>
<td>81(8)</td>
<td>86(2)</td>
<td>85(1)</td>
<td>76(4)</td>
<td>80(3)</td>
<td>80(5)</td>
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<tr>
<td>Octahedron [d]</td>
<td>1.88</td>
<td>0.91</td>
<td>0.75</td>
<td>3.0(4)[f]</td>
<td>2.7(2)[f]</td>
<td>2.79</td>
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<td>Trig. prism [d]</td>
<td>14.40</td>
<td>15.07</td>
<td>15.54</td>
<td>14.9(9)[f]</td>
<td>14.3(7)[f]</td>
<td>13.53</td>
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<tr>
<td>d_{M-Ln} /Å [e]</td>
<td>8.96</td>
<td>9.03</td>
<td>9.14</td>
<td>8.5(3)[f]</td>
<td>9.0(2)[f]</td>
<td>8.94</td>
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<tr>
<td>Reference</td>
<td>[18a]</td>
<td>[18b]</td>
<td>This work</td>
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<td>This work</td>
</tr>
</tbody>
</table>

[a] Bz = benzimidazole, py = pyridine, pz = pyrazine. [b] Interannular intraligand angle. [c] Interchelate angle. [d] SHAPE’s score for comparison with perfect octahedrons and trigonal prisms. [f] Average for the two independent complexes in the asymmetric unit.
The origin of these different spin states can be traced back to the considerable ligand-field splitting produced by heterocyclic nitrogen atoms, which favors low-spin configurations as found in \textit{mer-}[Fe(L2a)3]\textsuperscript{2+}. However, sterical constraints induced by the 3-methyl substituents in \textit{mer-}[Fe(L4)3]\textsuperscript{2+} prevent coplanarity within the didentate polyaromatic rings (interannular angle $\alpha = 41^\circ$ in \textit{mer-}[Fe(L4)3]\textsuperscript{2+} compared with $\alpha = 11^\circ$ in \textit{mer-}[Fe(L2a)3]\textsuperscript{2+}, Table 1). This reduces the ligand-field strength to such an extent that high-spin configuration becomes more stable in \textit{mer-}[Fe(L4)3]\textsuperscript{2+}.\cite{7}

Unfortunately, we were not able to isolate monocrystals of the facial isomers in the solid state for mononuclear complexes, but stoichiometric mixing of segmental ligands L5-L7 (3.0 eq) with M(CF$_3$SO$_3$)$_2$ (M = Fe, Zn; 1.0 eq) and Ln(CF$_3$SO$_3$)$_3$ (Ln = La, Eu, Lu; 1.0 eq) in dichloromethane/acetonitrile followed by slow diffusion of volatile ether provided fair yields (68-93\%) of microcrystalline [LnM(Lk)3](CF$_3$SO$_3$)$_5$ complexes (Table S2), among which monocrystals suitable for X-ray crystal structure analyses could be obtained after a second crystallization (sometimes in presence of ($^n$Bu)$_4$NClO$_4$) for [LaFe(L5)3](ClO$_4$)$_5$•5CH$_3$CN (6), [EuFe(L5)3](ClO$_4$)$_5$•6CH$_3$CN (7), [EuFe(L6)3](CF$_3$SO$_3$)$_5$•2.5CH$_3$CN•(CH$_3$)$_2$C(OCH$_3$) (8), \{[LaFe(L7)3](ClO$_4$)$_5$\}•2•6CH$_3$CN•1.5H$_2$O (9), \{[EuFe(L7)3](CF$_3$SO$_3$)$_5$\}•2•4CH$_3$CN•3•(CH$_3$)$_2$C(OCH$_3$) (10) and [LuFe(L7)3](CF$_3$SO$_3$)$_5$•2CH$_3$CN (11) (Figure 2 bottom, Tables S5-S10 and Figures S3-S8).

As previously reported for [EuZn(L5)]\textsuperscript{5+},\cite{15} [EuZn(L6)]\textsuperscript{5+} \cite{18a} and [LaFe(L6)]\textsuperscript{5+},\cite{18b} the three helical strands adopt a head-to-head-to-head (HHH) arrangement\cite{33} compatible with the formation of purely facial organization of the three didentate binding units around Fe$^{II}$ or Zn$^{II}$ (Figure 2 bottom). The intramolecular intermetallic distance (average $d_{M-Ln} = 9.0(2)$ Å) is roughly insensitive to the choice of the metals and to the nature of the terminal six-membered rings (substituted pyridine in L6 and L7 or pyrazine in L5). The Ln-O and Ln-N distances follow the expected lanthanide contraction along the La $>$ Eu $>$ Lu series (Figure 3 and Table S11 in the Supporting Information).\cite{34} On the contrary, the Fe-N distances in a given helicate are insensitive to the size of the various capping trivalent lanthanide cations (Figure 3), a trend in line with the lack of measurable constraints induced by the flexible non-covalent lanthanide tripod.\cite{16} In agreement with the analogous mononuclear \textit{mer-}
[Fe(L2a)3]2+ complex, the Fe-N distances (1.95-2.00 Å, Table 1) observed at 180 K for HHH-[LnFe(L6)3]5+ points to low-spin configuration, this whatever the meridional (mononuclear) or facial (dinuclear helicate) arrangements of the three (5-methylpyridin-2-yl)-benzimidazole binding units around FeII. Extension to (5-methylpyrazin-2-yl)-benzimidazoles in [LnFe(L5)]3 gives similar Fe-N distances (1.97-1.98 Å) and low-spin characteristics. On the contrary, constrained (6-methylpyridine-2-yl)-benzimidazole units in [LnFe(L7)]3 lead to high-spin configurations at 180 K with larger Fe-N distances (2.13-2.34 Å, Table 1) as previously discussed for mer-[Fe(L4)]32+.

**Figure 3.** Interatomic distances $d_{Ln-O}$, $d_{Ln-N}$ and $d_{Fe-N}$ measured for the HHH-[LnFe(L7)]35+ cations in the crystal structures of 9-11 at 180 K (py = pyridine, bz = benzimidazole; $R_{Ln}^{CN=9}$ = nine-coordinate lanthanide ionic radius).

The molar magnetic susceptibilities ($\chi_M$) corrected for diamagnetism and for FeIII contamination recorded at variable temperature for solid state samples confirm the spin states deduced by X-ray diffraction studies at 180 K with negligible $0.00 \leq C_L \leq 0.8 \text{ cm}^3\text{K.mol}^{-1}$ Curie constants for the low-spin FeII complexes with ligands L1, L2, L5 and L6 at this temperature (Figure 4; $C = \chi_M T = \left(N \beta^2/3k_B\right) g^2 S (S+1) = \left(g^2/8\right) S (S+1)$, where $N$ is Avagadro number, $\beta$ is Bohr magneton, $k_B$ is Boltzmann constant, $g = 2$ is Landé factor, $S$ is the total spin quantum number).

On the other hand, the homoleptic tris-didentate FeII complexes with sterically demanding ligands L4 and L7 possess significant Curie constants ($3.5 \leq C_L \leq 3.8 \text{ cm}^3\text{K.mol}^{-1}$, Figure 4) diagnostic for high-spin FeII ($S = 2$) configuration at this temperature. Upon warming the samples, $\chi_M T$ for complexes...
with ligands \textbf{L4} and \textbf{L7} do not significantly change, a trend in line with the existence of pure high-spin configuration. The abrupt decrease of $\chi_M T$ at very low temperature is diagnostic for the existence of axial zero-field splittings fitted to $D = 1.37 \text{ cm}^{-1}$ and $g = 2.26$ for $[\text{Fe(}\text{L4})_3]\text{(PF}_6)_2$.\cite{37}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{$\chi_M T$ versus $T$ plot of the molar magnetic susceptibilities ($\chi_M$) corrected for diamagnetism and for Fe$^{\text{III}}$ contamination recorded for a) mononuclear and b) dinuclear homoleptic tris-diimine Fe$^{\text{II}}$ complexes (solid state, Otf$^-$ = CF$_3$SO$_3^-$). The temperature at which the X-ray crystal structures have been measured is highlighted (180 K).}
\end{figure}

For complexes with ligands \textbf{L1}, \textbf{L2}, \textbf{L5} and \textbf{L6}, $\chi_M T$ values smoothly increase with temperature, a behavior diagnostic for the operation of thermodynamic temperature-driven spin state equilibria. All curves can be satisfyingly fitted with standard Eq. (2), where $C_{\text{ls}}, C_{\text{hs}}$ and $C_{\text{Fe(III)}}$ correspond to the Curie constants of the incriminated electronic configurations and $TIP_{\text{hs}}$ and $TIP_{\text{hs}}$ refer to the temperature independent paramagnetic contributions, see next section.\cite{24,38} The mole fraction of high-spin complexes ($x_{\text{hs}}$) can be further deduced with Eq. (3) when one takes into account the mass balance $x_{\text{ls}} + x_{\text{hs}} + x_{\text{Fe(III)}} = 1$. 

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In the solid state, the spin transition leads to 25 to 100% of high-spin FeII at the highest accessible temperature (400 K, Figure S9, Supporting information), but no rational correlation can be drawn between the local molecular structures (mer/fac isomerism or pyridine versus pyrazine donor groups) and the SCO properties. Major variations are observed upon exchange of non-coordinated (i.e., ionic) counter-anions, which indicates that intermolecular contributions and packing effects largely dominate local effects in the solid state. The record of heating/cooling cycles shows no evidence of cooperativity for the SCO processes in the solid state. A thorough study of the temperature dependence of the volume of the crystallographic unit cell of [Fe(L2a)3](PF6)2 (4) confirms the operation of a complete smooth spin transition for this complex in the 200-350 K range with an unit cell expansion of 31.2(6) Å (Appendix 1).

**Solution SCO processes for Fe(II) complexes with ligands L1-L4: a molecular approach to spin-state equilibria.** In solution, the minor second-sphere interactions between the solvent molecules and six-coordinate homoleptic tris-diimine [Fe(Lk)3]2+ cations are expected to produce only minor energy contributions, thus allowing the deciphering of chemically-programmable structural effects. Following the procedure previously detailed for analogous [Zn(Lk)3]2+ with the didentate ligands L1a, L1b, L2a and L2b,15] spectrophotometric titrations of these ligands with Fe(CF3SO3)2 in dry acetonitrile (Figure 5a,b and Figures S10a,b-S12a,b) show the successive formation of the expected three absorbing complexes [Fe(Lk)n]2+ (n = 3, 2, 1) as ascertained by their independent eigenvectors found in the factor analyses (Figures 5c and S10c-S12c)21] and their satisfying re-constructed absorption spectra (Figures 5d and S10d-S12d).
Figure 5. a) Variation of absorption spectra and b) corresponding variation of observed molar extinctions at different wavelengths recorded for the spectrophotometric titration of L1a with Fe(CF3SO3)2 (total ligand concentration: 2.3·10^{-4} mol.dm^{-3} in acetonitrile, 298 K). c) Evolving factor analysis using four absorbing eigenvectors,\cite{21} d) re-constructed individual electronic absorption spectra\cite{22} and e) associated speciation.\cite{39}

Beyond (i) the diagnostic 2000 cm^{-1} red-shift of the ligand-centered $\pi^* \leftrightarrow \pi$ transition observed upon complexation to FeII (Figure 5a,d and S10a,d-S12a,d)\cite{40} and (ii) the stepwise increase of the molar absorption coefficients along the [Fe(Lk)]^{2+} → [Fe(Lk)2]^{2+} → [Fe(Lk)3]^{2+} series (Figure 5d and S10d-S12d), the absorption spectrum of [Fe(Lk)3]^{2+} displays a supplementary broad absorption band...
covering the visible domain (440-600 nm), which can be unambiguously assigned to the $\text{LK} \leftarrow \text{Fe}^{\text{II}}$ metal-to-ligand charge transfer transition (MLCT) occurring in the low-spin iron(II) complex.\textsuperscript{[41]} Non-linear least-square fits\textsuperscript{[22]} of the spectrophotometric data to equilibria (4)-(6) provided the macroscopic cumulative formation constants gathered in Table S1 together with speciation curves (Figures 5e and S10e-S12e),\textsuperscript{[39]} which indicate that the target complexes $[\text{Fe(\text{LK})}_3]^{2+}$ are quantitatively formed for 1:3 stoichiometric ratio at sub-millimolar concentrations.

$$\text{Fe}^{2+} + \text{LK} \rightleftharpoons [\text{FeLK}]^{2+} \quad \beta_{1,1}^{\text{Fe,\text{LK}}}$$

$$\text{Fe}^{2+} + 2 \text{LK} \rightleftharpoons [\text{Fe(LK)}_2]^{2+} \quad \beta_{1,2}^{\text{Fe,\text{LK}}}$$

$$\text{Fe}^{2+} + 3 \text{LK} \rightleftharpoons [\text{Fe(LK)}_3]^{2+} \quad \beta_{1,3}^{\text{Fe,\text{LK}}}$$

Application of the site-binding model summarized in Eqs (7)-(9)\textsuperscript{[15]} dissects the free energy changes accompanying the complexation processes into (1) a pure entropic contribution produced by the change in rotational entropies accompanying the transformation of the reactants into products, a parameter often referred to as the statistical factor,\textsuperscript{[42]} (2) a simple intermolecular affinity $f_{\text{Fe,\text{LK}}}$ between the didentate ligand and the entering Fe$^{\text{II}}$ cation (including the change in solvation) and (3) allosteric cooperativity factors $u_{i,j}^{\text{L,L,L}}$ measuring the extra energy cost ($u_{i,j}^{\text{L,L,L}} < 1$), respectively energy benefit ($u_{i,j}^{\text{L,L,L}} > 1$) produced by an already bound ligand for the connection of the next one around Fe$^{\text{II}}$.\textsuperscript{[43]} Since different microspecies contribute to the $[\text{Fe(LK)}_2]^{2+}$ and $[\text{Fe(LK)}_3]^{2+}$ macrospecies in solution (Figure S13),\textsuperscript{[15]} various intramolecular interligand cooperativity factors $u_{i,j}^{\text{L,L,L}}$ should be considered (Eqs (7)-(9)).

$$\beta_{1,1}^{\text{Fe,\text{LK}}} = 24 f_{\text{Fe,\text{LK}}}$$

$$\beta_{1,2}^{\text{Fe,\text{LK}}} = 12 \left( f_{\text{Fe,\text{LK}}} \right)^2 \left( u_{\text{trans, fac}}^{\text{L,L,L}} + u_{\text{trans, mer}}^{\text{L,L,L}} + 4 u_{\text{cis, fac}}^{\text{L,L,L}} + 4 u_{\text{cis, mer}}^{\text{L,L,L}} \right)$$

$$\beta_{1,3}^{\text{Fe,\text{LK}}} = 16 \left( f_{\text{Fe,\text{LK}}} \right)^3 \left( u_{\text{cis, fac}}^{\text{L,L,L}} \right)^2 \left( u_{\text{cis, fac}}^{\text{L,L,L}} \right)^2 + 3 \left( u_{\text{cis, mer}}^{\text{L,L,L}} \right)^2$$
With the only resort to the three macroscopic formation constants obtained by spectrophotometric titrations, one roughly assumes that \( u_{\text{cis, fac}}^{\text{Lk}, \text{fac}, \text{cis}} = u_{\text{cis, mer}}^{\text{Lk}, \text{mer}, \text{cis}} = u_{\text{trans, fac}}^{\text{Lk}, \text{fac}, \text{trans}} = u_{\text{trans, mer}}^{\text{Lk}, \text{mer}, \text{trans}} = u_{\text{Lk}}^{\text{Lk}} \), and the multi-linear fits of the experimental \( \beta_{\text{Fe, Lk}}^{\text{Lk}} \) to Eqs (7)-(9) gives the intrinsic metal-ligand affinities \( \Delta G_{\text{Fe, Lk}}^{\text{Fe, Lk}} = -RT \ln(f_{\text{Fe, Lk}}) \) and allosteric interligand interactions \( \Delta E_{\text{Lk}, \text{Lk}}^{\text{Lk}, \text{Lk}} = -RT \ln(u_{\text{Lk}, \text{Lk}}) \) illustrated in Figure 6 and tabulated in Table S12.

![Figure 6](image_url)

**Figure 6.** a) Intrinsic affinities \( \Delta G_{\text{M, Lk}}^{\text{M, Lk}} = -RT \ln(f_{\text{M, Lk}}) \) and b) global interligand interactions \( \Delta E_{\text{Lk}, \text{Lk}}^{\text{Lk}, \text{Lk}} = -RT \ln(u_{\text{Lk}, \text{Lk}}) \) for the complexation of M(CF\(_3\)SO\(_3\))\(_2\) with ligands \( \text{Lk} \) obtained by fitting equilibria (4)-(6) with the help of the site-binding model (Eqs (7-9); \( u_{\text{cis, fac}}^{\text{Lk}, \text{fac}, \text{cis}} = u_{\text{cis, mer}}^{\text{Lk}, \text{mer}, \text{cis}} = u_{\text{trans, fac}}^{\text{Lk}, \text{fac}, \text{trans}} = u_{\text{trans, mer}}^{\text{Lk}, \text{mer}, \text{trans}} = u_{\text{Lk}}^{\text{Lk}} \); acetonitrile at 298 K).

In line with the Irving-Williams series,[44] the affinities of ligands \( \text{Lk} \) for Fe\(^{\text{II}}\) is marginally smaller than those with Zn\(^{\text{II}}\) (Figure 6a). The ethyl substituents connected to the benzimidazole units in \( \text{L1b} \) and \( \text{L2b} \) reduce the affinity for any entering metal by *circa* 10 kJ/mol because of the sterical constraints produced in the bound *cis-cis*-chelate conformation.[15] Remarkably, the recurrent global positive cooperativity accompanying the successive complexation of didentate ligands to Fe\(^{\text{II}}\) (-5 ≤...
\( \Delta E_{Fe}^{LL,kk} \leq -3 \text{kJ/mol} \) is at least twice as large as that measured in the Zn(II) analogues \((-2 \leq \Delta E_{Zn}^{LL,kk} \leq 1 \text{kJ/mol}, \text{Figure 6b})\). This trend is reminiscent of \( \Delta E_{M}^{\text{bipy,bipy}} \) estimated with Eqs. (7)-(9) for \([M(\text{bipy})_2]^{2+}\) in water, where the minor values found for \( M = \text{Zn} \), \( \Delta E_{Zn}^{\text{bipy,bipy}} = -0.57(7) \text{kJ/mol} \) becomes much more negative in \([\text{Fe(\text{bipy})}_3]^{2+} \) \( \Delta E_{Fe}^{\text{bipy,bipy}} = -18(7) \text{kJ/mol} \) because the coordination of a third ligand to high-spin \([\text{Fe(\text{bipy})}_2]^{2+} \) (possessing two anti-bonding electrons) gives low-spin \([\text{Fe(\text{bipy})}_3]^{2+} \) with no anti-bonding electron. The less drastic effect observed in going from \([\text{Fe(\text{L}k)2}]^{2+} \) and \([\text{Fe(\text{L}k)3}]^{2+} \) can be tentatively assigned to the smaller ligand-field strength produced by \( \text{L1} \) or \( \text{L2} \), compared with \( \text{bipy} \), thus leading to spin-crossover \([\text{Fe(\text{L}k)3}]^{2+} \) complexes instead of pure low-spin entities.

Since Fe(II) complexes are kinetically less labile than their Zn(II) analogues, separated \(^1\text{H} \text{NMR signals for the microspecies } \text{mer-[Fe(\text{L}k)3]}^{2+} \) and \( \text{fac-[Fe(\text{L}k)3]}^{2+} \) (\( \text{L}k = \text{L1a, L2a}; \text{Figure S14} \)) can be observed in the 233-293 K range (Figure S15), while coalescence due to fast exchange processes on the NMR time scale already occurs at 250 K for Zn(II) analogues. The integration of the \(^1\text{H} \text{NMR signals at variable temperatures gives } K_{\text{mer} \rightarrow \text{fac}}^{\text{Fe,Lk}} \text{ (Eq. (10)), from which the enthalpic } \Delta H_{\text{mer} \rightarrow \text{fac}}^{\text{Fe,Lk}} \text{ and entropic } \Delta S_{\text{mer} \rightarrow \text{fac}}^{\text{Fe,Lk}} \text{ contributions are deduced with the help of van’t Hoff plots (Table S13 and Figure S16).}

\[
\text{mer-[Fe(\text{L}k)3]}^{2+} \rightleftharpoons \text{fac-[Fe(\text{L}k)3]}^{2+} \quad K_{\text{mer} \rightarrow \text{fac}}^{\text{Fe,Lk}} \quad (10)
\]

In agreement with an identical analysis performed for Zn(II) analogues, a weak, but non-negligible enthalpic driving force \((-5 \leq \Delta H_{\text{mer} \rightarrow \text{fac}}^{\text{Fe,Lk}} \leq -3 \text{kJ/mol})\) favors the formation of the facial isomers \( \text{fac-[Fe(\text{L}k)3]}^{2+} \), the signature of a weak thermodynamic \( trans \)-influence. Specific solvation effects produce negative entropic contributions \((-17 \leq \Delta S_{\text{mer} \rightarrow \text{fac}}^{\text{Fe,Lk}} \leq -13 \text{J/mol\cdotK})\), which (i) exceed the expected statistical factor \( \Delta S_{\text{mer} \rightarrow \text{fac}}^{\text{Fe,Lk,stat}} = -R \ln (1/3) = -9.1 \text{J/mol\cdotK} \) and (ii) oppose the enthalpic trend thus making \( \text{mer-[Fe(\text{L}k)3]}^{2+} \) the major isomer in acetonitrile at room temperature. Application of the site-binding model to Equilibrium (10) yields Eq. (11), which can be combined with Eqs (7)-(9) to
partition the rough cooperativity factors $u^{LL,gg}$ into $u^\text{trans, fac}$, $u^\text{trans, mer}$, $u^\text{cis, fac}$, and $u^\text{cis, mer}$ (Table S12).

\[
K_{\text{mer} \rightarrow \text{fac}}^{\text{Fe(Lk)}} = K_{\text{mer} \rightarrow \text{fac}}^{\text{Fe(Lk)}} = \frac{1}{3} \left( \frac{u^{\text{LLL,gg}}}{u^{\text{LLL,gg}}} \right)^2
\]  

(11)

With this thermodynamic toolkit in hand, we are able to catch the meridional/facial speciation of $[\text{Fe(Lk)}_3]^{2+}$ at any temperature in acetonitrile solution (Figure S17), a prerequisite for assigning specific magnetic SCO properties to each isomer. Moreover, the stability constants collected for FeII and ZnII (Table S12) are strong support for assuming that the closely related homoleptic pseudo-octahedral $[\text{Ni(Lk)}_3]^{2+}$ complexes (existing as mixtures of mer/fac isomers) are quantitatively formed in acetonitrile at 0.1 M, where well-resolved absorption spectra can be recorded for the Ni$(^3T_2g \leftrightarrow ^3A_2g)$, Ni$(^3T_1g \leftrightarrow ^3A_2g)$ and Ni$(^1E_g \leftrightarrow ^3A_2g)$ d-d transitions (the symmetry labels assume $O_h$ symmetry, Figure S18). Non-linear least-square fits of the experimental energies at the maximum of the absorption bands (Table S14) with the ligand-field Eqs (12-15) pertinent to octahedral d$^8$ systems give the ligand-field strengths $\Delta_{\text{oct}}$ and Racah parameters $B$ and $C$ collected in Table 2.

\[
E^\left( ^3A_{2g} \right) = 0
\]  

(12)

\[
E^\left( ^1E_g \right) = 8B + 2C - 6B^2 \over 2A_{\text{oct}}
\]  

(13)

\[
E^\left( ^3T_{2g} \right) = \Delta_{\text{oct}}
\]  

(14)

\[
E^\left( ^3T_{1g} \right) = 1.5\Delta_{\text{oct}} + 7.5B - 0.5\sqrt{225B^2 + 18\Delta_{\text{oct}}^2} + 18\Delta_{\text{oct}} B
\]  

(15)

This well-established procedure overcomes the difficult detection of weak d-d transitions masked by intense charge transfer band found in FeII complexes.\cite{49} Ligand-field strength in the 11200 $\Delta_{\text{oct}} $ (NiII) $\leq$ 12400 cm$^{-1}$ range corresponds to the accepted limits for inducing accessible SCO behavior in FeII analogues,\cite{2a} but it may induce some uncertainties for the calculation of the exact values of $\Delta_{\text{oct}}$ due to the mixing of spin-allowed $^3T_{2g} \leftrightarrow ^3A_{2g}$ with the spin-forbidden $^1E_g \leftrightarrow ^3A_{2g}$.\cite{50} Further refinements using the improved equation proposed by Hart et al\cite{50} provide $\Delta_{\text{oct}}$(Ni(L1a)) = 11730
cm⁻¹, \( \Delta_{\text{oct}}(\text{Ni}(\text{L}1\text{b})_3) = 11880 \text{ cm}^{-1} \), \( \Delta_{\text{oct}}(\text{Ni}(\text{L}2\text{a})_3) = 11680 \text{ cm}^{-1} \) and \( \Delta_{\text{oct}}(\text{Ni}(\text{L}2\text{b})_3) = 11780 \text{ cm}^{-1} \), which deviate by less than 2% of those estimated in absence of mixing (eq. 14, column 2 in Table 2).

**Table 2.** Ligand-field strengths (\( \Delta_{\text{oct}} \)), Racah parameters \( B \) et \( C \) and nephelauxetic parameters \( \beta \) for homoleptic \([\text{Ni}(\text{L}k)_3]^{2+}\) complexes (acetonitrile, 293 K).

<table>
<thead>
<tr>
<th>complexes</th>
<th>( \Delta_{\text{oct}} / \text{cm}^{-1} )</th>
<th>( B / \text{cm}^{-1} )</th>
<th>( C / \text{cm}^{-1} )</th>
<th>( C/B )</th>
<th>( \Delta_{\text{oct}}/B )</th>
<th>( \beta ) ([a])</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni}(\text{bipy})_3]^{2+})</td>
<td>12699</td>
<td>741</td>
<td>2801</td>
<td>3.78</td>
<td>17.1</td>
<td>0.71</td>
<td>This work</td>
</tr>
<tr>
<td>([\text{Ni}(\text{L}1\text{a})_3]^{2+})</td>
<td>11476</td>
<td>866</td>
<td>3149</td>
<td>3.64</td>
<td>13.3</td>
<td>0.83</td>
<td>This work</td>
</tr>
<tr>
<td>([\text{Ni}(\text{L}1\text{b})_3]^{2+})</td>
<td>11628</td>
<td>878</td>
<td>3072</td>
<td>3.50</td>
<td>13.2</td>
<td>0.84</td>
<td>This work</td>
</tr>
<tr>
<td>([\text{Ni}(\text{L}2\text{a})_3]^{2+})</td>
<td>11423</td>
<td>889</td>
<td>3096</td>
<td>3.48</td>
<td>12.9</td>
<td>0.85</td>
<td>This work</td>
</tr>
<tr>
<td>([\text{Ni}(\text{L}2\text{b})_3]^{2+})</td>
<td>11567</td>
<td>882</td>
<td>3067</td>
<td>3.48</td>
<td>13.1</td>
<td>0.85</td>
<td>This work</td>
</tr>
<tr>
<td>([\text{Ni}(\text{L}3)_3]^{2+})</td>
<td>9644</td>
<td>994</td>
<td>2614</td>
<td>2.63</td>
<td>9.7</td>
<td>0.95</td>
<td>This work</td>
</tr>
<tr>
<td>([\text{Ni}(\text{L}4)_3]^{2+})</td>
<td>10681</td>
<td>918</td>
<td>2800</td>
<td>3.05</td>
<td>11.6</td>
<td>0.88</td>
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<tr>
<td>([\text{Ni}(\text{CH}_3\text{CN})_6]^{2+})</td>
<td>10100</td>
<td>864</td>
<td>3708</td>
<td>4.29</td>
<td>11.7</td>
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<tr>
<td>([\text{Ni}(\text{NH}_3)_6]^{2+})</td>
<td>10730</td>
<td>830</td>
<td>[b]</td>
<td>[b]</td>
<td>12.9</td>
<td>0.80</td>
<td>[48]</td>
</tr>
<tr>
<td>([\text{Ni}(\text{H}_2\text{O})_6]^{2+})</td>
<td>8580</td>
<td>929</td>
<td>[b]</td>
<td>[b]</td>
<td>9.2</td>
<td>0.89</td>
<td>[48]</td>
</tr>
</tbody>
</table>

[a] Nephelauxetic parameter \( \beta = B/B^0 \) with \( B^0 = 1042 \text{ cm}^{-1} \) for free \( \text{Ni}^{2+} \).\([6b]\) [b] Not computed in reference [48].

**Figure 7.** Tanabe-Sugano diagram built for the d⁸ electronic configuration (\( C^o/B^o = 4.71 \) taken for the free \( \text{Ni}^{2+} \))\([8]\) highlighting the \( \Delta_{\text{oct}}/B \) ratio observed for \([\text{Ni}(\text{L}k)_3]^{2+}\) in acetonitrile solution.\([8]\)
Neglecting this minor effect, Table 2 predicts that [Fe(L1)_3]^{2+} and [Fe(L2)_3]^{2+} display SCO behavior in solution, whereas [Fe(L3)_3]^{2+} and [Fe(L4)_3]^{2+} adopt pure high-spin state. Furthermore, the slightly larger nephelauxetic effect produced by the remarkable \( \pi \)-accepting properties of terminal pyrazine groups in \( \text{L1} \) shifts \( \Delta_{\text{oct}}/B \) toward high values. The associated SCO behavior is thus expected to occur at higher temperature for [Fe(L1)_3]^{2+} than for [Fe(L2)_3]^{2+} (Figure 7), a trend previously documented for related replacements of pyridine rings with pyrazine analogues.\(^{[52]}\) Since the NMR spectra recorded for [Fe(Lk)_3]^{2+} in acetonitrile are complicated by \textit{mer}/\textit{fac} isomerization and by paramagnetic line broadening (Figure S15), we gave up chemical shifts techniques\(^{[53]}\) and preferred to use the Evans’ method\(^{[24],[27]}\) adapted for systems with non-negligible diamagnetic contributions (Eq. 16).\(^{[28]}\) The corrected magnetic susceptibilities \( \chi_M \) are obtained from the balance between the shifts in frequency of the paramagnetic sample \( \Delta\nu_{\text{para}} \) (Hz) with respect to \textit{tert}-butanol taken as the reference (measured for the [Fe(Lk)_3]^{2+} complex of molecular mass \( M_{\text{para}} \) (g\cdot mol\(^{-1}\)) and at concentration \( m_{\text{para}} \) (g\cdot cm\(^{-3}\))) and that of the diamagnetic analogue \( \Delta\nu_{\text{dia}} \) (measured for [Zn(Lk)_3]^{2+} of molecular mass \( M_{\text{dia}} \) at concentration \( m_{\text{dia}} \)). In Eq (16), \( \nu_0 \) stands for the operating frequency of the NMR spectrometer in Hz and \( S_f = 4\pi/3 \) is the shape factor of the superconducting magnet.\(^{[28]}\)

\[
\chi_M = -\frac{1}{\nu_0 S_f} \left( \frac{\Delta\nu_{\text{para}} M_{\text{para}}}{m_{\text{para}}} - \frac{\Delta\nu_{\text{dia}} M_{\text{dia}}}{m_{\text{dia}}} \right) \tag{16}
\]

Plots of \( \chi_M T \) products versus \( T \) collected in Figure 8 show pure high-spin character for [Fe(L3)_3]^{2+} and [Fe(L4)_3]^{2+} and pure low-spin character for [Fe(bipy)_3]^{2+} in complete agreement with previous solid state measurements (Figure 4a).\(^{[45b],[54]}\) Non-linear least-squares fits using Eq. (2) provide Curie constants of \( 3.41 \leq C_{\text{hs}} \leq 3.44 \) cm\(^3\)\cdot K\cdot mol\(^{-1}\) typical for high-spin [Fe(L3)_3]^{2+} and [Fe(L4)_3]^{2+} (expected range 3.13-3.65 cm\(^3\)\cdot K\cdot mol\(^{-1}\))\(^{[55]}\) and \( C_{\text{ls}} = 0.00(8) \) cm\(^3\)\cdot K\cdot mol\(^{-1}\) typical for low-spin [Fe(bipy)_3]^{2+}. The contributions of temperature-independent paramagnetism are opposite, but in the same range as the diamagnetic response for [Fe(L4)_3]^{2+} (\( TIP_{\text{hs}} = 358(57)\cdot 10^{-6} \) cm\(^3\)\cdot K\cdot mol\(^{-1}\)) and for [Fe(bipy)_3]^{2+} (\( TIP_{\text{ls}} = 351(55)\cdot 10^{-6} \) cm\(^3\)\cdot K\cdot mol\(^{-1}\), Table 3). Using these values for pure high-spin, respectively pure low
spin configurations allows the non-linear least-square fit of the $\chi_M T$ versus $T$ curves recorded for the spin crossover complexes $[\text{Fe(L1)}_3]^{2+}$ and $[\text{Fe(L2)}_3]^{2+}$ with the help of Eqs (1)-(2) (see Appendix 2 for details). In solution, the estimated enthalpic ($\Delta H_{SCO}$) and entropic ($\Delta S_{SCO}$) contributions to the spin state equilibria (Table 3) are essentially independent from the choice of the counter anions (Table 3). However, the replacement of pyrazine rings in $[\text{Fe(L1)}_3]^{2+}$ with pyridine rings in $[\text{Fe(L2)}_3]^{2+}$ significantly decreases $\Delta H_{SCO}$, while $\Delta S_{SCO}$ is poorly affected. As a result, the ‘transition’ temperature $T_{1/2}$ at which $x_{ls} = x_{hs} = 0.5$ is shifted by 40 K toward high temperature for $[\text{Fe(L1)}_3]^{2+}$ (Figure 8 and Table 3), a trend in line with stronger Fe-N interactions and a larger $\Delta \sigma_{el}/B$ parameter found for this ligand (larger $\pi$-backbonding, vide infra).

**Figure 8.** Corrected $\chi_M T$ products plotted as a function of the temperature for 0.01 M solution of $[\text{Fe(Lk)}_3](\text{CF}_3\text{SO}_3)_2$ (discs) or $[\text{Fe(Lk)}_3](\text{PF}_6)_2$ (squares) in CD$_3$CN. The dotted traces correspond to non-linear least-square fits obtained with Eqs (1)-(2) and using the parameters gathered in Table 3.

Two additional points merit to be highlighted here. Firstly, an especially large $TIP_{hs} = 1321(88) \cdot 10^{-6}$ cm$^3$.K.mol$^{-1}$ is found for high-spin $[\text{Fe(L3)}_3]^{2+}$ because the sterically hindered approach of the 6-methyl-pyridine rings produces very weak ligand-field (Table 2) and, consequently, large second-order Zeeman contributions via the spin-orbit coupling mechanism. Secondly, the thermodynamic parameters $\Delta H_{SCO}$ and $\Delta S_{SCO}$ recorded for $[\text{Fe(L1)}_3]^{2+}$ and $[\text{Fe(L2)}_3]^{2+}$ refer to average values characterizing a mixture of temperature-dependent *mer*/*fac* isomers, probably both displaying specific and different SCO behaviors (see next section).
Solution SCO processes for LnFe(II) helicates with ligands L5-L7: deciphering meridional/facial contributions. Stoichiometric mixing of segmental ligands L5-L7 (3 eq.) with M(CF3SO3)2 (1 eq., M = FeII, ZnII) and Ln(CF3SO3)3 (1 eq., Ln = LaIII, EuIII) in acetonitrile at millimolar concentrations quantitatively form C3-symmetrical \[\text{HHH-}[\text{LnM(Lk3)}]\]3\textsuperscript{5+} triple-stranded helicates as ascertained by ESI-MS data (qualitative speciation, Figure S19 and Table S15) and 1H NMR spectra (quantitative speciation, Figures S20-S24). These results corroborate detailed solution studies previously reported for \([\text{EuZn(L5)}]3\)\textsuperscript{5+} [15] and \([\text{LnM(L6)}]3\)\textsuperscript{5+}[18] and they unambiguously establish that the divalent d-block FeII or ZnII cations are facially coordinated by three unsymmetrical diimine units in these C3-symmetrical dinuclear complexes in solution, as depicted in their crystal structures (Figure 2). The associated corrected magnetic susceptibilities \(\chi_M\), recorded using Evans’ method in CD₃CN (Eq. (16)) and plotted as \(\chi_M T\) versus \(T\) curves (Figure 9), show pure high-spin behavior for \([\text{LaFe(L7)}]3\)\textsuperscript{5+} with the constrained ligand L7. The magnetic behavior of the latter complex provides reliable estimates for \(C_{hs} = 3.44(4) \text{ cm}^3\text{-K}^{-1}\text{-mol}^{-1}\) and \(TIP_{hs} = 310(15) \times 10^{-6} \text{ cm}^3\text{-mol}^{-1}\) using Eq. (2), two parameters very similar to those found for the mononuclear parent high-spin complex \([\text{Fe(L4)}]3\)\textsuperscript{5+} (Table 3).

**Figure 9.** Corrected \(\chi_M T\) products plotted as a function of the temperature for 0.01 M solution of \([\text{LaFe(L5)}]3\)\textsuperscript{5+}, \([\text{CaFe(L5)}]3\)\textsuperscript{4+}, \([\text{YFe(L5)}]3\)\textsuperscript{5+}, \([\text{LaFe(L6)}]3\)\textsuperscript{5+} and \([\text{LaFe(L7)}]3\)\textsuperscript{5+} in CD₃CN. The dotted traces correspond to non-linear least-square fits obtained with Eqs (1)-(2) and using the parameters gathered in Table 3.
<table>
<thead>
<tr>
<th>complexes</th>
<th>X</th>
<th>$C_{hs}$</th>
<th>$TIP_{hs} \times 10^{-6}$</th>
<th>$C_{ls}$</th>
<th>$TIP_{ls} \times 10^{-6}$</th>
<th>$\Delta H_{SCO}$</th>
<th>$\Delta S_{SCO}$</th>
<th>$T_{1/2}$ $^{[a]}$</th>
<th>$X_{Fe(III)}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(bipy)$_3$]X$_2$</td>
<td>CF$_3$SO$_3$</td>
<td>-</td>
<td>-</td>
<td>0.00(8)</td>
<td>351(55)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.00</td>
<td>This work</td>
</tr>
<tr>
<td>[Fe(L1a)$_3$]X$_2$</td>
<td>CF$_3$SO$_3$</td>
<td>3.44$^{[b]}$</td>
<td>358$^{[b]}$</td>
<td>0.00$^{[c]}$</td>
<td>351$^{[c]}$</td>
<td>35.0(3)</td>
<td>100(1)</td>
<td>349(5)</td>
<td>0.032</td>
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</tr>
<tr>
<td>[Fe(L1a)$_3$]X$_2$</td>
<td>PF$_6$</td>
<td>3.44$^{[b]}$</td>
<td>358$^{[b]}$</td>
<td>0.00$^{[c]}$</td>
<td>351$^{[c]}$</td>
<td>35.7(3)</td>
<td>101(1)</td>
<td>354(5)</td>
<td>0.00</td>
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<tr>
<td>[Fe(L2a)$_3$]X$_2$</td>
<td>CF$_3$SO$_3$</td>
<td>3.44$^{[b]}$</td>
<td>358$^{[b]}$</td>
<td>0.00$^{[c]}$</td>
<td>351$^{[c]}$</td>
<td>28.3(4)</td>
<td>91(1)</td>
<td>309(6)</td>
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<td>This work</td>
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<tr>
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<td>PF$_6$</td>
<td>3.44$^{[b]}$</td>
<td>358$^{[b]}$</td>
<td>0.00$^{[c]}$</td>
<td>351$^{[c]}$</td>
<td>28.6(3)</td>
<td>91.5(8)</td>
<td>313(4)</td>
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<td>This work</td>
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<tr>
<td>[Fe(L3)$_3$]X$_2$</td>
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<td>-</td>
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<td>3.44(2)</td>
<td>358(57)</td>
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<td>CF$_3$SO$_3$</td>
<td>3.44$^{[b]}$</td>
<td>358$^{[b]}$</td>
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<td>351$^{[c]}$</td>
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<td>412(8)</td>
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<td>[YFe(L5)$_3$]X$_5$</td>
<td>CF$_3$SO$_3$</td>
<td>3.44$^{[b]}$</td>
<td>358$^{[b]}$</td>
<td>0.00$^{[c]}$</td>
<td>351$^{[c]}$</td>
<td>34(2)</td>
<td>83(5)</td>
<td>412(33)</td>
<td>0.08$^{[d]}$</td>
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<tr>
<td>[CaFe(L5)$_3$]X$_4$</td>
<td>CF$_3$SO$_3$</td>
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<td>358$^{[b]}$</td>
<td>0.00$^{[c]}$</td>
<td>351$^{[c]}$</td>
<td>36.8(2)</td>
<td>90.4(6)</td>
<td>407(3)</td>
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</tr>
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<td>[LaFe(L6)$_3$]X$_5$</td>
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<td>358$^{[b]}$</td>
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<td>351$^{[c]}$</td>
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<td>0.00$^{[c]}$</td>
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<td>30.0(2)</td>
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<td>-</td>
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<tr>
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<td>ClO$_4$</td>
<td>3.44(4)</td>
<td>310(15)</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
<td>[19]</td>
</tr>
</tbody>
</table>

$^{[a]} T_{1/2} = \Delta H_{SCO}/\Delta S_{SCO}$. $^{[b]} C_{hs}$ and $TIP_{hs}$ found for [Fe(L4)$_3$](CF$_3$SO$_3$)$_2$ are used for fitting the SCO behaviors. $^{[c]} C_{ls}$ and $TIP_{ls}$ found for [Fe(bipy)$_3$](CF$_3$SO$_3$)$_2$ are used for fitting the SCO behaviors. $^{[d]}$ Deduced from low-temperature data fitted for pure low-spin complex.
For \([\text{CaFe(L5)}_3]^{4+}\), \([\text{YFe(L5)}_3]^{5+}\) and \([\text{LaFe(L6)}_3]^{5+}\), the \(\chi_M T\) versus \(T\) plots are diagnostic for spin-crossover processes (Figure 9), the thermodynamic characteristics of which could be extracted with Eqs (1)-(2) (see Appendix 2) and collected in Table 3. Since only a limited temperature range is available for collecting SCO data for \([\text{CaFe(L5)}_3]^{4+}\), \([\text{YFe(L5)}_3]^{5+}\) and \([\text{LaFe(L5)}_3]^{5+}\) in solution (Figure 9), \(\Delta H_{\text{SCO}}\) and \(\Delta S_{\text{SCO}}\) are the only adjusted parameters within the SCO domain using Eqs (1)-(2) for these complexes, while \(TIP_{\text{hs}}, TIP_{\text{ls}}\) and \(x_{\text{Fe(III)}}\) are fixed (see caption in Table 3). Taking into account that no cooperativity factor can influence mononuclear SCO processes, the known linear dependence of the van’t Hoff equation correlating \(\Delta H_{\text{SCO}}\) and \(\Delta S_{\text{SCO}}\) with \(\ln(K_{\text{SCO}})\) implies that both parameters can be obtained with a similar precision, obviously limited by experimental dispersion and by the restricted accessible temperature range.\[^{[57]}\]

Considering that \(\Delta H_{\text{SCO}}\) and \(\Delta S_{\text{SCO}}\) measured for \(C_3\)-symmetrical helicates \(\text{HHH-[LaFe(Lk)]}_3\)^{5+}\) strictly refer to pure facial isomer \((\text{Lk} = \text{L5-L6})\), it is not so surprising that the enthalpic contributions are 1-2 kJ/mol larger than those found in related mixtures of \(\text{mer/fac-[Fe(Lk)]}_3\)^{2+}\) complexes \((\text{Lk} = \text{L1-L2})\), Table 3) because the latter mixtures are largely dominated by the meridional isomers (see Figure S17). It is indeed the facial arrangement which benefits from the largest thermodynamic trans-influence (Table S13) and consequently possesses the strongest Fe-N bonds. Interestingly, the entropic contributions \(\Delta S_{\text{SCO}}\) is reduced by 6-10 J mol\(^{-1}\) K\(^{-1}\) in the pure facial isomer found in the \([\text{LaFe(Lk)}_3]^{5+}\) helicate, a trend which can be assigned to the larger dipole moments of the facial isomers (compared with the meridional isomers) and their detrimental effect on the solvation free energy changes upon molecular size expansions accompanying low-spin \(\rightarrow\) high-spin transition (Eq(18), \textit{vide supra}).\[^{[58]}\] Let’s stress here that changing the size or the charge of the innocent (\textit{i.e.} non-paramagnetic) capping cations (\(\text{Ca}^{2+}, \text{Y}^{3+}, \text{La}^{3+}\)) in the helicates \([\text{CaFe(L5)}_3]^{4+}\), \([\text{YFe(L5)}_3]^{5+}\) and \([\text{LaFe(L5)}_3]^{5+}\) has very limited impact on the Fe\(^{II}\)-centered spin-crossover processes, a consequence of the large flexibility of the capping unit and its minor influence on the Fe\(^{II}\) coordination sphere, except for the preorganization of a single facial isomer (Figure S25).\[^{[18b],[49d],[59]}\] Altogether, the opposite trends displayed by \(\Delta H_{\text{SCO}}\) (\textit{i.e.} increase) and \(\Delta S_{\text{SCO}}\) (\textit{i.e.} decrease) in going from the
mononuclear \([\text{Fe}(Lk)_3]^{2+}\) complexes (i. e. mixture of \textit{mer/fac} isomers) to the dinuclear helicates \([\text{LnM}(Lk)_3]^{5+}\) (i. e. pure facial isomer) produces a significant shift of \(T_{1/2} = \Delta H_{\text{SCO}}/\Delta S_{\text{SCO}}\) toward higher temperature (\(\Delta T_{1/2} = 30-60\) K), which eventually delays the SCO process in the pure facial isomers found in the helicates. Assuming that \([\text{LaFe}(L5)_3]^{5+}\) and \([\text{LaFe}(L6)_3]^{5+}\) are acceptable thermodynamic models for the SCO transitions occurring in \textit{fac}-[\text{Fe}(L1)_3]^{2+} and \textit{fac}-[\text{Fe}(L2)_3]^{2+} respectively, the assignment of specific spin state equilibria for the facial isomer (\(K_{\text{SCO}}^{\text{fac-Fe(L1)_3}} = x_{\text{hs}}^{\text{fac}}/x_{\text{hs}}^{\text{fac}} = K_{\text{SCO}}^{\text{LnFe(L5)_3}}\) and \(K_{\text{SCO}}^{\text{fac-Fe(L2)_3}} = x_{\text{hs}}^{\text{fac}}/x_{\text{hs}}^{\text{fac}} = K_{\text{SCO}}^{\text{LnFe(L6)_3}}\), Table 3) and for the meridional isomer (\(K_{\text{SCO}}^{\text{mer-Fe(L1)_3}} = x_{\text{hs}}^{\text{mer}}/x_{\text{hs}}^{\text{mer}}\)) in the mononuclear \([\text{Fe}(Lk)_3]^{2+}\) complexes transforms Eq. (2) into Eq. (17) (Appendix 3).

\[
\chi_M T = \left(x_{\text{hs}}^{\text{fac}} + x_{\text{hs}}^{\text{mer}}\right) \cdot \left(C_{\text{hs}} + T \cdot TIP_{\text{hs}}\right) + \left(x_{\text{hs}}^{\text{fac}} + x_{\text{hs}}^{\text{mer}}\right) \cdot \left(C_{\text{hs}} + T \cdot TIP_{\text{hs}}\right) + x_{\text{Fe(III)}} \cdot C_{\text{Fe(III)}} \tag{17}
\]

The various mole fractions involved in Eq. (17) must obey the mass balance \(x_{\text{hs}}^{\text{fac}} + x_{\text{hs}}^{\text{fac}} + x_{\text{hs}}^{\text{mer}} + x_{\text{hs}}^{\text{mer}} + x_{\text{Fe(III)}} = 1\), together with the thermodynamic constraint accompanying meridional \(\rightarrow\) facial isomerization \(K_{\text{mer}\rightarrow\text{fac}}^{\text{Fe(Lk)_3}} = \left(x_{\text{hs}}^{\text{fac}} + x_{\text{hs}}^{\text{fac}}\right)/\left(x_{\text{hs}}^{\text{mer}} + x_{\text{hs}}^{\text{mer}}\right)\) (Eq. (10) and Table S13).

With this ultimate model in hand, the non-linear least-square fits of the \(\chi_M T\) versus \(T\) plots recorded for the SCO processes displayed by \([\text{Fe}(L1a)_3]^{2+}\) and \([\text{Fe}(L2a)_3]^{2+}\) in acetonitrile yield the two missing parameters \(\Delta H_{\text{SCO}}^{\text{mer-Fe(Lk)_3}}\) and \(\Delta S_{\text{SCO}}^{\text{mer-Fe(L1a)_3}}\) (Figure 10, Table 4; see Appendix 3 for details). In all rigor, a calibration by a spectroscopic technique (ie. Mössbauer spectrometry) is necessary for the estimation of the residual fractions LS (high temperature) and HS (low temperature) which slightly modify the parameters of the fitting process (\(\Delta H\) and \(\Delta S\)). However, the impossibility of carrying out Mössbauer spectrometry in solution leads us to consider only the magnetic susceptibility measurements for comparison of the different compounds, what remains valid for our analysis.
Table 4. Thermodynamic parameters obtained by non-linear least-square fits using Eq. (17) for the $\chi_M T$ versus $T$ plots recorded for the homoleptic $[\text{Fe}(Lk)_3]X_2$ complexes in solution (CD$_3$CN).

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$\Delta H_{soc}$ / kJ·mol$^{-1}$</th>
<th>$\Delta S_{soc}$ / J·mol$^{-1}$·K$^{-1}$</th>
<th>$T_{1/2}$ / K</th>
<th>$x_{\text{Fe(III)}}$ / %</th>
<th>$AF$ $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrazines</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fac-[Fe(L1a)$_3$]$^{2+}$ $^a$</td>
<td>37.9(5)</td>
<td>92(1)</td>
<td>412(8)</td>
<td>1.16(2)</td>
<td>2.50·10$^{-3}$</td>
</tr>
<tr>
<td>mer-<a href="Otf">Fe(L1a)$_3$</a>$_2$</td>
<td>35.9(6)</td>
<td>106(2)</td>
<td>339(8)</td>
<td>3.3(1)</td>
<td>1.04·10$^{-2}$</td>
</tr>
<tr>
<td>mer-<a href="PF$_6$">Fe(L1a)$_3$</a>$_2$</td>
<td>35.9(3)</td>
<td>104.1(9)</td>
<td>345(4)</td>
<td>0.00(7)</td>
<td>5.13·10$^{-3}$</td>
</tr>
<tr>
<td>Pyridines</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fac-[Fe(L2a)$_3$]$^{2+}$ $^b$</td>
<td>29.6(2)</td>
<td>86.2(5)</td>
<td>344(3)</td>
<td>2.83(6)</td>
<td>3.89·10$^{-3}$</td>
</tr>
<tr>
<td>mer-<a href="Otf">Fe(L2a)$_3$</a>$_2$</td>
<td>29.3(6)</td>
<td>97(2)</td>
<td>303(8)</td>
<td>1.4(4)</td>
<td>1.13·10$^{-2}$</td>
</tr>
<tr>
<td>mer-<a href="PF$_6$">Fe(L2a)$_3$</a>$_2$</td>
<td>29.2(3)</td>
<td>95.0(8)</td>
<td>307(4)</td>
<td>0.0(2)</td>
<td>5.51·10$^{-3}$</td>
</tr>
</tbody>
</table>

$^a$ [LaFe(L5)$_3$](Otf)$_5$ is taken as model (see text). $^b$ [LaFe(L6)$_3$](Otf)$_5$ is taken as model (see text).

$^c$ Agreement factor $AF = (\Sigma (\chi_M T_{exp} - \chi_M T_{calc})^2 / \Sigma (\chi_M T_{exp})^2)^{1/2}$.

Figure 10. High-spin mole fraction ($x_{hs}$) as a function of the temperature for 0.01 M CD$_3$CN solution of a) [Fe(L1a)$_3$](CF$_3$SO$_3$)$_2$ (black) (and its partition between fac-[Fe(L1a)$_3$]$^{2+}$ (green) and mer-[Fe(L1a)$_3$]$^{2+}$ (red)) and b) [Fe(L2a)$_3$](CF$_3$SO$_3$)$_2$ (black) (and its partition between fac-[Fe(L2a)$_3$]$^{2+}$ (green) and mer-[Fe(L2a)$_3$]$^{2+}$ (red)) in CD$_3$CN. The traces correspond to non-linear least-square fits obtained with Eq. (17) and using the parameters gathered in Table 4.
For both pyrazine-type (L1a) and pyridine-type (L2a) ligands, the temperature $T_{1/2} = \Delta H_{SCO}/\Delta S_{SCO}$ at which $x_{hs} = x_{ls} = 0.5$ is shifted toward higher values in going from $\text{mer-}[\text{Fe(Lk)}_3]^{2+}$ to $\text{fac-}[\text{Fe(Lk)}_3]^{2+}$ (Figure 10) due to the concomitant (minor) increase of $\Delta H_{SCO}$ and decrease of $\Delta S_{SCO}$ in the facial isomer (Table 4), this whatever the helicate $[\text{LaFe(L5)}_3]^{2+}$, $[\text{YFe(L5)}_3]^{2+}$ or $[\text{CaFe(L5)}_3]^{4+}$ chosen for modelling $\text{fac-}[\text{Fe(L1a)}]^{2+}$ (Table S16). The enthalpic trend can be assigned to the minor, but non-negligible thermodynamic trans-influence, which strengthens the Fe-N bonds in the facial isomer, especially for $\text{fac-}[\text{Fe(L1a)}]^{2+}$ (Table S13). The entropic tendency is rather counter-intuitive since it opposes the gain in electronic degeneracy upon spin transition, which is larger for $C_3$-symmetrical $\text{fac-}[\text{Fe(Lk)}_3]^{2+}$ ($\Delta S_{el}(1A \rightarrow 5E) = R \ln(10) = 19.1 \text{ J-K}^{-1}\cdot\text{mol}^{-1}$) than for $C_1$-symmetrical $\text{mer-}[\text{Fe(Lk)}_3]^{2+}$ ($\Delta S_{el}(1A \rightarrow 4A) = R \ln(5) = 13.4 \text{ J-K}^{-1}\cdot\text{mol}^{-1}$). The global decrease of the entropic contribution to the spin crossover transition occurring in $\text{fac-}[\text{Fe(Lk)}_3]^{2+}$ can be thus tentatively traced back to the change in solvation energies accompanying the 1-2 % volume expansion of the complexes (see Appendix 1). Since $\text{mer-}[\text{Fe(Lk)}_3]^{2+}$ and $\text{fac-}[\text{Fe(Lk)}_3]^{2+}$ have similar volume and charge, the dominant monopole contribution (produced by the doubly charged pseudo-spherical cations) to solvation energies would be identical for both isomers. On the contrary, the dipole contribution will be different since $\text{fac-}[\text{Fe(Lk)}_3]^{2+}$, which possess up-up-up arrangements of the three ligands (Figure 1), are expected to have large electric dipoles along the threefold axis ($\mu_{\text{dip}} = 7.5(5) \text{ Debye}$ could be computed for the optimized gas-phase structure of $\text{fac-}[\text{Zn(L1a)}]^{2+}$). On the contrary, the $\text{mer-}[\text{Fe(Lk)}_3]^{2+}$ isomers (up-down arrangement of the ligand strands, Figure 1) possess lower electric dipoles ($\mu_{\text{dip}} = 5.2(6) \text{ Debye}$ computed for $\text{mer-}[\text{Zn(L1a)}]^{2+}$). Rough estimations of the contribution to solvation free energy $\Delta_{\text{solv}}G$ of a dipolar guest dissolved in a dielectric continuum can be then obtained by using Onsager Equation (18), where $N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$ is Avogadro’s number, $e = 1.602 \cdot 10^{-19} \text{ C}$ is the elementary charge, $\varepsilon_0 = 8.854 \cdot 10^{-12} \text{ C}^2\cdot\text{N}^{-1}\cdot\text{m}^{-2}$ is the vacuum permittivity, $\varepsilon_r$ is the relative dielectric permittivity ($\varepsilon_r = 37.5$ in acetonitrile), $\mu_0$ is the dipole moment of the particle and $R_i$ is the radius of a spherical cavity cut from the dielectric when a spherical solute is immersed into the solvent.
Assuming that the dipole moment is similar in low-spin and high-spin configurations, the variation of free energy of solvation \( \Delta \Delta \text{solv} G^0 = \Delta \text{solv} G^0_{\text{hs}} - \Delta \text{solv} G^0_{\text{ls}} \) during the SCO transition is systematically positive since \( R_{\text{hs}} > R_{\text{ls}} \) and therefore maximized for the facial isomers possessing the larger dipole moments. An exact partition of the solvation effects between enthalpic and entropic effects is currently under investigation, but beyond the scope of this contribution.

### Conclusion

Chemical intuition and semi-quantitative structural criteria\(^7\) remain the most popular and the most exploited strategies for designing novel spin-crossover complexes\(^2\). According that unpredictable intermolecular interactions operating in bulk solids\(^6\) largely dominate the rational minor enthalpic and entropic tunings induced by molecular design\(^,\)\(^6\) the latter empirical approach is fully justified and leads to noticeable advances in the design of switchable and/or bistable macroscopic materials displaying positive cooperativities\(^{2c,9c}\). However, microscopic structure-properties correlations remain attractive for pushing novel concepts into the arena of empirical exploration, this at the condition that pertinent test benches are available for evaluating which molecular effects are at the origin of specific thermodynamic trends in SCO complexes. Solution studies play a crucial role in this field since intermolecular interactions are limited to solvation energies, which display faint variations upon spin-state equilibria, thus allowing a reliable analysis of structure-properties correlations. However, molecular structure and speciation are much more challenging to address in solution compared to solid state, particularly for (semi)-labile complexes such as homoleptic \([\text{Fe(Lk)}_3]^{2+}\) complexes (\(\text{Lk} = \text{L1-L4}\)), which are quantitatively formed only at exact stoichiometric ratio and at sufficiently high concentration in acetonitrile. Moreover, \([\text{Fe(Lk)}_3]^{2+}\) exist as temperature-dependent mixtures of meridional/facial isomers. If specific magnetic and thermodynamic parameters have been characterized for related homoleptic tris-didentate complexes in the solid state, where a single isomer (facial or meridional) could be crystallized by chance,\(^{11}\) the use of an ultra-flexible
non-covalent lanthanide podate in \( HHHH-[\text{LnFe}(Lk)_3]^{5+} \) for modelling facial arrangement could become a novel attractive toolkit for addressing the SCO properties of these different isomers in solution. Applying this strategy, we showed here that:

1) Pyrazine is a weaker \( \sigma \)-donor, but a much stronger \( \pi \)-acceptor than pyridine for \( \text{M}^{II} \) in the \([\text{M}(Lk)_3]^{2+}\) complexes. This ultimately (and counter-intuitively) produces larger \( \Delta \text{bond}/B \) ratios and delayed spin crossover transitions occurring at higher temperature for \( L1 \) or \( L5 \)-type ligands.

2) Weak but non-negligible thermodynamic \( \text{trans} \)-influence enthalpically favors the formation of \( \text{fac-}[\text{M}(Lk)_3]^{2+} \) (\( \text{M} = \text{Fe}^{II}, \text{Zn}^{II} \)), a trend offsets at room temperature by opposite entropic contributions produced by the larger dipole moment of the latter isomer. This effect is maximum for pyrazine-benzimidazole units in \( L1 \), which contributes to the larger \( \Delta H^{\text{SCO}} \) parameters found for \( \text{fac-}[\text{Fe}(L1)_3]^{2+} \).

3) The SCO transition temperature \( T_{1/2} \) of the facial isomer is shifted by several tenths of degrees toward high values compared with the meridional isomer in solution as the result of concomitant enthalpic (\( \text{trans} \)-influence) and entropic (solvation) effects. Since the latter entropic effect depends on the dielectric constant of the medium (see Eq. (18)), further fine tuning could be envisioned via a judicious choice of the solvent.

Altogether, we are now equipped for attempting some \textit{de novo} design of spin-crossover d-f dinuclear helicates \([\text{LnFe}(L)_3]^{5+}\), in which the facial arrangement of three homoleptic diimine units ensures transition temperatures \( T_{1/2} \) below room temperature, a characteristic compatible with the optical sensing of the magnetic switch via a neighboring luminescent lanthanide in a (supra)molecular object.\(^{[10],[19]}\)

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Spin transition, magnetism, thermodynamics, isomers, iron, facial-meridional

References


[57] Once the mathematical model is fixed for a linear correlation, the two parameters can be obtained with the same accuracy, see G. Lente, I. Fabian, A. J. Poe, *New J. Chem.* 2005, 29, 759-760.


Though many pseudo-octahedral non-symmetrical homoleptic tris-diimine Fe$^{II}$ spin crossover complexes [FeL$_3$]$^{2+}$ have been designed for exploring magnetic bistability and switching, specific characteristics assigned to meridional/facial isomers are essentially missing. This work proposes a strategy for overcoming this limitation.