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Switching the Spin-Crossover Phenomenon by Ligand Design on Imidazole–Diazineiron(II) Complexes

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S Supporting Information

ABSTRACT: The iron(II) complexes of two structural isomers of 2-(1H-imidazol-2-yl)diazine reveal how ligand design can be a successful strategy to control the electronic and magnetic properties of complexes by fine-tuning their ligand field. The two isomers only differ in the position of a single diazinic nitrogen atom, having either a pyrazine (\mathbf{Z}) or a pyrimidine (M) moiety. However, $[Fe(M)_3](ClO_4)_2$ is a spincrossover complex with a spin transition at 241 K, whereas $[Fe(Z)_3](ClO_4)_2$ has a stable magnetic behavior between 2 and 300 K. This is corroborated by temperature-dependent



Mössbauer spectra showing the presence of a quintet and a singlet state in equilibrium. The temperature-dependent singlecrystal X-ray diffraction results relate the spin-crossover observed in $[Fe(M)_3](ClO_4)_2$ to changes in the bond distances and angles of the coordination sphere of iron(II), hinting at a stronger σ donation of ligand Z in comparison to ligand M. The UV/ vis spectra of both complexes are solved by means of the multiconfigurational wave-function-based method CASPT2 and confirm their different spin multiplicities at room temperature, as observed in the Mössbauer spectra. Calculations show larger stabilization of the singlet state in $[Fe(Z)_3]^{2+}$ than in $[Fe(M)_3]^{2+}$, stemming from the slightly stronger ligand field of the former (506 cm⁻¹ in the singlet). This relatively weak effect is indeed capable of changing the spin multiplicity of the complexes and causes the appearance of the spin transition in the M complex.

INTRODUCTION

Memory storage on digital electronics requires materials capable of switching between two stable and distinguishable states that represent the 1 and 0 bits of information. Ideally, such materials should have two long-lived states with different magnetic or electronic properties under the same external conditions and allow a fast transition between them triggered by some external stimuli. Enticing compounds to be used in these technological applications can be found in the family of spin-crossover (SCO) materials. The SCO phenomenon occurs on systems with two spin states of different total spin number, where the spin transition is accompanied by some structural change. It is typically found in octahedral transitionmetal complexes of the fourth period with a $3d^4$ to $3d^7$ metal center in a ligand field (LF) close to the limit between the lowspin (LS) and high-spin (HS) regimes. The LS-HS transition in these complexes induces an expansion of the coordination sphere and a corresponding change of the LF. The equilibrium between both spin states of the system is governed by two competing processes, the enthalpy change related to the

different metal-ligand length and the entropy change related to the electronic and vibrational degrees of freedom.^{1–12}

Hence, it is possible to trigger the spin transition by external stimuli affecting the molecular structure (pressure)^{13,14} or the vibrational entropy (temperature)¹⁵⁻¹⁷ or through an electronic excitation induced by light radiation in the so-called light-induced excited spin trapping.¹⁸⁻²⁴

The complex interplay of geometrical and electronic factors behind the SCO phenomenon calls for thorough systematic studies to unravel the structure-function relationship governing the SCO.^{25,26} Available data for many different SCO complexes and their derivatives reveal that too large distortions between the LS and HS states overstabilize one of them, thus hindering the spin transition. Nonetheless, a sufficient distortion is needed during the spin transition to switch the LF between the LS and HS regimes. Hence, many pseudooctahedral iron(II) complexes with nitrogen-donor

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chelating ligands are very successful SCO compounds because they show relatively large structural changes (~10% on the Fe–N bond) while still allowing the forward and backward spin transition to occur. At the molecular level, not only do the distortions affect the coordination sphere, but they may also extend to the ligands. Therefore, the bulkiness, flexibility, and denticity of the ligands can have an impact on thermal SCO and its transition temperature ($T_{1/2}$, temperature at 50:50 of LS and HS), which is a measure of the zero-point-corrected energy difference between the HS and LS states ($\Delta E_{\rm HL}^0 = E_{\rm HS}^0$).^{27,28} Relative stabilization of the more voluminous HS state should lead to lower $T_{1/2}$, while stabilization of the compact LS state should increase $T_{1/2}$. However, even at the molecular level, control over $T_{1/2}$ is not straightforward due to the sensitiveness of $\Delta E_{\rm HL}^0$ to structural factors.

The effect of stereoisomerism on the magnetic properties of complexes has been extensively studied. The SCO properties can be very different from one isomer to another because of the different LFs experienced by the metal ion.^{29–32} Structural isomerism also has a very important influence on the magnetic properties, and several examples show that both linkage³³⁻³⁵ and substitutional isomers have quite different magnetic properties.^{36–41} Isomerism can change the magnetic behavior of materials even when the structural difference is centered on counterions.⁴² The resulting geometric changes are generally accompanied by changes in both the LF and intermolecular interactions responsible for the packing in the solid. Associated with it, cooperative effects are sometimes present in one isomer and absent in another and, as a consequence, it is difficult to disentangle the relative importance of both factors in defining the magnetic properties.

The effect of changing the positions of the heteroatoms in the ligands has been studied before for the case of tridentated ligands analogous to terpyridine. Goodwin and co-workers have reported a comparison between the two isomers of homoleptic iron(II) complexes obtained with 2,6-di(thiazol-4yl)pyridine⁴³ and 2,6-di(thiazol-2-yl)pyridine;⁴⁴ however, both are LS at room temperature. The substitution of thiazolyl by pyrazolyl groups has recently been reviewed, and these ligands have been extensively used to study homoleptic iron(II) complexes with the formula $[Fe(bpp)_2]^{2+}$, in which bpp can be either 2,6-di(pyrazol-1-yl)pyridine or 2,6-di(1H-pyrazol-3-yl)pyridine.⁴⁵ Again, both isomers have similar magnetic properties showing SCO but very sensitive to differences in packing. Further modification of the ligand by a change from pyridine to pyrazine as the central ring does not show a significant difference in the SCO properties.⁴⁶ More recent examples report bidentate isomeric ligands used to obtain iron(II) showing SCO; however, the same combined effects (LF/packing) cannot be easily isolated.^{47,48}

The aim of the present work is to achieve better control of the SCO phenomenon by tuning the LF on the metal center through structural isomerism of the ligands without serious perturbation of the packing in the solid state. We will show that small changes in the ligand structure involving the position of a single heteroatom can fully switch the SCO behavior of the complex. Such a limited structural alteration leads to structure-function relationships lying in the molecular domain, acting on the LF, and not involving cooperative effects. Thus, the knowledge obtained from these experiments is less system-dependent and more likely to be transferred to a wider range of compounds, which is helpful to attaining the major goal of designing functional materials with tailored SCO properties.^{49,50}

We have synthesized and characterized two structural isomers of 2-(1*H*-imidazol-2-yl)diazine (Scheme 1) and their





^{*a*}The structures correspond to *mer* isomers because the *fac* ones were not observed experimentally.

respective iron(II) complexes. This family of ligands combines an electron-deficient diazine with an electron-rich imidazole, conferring them high versatility. The two isomers differ in the diazine moiety, having either a pyrazine (\mathbf{Z}) or a pyrimidine (\mathbf{M}) , and were partially explored as ligands in the literature.⁵ Diazines are electron-deficient heterocycles well-known for their strong π -acceptor character related to their optic properties and noninnocent behavior.52,53 Conversely, imidazole-based ligands are prominent not only for their electronrich character, being stronger σ donors than azines, ^{54,55} but also for the possibility of altering the electronic structure and reactivity of the compound through deprotonation, hydrogenbonding modulation, or derivatization of the NH group.⁵ Thus, the combination of such properties in this class of ligands has the potential to provide a tunable LF through chemical modifications. Moreover, the related SCO iron(II) complexes can have the required stability and solubility to be used in the development of novel materials, such as the 2-(1Himidazol-2-yl)pyridineiron(II) complex used by Coronado et al. in a hybrid multifunctional material combining superconductivity and SCO magnetism.⁶⁰

The homoleptic complexes $[Fe(Z)_3](ClO_4)_2$ (1) and $[Fe(M)_3](ClO_4)_2$ (2) show strikingly different optical and magnetic properties. The preeminent one is the appearance of a spin transition at 241 K for 2, whereas 1 shows an almost flat magnetic susceptibility in the same range of temperatures. We explain the origin behind such differential behavior through a detailed characterization of the compounds and an in-depth computational study using multiconfigurational wave-functionbased methods. We have used temperature-dependent experiments with a combination of single-crystal crystallography, magnetic susceptibility, and Mössbauer spectroscopy to unveil the spin states of both complexes. Mössbauer spectroscopy is a powerful tool in probing the oxidation and spin states of iron in coordination compounds. In particular, because of the isomer shift δ and the quadrupole splitting ΔE_{0} , which presents significantly different values between HS and LS iron(II),⁶¹ we were able to unambiguously assign the spin state of each complex in different temperatures. We also use highly elaborate correlated wave-function methods (CASPT2/CC = second-order perturbation theory based on a multiconfigurational reference wave function, combined with CCSD(T) for a description of the 3s3p correlation on the metal⁶²) to describe

the spin-state energetics of these two complexes and to settle the electronic structure of their ground state. CASPT2 is also used to evaluate the transitions to the first manifold of metalto-ligand charge-transfer (MLCT) states to resolve their UV/ vis absorption spectra.

EXPERIMENTAL SECTION

Syntheses of Ligands. All reagents were obtained from commercial sources and used without purification. Ligands Z and M were synthesized following an adaptation of the procedure described by Voss et al. $^{63-65}$

2-(1H-Imidazol-2-yl)pyrazine (Z). In a 50-mL round-bottom flask, a mixture of 0.471 mL (5 mmol) of 2-pyrazinecarbonitrile, 5 mL of methanol (MeOH), and 0.47 mL (1 mmol) of a 30% solution of sodium methoxide was stirred at room temperature for 20 min. A total of 0.727 mL (5 mmol) of 2,2-diethoxyethanamine was added, followed by the dropwise addition of 0.6 mL of acetic acid. The system was kept under reflux for 1 h at 50 °C. A total of 10 mL of MeOH and 2.5 mL of 6 mol L⁻¹ HCl were added after the mixture was cooled to room temperature, after which the system was kept under reflux for 5 h. The solution was evaporated, and the residue was dissolved in 15 mL of water (H2O) and extracted with 15 mL of diethyl ether (Et₂O), which resulted in a brown solution. After the pH was adjusted to 8-9 with 2 mol L⁻¹ NaOH, the product precipitated as a brown solid, which was filtered and washed with Et₂O. Yield: 41%. Anal. Calcd for C₇H₆N₄: C, 57.53; H, 4.14; N, 38.33. Found: C, 57.63; H, 4.16; N, 38.14. ESI-MS (MeOH): 147.1 ([M + H]⁺). ¹H NMR (500 MHz, DMSO- d_6): δ 13.058 (s, 1H), 9.23 (d, 1H, J = 1.5Hz), 8.649 (dd, 1H, J = 2.5 and 1.5 Hz), 8.595 (d, 1H, J = 2.5 Hz), 7.25 (s, 1H), 7.17 (s, 1H). ¹³C NMR (125.7 MHz, DMSO- d_{δ}): δ 144.90, 144.24, 143.92, 143.70, 141.80, 130.66, 120.27. $pK_{aH} = 4.51 \pm$ 0.05

2-(1H-Imidazol-2-yl)pyrimidine (M). A mixture of 2.62 g (25 mmol) of 2-pyrimidinecarbonitrile, 10 mL of MeOH, and 0.47 mL of a 30% solution of sodium methoxide in MeOH was kept under vigorous stirring at room temperature for 1.5 h in a 100 mL flask. Then, 1.63 mL (15 mmol) of 2,2-dimethoxyethylamine was added to the mixture, followed by the dropwise addition of 2.75 mL of acetic acid. The system was kept under reflux for 30 min. After cooling to room temperature, 15 mL of MeOH and 12.5 mL of 6 mol L⁻¹ HCl were added to the solution, which was heated again and kept under reflux for 5 h. After the reaction time, the solvent was evaporated and 27.5 mL of a warm 1 g mL⁻¹ K₂CO₃ solution was carefully added to the residue, yielding a yellowish suspension, which was filtered. Extraction of the precipitate with 3×50 mL of MeOH yielded a yellowish solution, which was concentrated until precipitation. The resulting pale-yellow solid was filtered, washed with Et₂O, and dried under vacuum. Yield: 65%. Anal. Calcd for C7H6N4: C, 57.53; H, 4.14; N, 38.33. Found: C, 57.76; H, 4.22; N, 38.24. ESI-MS (MeOH): 147.1 ($[M + H]^+$). ¹H NMR (600 MHz, DMSO- d_6): δ 12.97 (s, 1H), 8.865 (d, 2H, J = 4.8 Hz), 7.43 (t, 1H, J = 4.8 Hz), 7.22 (s, 2H). ¹³C NMR (100.6 MHz, DMSO-d₆): δ 158.11, 157.41, 144.85, 125.98, 120.41. p $K_{\rm aH}$ = 5.07 \pm 0.07.

Syntheses of the Iron(II) Complexes. Complexes were obtained using the procedure given by Stupka et al.⁶⁶ A solution of $Fe(ClO_4)_2$. $6H_2O$ (41.7 mg, 0.115 mmol) in ethanol (EtOH; 2.5 mL) was added dropwise to a solution of 50 mg (0.345 mmol) of the corresponding ligand in EtOH (2.5 mL). The color of the mixture turned immediately to violet in the case of $[Fe(Z)_3]^{2+}$ and reddish orange for $[Fe(M)_3]^{2+}$. Thereafter, the mixture was stirred for 4 h and concentrated using a rotary evaporator. The resulting concentrated solution was left in a refrigerator overnight, which resulted in a colored powder of the desired complexes. In both cases, the powder was filtered from the corresponding mixture, washed with Et₂O, and dried under reduced pressure. Both complexes are soluble in H₂O, EtOH, MeOH, acetonitrile (CH₃CN), dimethyl sulfoxide (DMSO), acetone, and pyridine. (*Caution! Perchlorate compounds should be handled with care due to the risk of explosion.*) $[Fe(Z)_3](ClO_4)_2$ (1). Yield: 60% Anal. Calcd for $[Fe(C_7H_6N_4)_3]$ -(ClO₄)₂(H₂O): C, 35.46; H, 2.83; N, 23.63. Found: C, 35.88; H, 2.8; N, 23.43. ESI-MS (CH₃CN): 247.0 ($[M]^{2+}$). Molar conductivity in H₂O: 230 S cm² mol⁻¹. FTIR: 637, 760, 1122, 1461, 1633, 3488 cm⁻¹. Single crystals were obtained by slow diffusion of an CH₃CN solution of the complex into toluene at room temperature.

 $[Fe(M)_3](ClO_4)_2$ (2). Yield: 64% Anal. Calcd for $[Fe(C_7H_6N_4)_3]$ -(ClO₄)₂(3H₂O): C, 33.75; H, 3.23; N, 22.49. Found: C, 34.09; H, 3.2; N, 22.08. ESI-MS (CH₃OH): 279.0 ($[M + 2CH_3OH]^{2+}$). Molar conductivity in H₂O: 155.3 S cm² mol⁻¹. FTIR: 626, 708, 1090, 1411, 1470, 1586, 3101, 3403 cm⁻¹. Single crystals were obtained by slow evaporation of a solution of the complex in a 1:1 mixture of EtOH and MeOH at room temperature.

Physical Measurements. Electronic spectra in the 190–1100 nm range were acquired by using a 1.00 cm quartz cuvette in a HP8453 diode-array UV/vis absorption spectrophotometer equipped with a Peltier HP89090A.

IR spectra were obtained with an Agilent Cary 630 Fourier transform infrared (FTIR) spectrometer, using the attenuated total reflectance method, with a diamond cell. The spectra were recorded in the 4000–400 cm⁻¹ range, with 64 scans and a resolution of 4 cm⁻¹.

Electrospray ionization mass spectrometry (ESI-MS) measurements were carried out using a Waters Quattro Micro API spectrometer. Samples were evaluated in the positive mode either in a 1:1 MeOH/H₂O solution with the addition of 0.10% (v/v) formic acid or in CH₃CN.

Elemental analyses for carbon, hydrogen, and nitrogen were performed using a PerkinElmer 2400 CHN analyzer.

Conductivity measurements of the complex solutions were obtained using a LAB1000 conductometer and a standard platinum electrode cell with K = 0.1. Data were obtained with 10^{-3} mol L⁻¹ aqueous solutions of the complexes.

Potentiometric titrations were used to calculate the pK_{aH} values of the ligands using a 827 pH Lab Metrohm pH meter and a standard electrode using 1.12×10^{-2} mol L⁻¹ HCl as the titrant. The initial pH values for the ligand solutions were 6.82 and 7.78 for Z and M, respectively.

¹H and ¹³C NMR spectra were acquired in deuterated dimethyl sulfoxide (DMSO- d_6) solutions using Bruker Avance III 500 MHz (11.7 T) and 600 MHz (14.09 T) spectrometers.

Temperature-dependent direct-current magnetic susceptibilities were obtained from dried powder samples (ca. 50 mg) mounted in a sealed plastic sample holder on a Quantum Design MPMS XL superconducting quantum interference device (SQUID) magnetometer in the temperature range of 2–300 K under an applied field of 0.1 T. The magnetization data for the samples were corrected by subtraction of the background due to the sample holder and also for diamagnetic contributions estimated by Pascal constants.⁶⁷

Mössbauer spectra were recorded in transmission geometry, using a ⁵⁷Co/Rh source, with a 50 mCi nominal starting activity. A closedcycle helium cryostat was used for low-temperature measurements. The spectrometer was calibrated with a metallic iron foil as the absorber at room temperature, and the spectra were fitted by taking the absorption lines as Lorentzian functions.

Crystal Structure Determination. Data collection for single crystals was performed with a Bruker Apex II CCD diffractometer using either Mo K α (λ = 0.71703 Å) or Cu K α (λ = 1.54178 Å) radiation. An Oxford Cryosystems controller was used in all cases. Unit cell dimensions and orientation matrices were determined by least-squares refinement of the reflections obtained by $\phi-\omega$ scans. The data were indexed and scaled with the *ApexII* suite [*APEX2*, v2014.1-1 (Bruker AXS Inc.), and *SAINT*, V8.34A (Bruker AXS Inc., 2013)]. Bruker *SAINT* and *SADABS* were used for integration and scaling of the data, respectively. Using *Olex2*,⁶⁸ the structure was solved with the *ShelXT*⁶⁹ structure solution program using direct methods and refined with *ShelXL*⁷⁰ by a full-matrix least-squares technique on F^2 . All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to the structure in idealized positions and further refined according to the riding model.

Powder X-ray diffraction (XRD) data were collected with a Shimadzu XRD-7000 diffractometer with Bragg–Brentano geometry and a graphite monochromator. The Cu K α (1.5406 Å) X-ray radiation source was operated at 40 kV and 30 mA. The collected 2θ range was from 5.0 to 50.0° under 2° min⁻¹ (2θ). The apertures of the divergence, scattering, and receiving slits were at 1.0, 1.0, and 0.3 mm, respectively.

Computational Details. We optimized the geometry of the *mer*- $[Fe(M)_3]^{2+}$ and *mer*- $[Fe(Z)_3]^{2+}$ complexes in a vacuum using density functional theory (DFT) with the PBE0 functional⁷¹⁻⁷³ and Def2-TZVP basis set.⁷⁴ The choice of the PBE0 functional is based on previous experience showing that it produces accurate molecular structures of transition-metal complexes.⁷⁵⁻⁷⁷ Because the *mer* isomers have no spatial symmetry (C_1) because of the orientation of the three bidentate ligands (M or Z), all calculations were performed without symmetry constraints. The character of the stationary points on the potential energy surface of the optimized structures was verified by frequency analysis. DFT/PBE0 calculations were carried out with the *TURBOMOLE v6.4* package.⁷⁸

We evaluated the spin-state energetics and metal-centered transitions of $[Fe(\mathbf{M})_3]^{2+}$ and $[Fe(\mathbf{Z})_3]^{2+}$ by means of the complete-active-space second-order perturbation theory (CASPT2),^{79,80} using a complete active space CAS[10,12] formed by 10 electrons in 12 molecular orbitals (MOs) that we built following established procedures.^{81,82} The 12 active MOs are five Fe(3d)-like orbitals, plus five Fe(4d)-like orbitals to account for the so-called double-shell effect⁸³ and two σ -type orbitals on the coordinating nitrogen atoms to account for the σ donation. π -backdonation to π^* orbitals of the ligands is negligible in the ground and LF excited states of both complexes.

For calculation of the CT spectra, the CAS[10,12] active space was extended to CAS[10,15] by adding the lowest π^* orbital of each ligand. This CAS[10,15] space allows us to estimate the vertical transitions in the Franck-Condon region to the first manifold of the MLCT states. These excitations consist of spin-allowed electron transfer from the doubly occupied Fe(3d)-like MOs to one π^* MO localized on a M or Z ligand. Hence, the size of the manifold depends on the total spin of the electronic state of departure, which varies from only one possible electron transfer per ligand for ⁵HS to three MLCTs per ligand for ¹LS. It is imperative to use a set of MOs fully adapted to the charge-transfer states to properly describe rearrangement of the charges between the metal center and ligands induced by the MLCTs.^{84,85} Thus, we use two different sets of MOs to evaluate each MLCT excitation. The ground state is described by a set of orbitals resulting from a state-specific CAS[10,12]SCF calculation, whereas the MOs for the MLCT states are obtained from a CAS[10,15]SCF state average including exclusively the MLCT excited states of the manifold in the orbital optimization procedure. Hence, the manifold of nine singlet MLCTs (three transitions per ligand) is described with a unique set of MOs obtained from a state average of those nine MLCT excited states, while for ⁵HS, we use a state average of three quintet MLCTs (one transition per ligand). Additionally, because the two states involved in the MLCT transitions are described with different MO sets, we performed a state-interaction step to ensure the orthogonality and estimate their oscillator strength.⁸⁶

CASPT2 calculations on the vertical LF and MLCT spectrum were performed with a basis set of the ANO-RCC type contracted to [7s6p5d3f2g1h] for iron, to [4s3p2d1f] for nitrogen and carbon, and to [3s1p] for hydrogen.^{87,88} In these calculations, all valence electrons and Fe(3s,3p) semicore electrons are correlated at the CASPT2 level. On the other hand, because we have shown recently that an accurate description of spin-state energetics requires considerably larger basis sets,⁶² calculation of the HS–LS splitting was also performed using correlation-consistent basis sets. For the ligands, we used a combination of aug-cc-pVTZ-DK on the heavy atoms and ccpVTZ-DK on hydrogen, while different basis sets were used for iron, of the type aug-cc-pwCVnZ-DK, with n = 3-5. Extrapolation to the complete basis set (CBS) limit on the metal was accomplished by making use of two-point extrapolation equations (separate for CASSCF and CASPT2) given in refs 89 and 90 and described in our previous paper.⁶² In this set of calculations, only the valence electrons were correlated at the CASPT2 level because it was shown before that CASPT2 generally fails in the description of the metal (3s,3p) correlation contribution to the spin-state energetics.⁹¹ Therefore, the latter contribution was instead obtained with CCSD(T), making use of much smaller ligand basis sets of the type MINAO (minimal basis sets constructed from the cc-pVTZ basis sets) combined with aug-cc-pwCVTZ-DK on iron. This approach, denoted as CASPT2/CC in our recent study, was shown to give highly accurate spin-state energetics for a broad series of iron complexes.⁶²

In all CASPT2 and CCSD(T) calculations, scalar relativistic effects were included using the standard second-order Douglas–Kroll–Hess Hamiltonian.⁹² The CASPT2 calculations use the default IPEA shift of 0.25 hartree⁹³ and an imaginary shift of 0.1 hartree to avoid possible weak intruder states.⁹⁴ The CASPT2 calculations were carried out with the *Molcas* 8 package.⁹⁵ Here, the two-electron integrals were decomposed by means of the Cholesky technique with a threshold of 10^{-6} hartree.⁹⁶ For the CCSD(T) calculations, we used the *Molpro* V.2012 package.⁹⁷ All CCSD(T) calculations are (partially) spin-restricted, on the basis of restricted open-shell Hartree–Fock orbitals.

Because characterization of the complexes is done in MeOH, we included solvent effects in the calculations of the electronic spectra through a polar continuum model (PCM)⁹⁸ with the dielectric constant of MeOH (32.63) and a surface element average area of 0.4 Å². For the excited states, only the fast component of the reaction field was calculated, while the slow component was taken from the ground state.⁹⁹ Each charge-transfer excitation was fully localized on a single ligand and, hence, each MLCT transition clearly identified based on its induced polarization. Therefore, we treat all transitions to the same ligand molecule with a specific PCM that has its fast response component equilibrated to one of those states. For instance, the nine ¹MLCT transitions of [Fe(Z)₃]²⁺ form three groups of three charge transfers to each Z ligand. Because all transitions to the same ligand induce the same qualitative polarizations, we use a common PCM for each of those three groups.

RESULTS AND DISCUSSION

The complexes were synthesized using an adapted procedure from Stupka et al. with iron(II) perchlorate.¹⁰⁰ Reaction kinetics were quick, and the color changed immediately after the addition of the metal salt to the ligand solution. The Z complex synthesis resulted in a violet powder, whereas the **M** complex was obtained as a reddish-orange powder. Hence, their electronic spectra are expected to be very distinct from one another, even though they are isomers (vide infra). Another important feature of the complexes is their ¹H NMR spectra showing broad bands preventing peak assignment, typical of paramagnetic samples.

Magnetic Susceptibilities and Mössbauer Spectra. Figure 1 shows the temperature dependence of the $\chi_M T$ product for both complexes in the 2–300 K range. Both samples are paramagnetic, with $\chi_M T$ larger than zero in all ranges but with very different temperature dependencies. At 300 K, 2 has a $\chi_M T$ value approximately 12 times larger than that of 1, which decreases until 100 K, where $\chi_M T$ becomes similar to that of the Z complex. The behavior of 2 indicates that a HS species predominates at room temperature with an incomplete conversion to a LS species upon cooling. Inspection of the curve below 20 K hints at a full depopulation of the HS state as the temperature is decreased. Although this decrease is more pronounced for 2, the same trend is observed for 1, indicating that the ground state for both complexes is a singlet state at 0 K and that the paramagnetic nature of the



Figure 1. Temperature dependence of the $\chi_{\rm M}T$ product for **2** and **1** in the 2–300 K range. The theoretical fitting of the curve exhibiting spin transition corresponds to an equilibrium between the ¹LS and ⁵HS iron(II) states with $T_{1/2} = 241$ K. The ideal O_h curve was simulated using van Vleck's equation for a ⁵T_{2g} ground state with $\lambda = -100$ cm⁻¹.

samples is a consequence of the thermal population of lowlying excited states.

Although a plateau is not observed at higher temperatures, the $\chi_{\rm M}T$ value for 2 tends to the value expected for an ideal O_h ${}^5T_{2g}$ state. Taking this into account and considering that the $\chi_{\rm M}T$ value for the ground state is zero, the molar fraction of the 5 HS species ($\gamma_{\rm HS}$) can be calculated as a function of the temperature using the theoretical values for the ideal ${}^{5}T_{2g}$ state. The theoretical fit is a sigmoidal curve and reproduces very well the experimental $\chi_{\rm M}T$ data with a root-mean-square deviation of 0.30 cm³ K mol⁻¹ (Figures 1 and S6). The sigmoidal behavior of the spin conversion is an indication that a ${}^{1}\text{LS}-{}^{5}\text{HS}$ equilibrium is in operation with $T_{1/2} = 241$ K (the derivative of the experimental curve gives a broad maximum ranging from 210 to 250 K).

The nature of the HS and LS species was confirmed by Mössbauer spectroscopy at two different temperatures. The spectra shown in Figure 2a,b were fitted using one or two doublets, and the hyperfine parameters are listed in Table 1. The recorded spectra confirm the paramagnetic nature of 2, even at low temperatures. It is clear from Figure 2a that complex 2 presents two doublets, confirming the coexistence of two different spin states at both temperatures. Doublet A always exhibits a large splitting ($\delta \ge 1.00 \text{ mm s}^{-1}$) consistent with a ⁵HS, whereas doublet B presents an isomer shift typical of a ¹LS. At room temperature, the HS area $A_{\rm HS}/A_{\rm tot}$ was found to be 64.5%, decreasing to 9.8% upon cooling to 22 K, in very good agreement with the values obtained from the fitting of the magnetic curve in which the ⁵HS molar fraction was calculated as 72.2% and 6.8%, respectively. The low isomer-shift increase with decreasing temperature is caused by a second-order Doppler effect, for both doublets.¹⁰¹ A pronounced change in the quadrupole splitting was found to accompany the spin conversion. This large quadrupole splitting found for ⁵HS $(\Delta E_Q > 2 \text{ mm s}^{-1})$ indicates that a strong electric-field gradient permeates the iron atom, suggesting a distorted ⁵HS octahedral complex. It is also worth noting that the subspectral areas change significantly from room temperature down to 22 K, clearly indicating a HS-LS crossover under decreasing



Figure 2. Mössbauer spectra recorded at 300 and 22 K of (a) 2 fitted using two doublets and (b) 1 fitted using one doublet.

temperature, in agreement with the $\chi_{\rm M}T$ versus T curve (Figure 1).

Complex 1 (Figure 2b) has only one iron(II) site, the isomer shift value of which may be attributed to a ¹LS state. The spin configuration does not change with decreasing temperature to 22 K, as can be verified by the small variation of the Δ and δ hyperfine parameters. Again, the δ increase is attributed to a second-order Doppler effect. The absence of the ⁵HS doublet in this case indicates that the observed increase in χT with the temperature for this sample (Figure 1) may be a consequence of temperature-independent paramagnetism (TIP). Indeed, the experimental data for this sample are very well reproduced if a TIP contribution of 7.7 × 10⁻⁴ cm³ mol⁻¹ is added to the Curie component (Figure S7).¹⁰²

Provided that a spin conversion is observed (as for 2) and assuming that the system can be described by a regularsolution model,¹⁰³ thermodynamic parameters can be obtained using eq 1, in which $\Delta H_{\rm HL}^0$ denotes the difference in enthalpy between the LS and HS states and Γ the interaction energy concerning magnetic cooperativity between metal centers.

$$\ln\left(\frac{1-\gamma_{\rm HS}}{\gamma_{\rm HS}}\right) = \frac{\Delta H_{\rm HL}^0 + \Gamma(1-2\gamma_{\rm HS})}{RT} - \frac{\Delta S_{\rm HL}^0}{R} \tag{1}$$

			HS $(mm s^{-1})$			LS (mm s^{-1})		
	T (K)	$A_{\rm HS}/A_{\rm tot}$ (%)	δ	ΔE_Q	Г	δ	ΔE_Q	Г
$[Fe(M)_3]^{2+}$	300	64.5	1.00	2.04	0.51	0.31	0.34	0.41
	22	9.8	1.30	2.37	0.84	0.47	0.43	0.45
$[Fe(Z)_3]^{2+}$	300					0.32	0.53	0.27
	22					0.40	0.55	0.39

Table 1. Hyperfine Parameters for 2 and 1 at 22 and 300 K

Table 2. Crystallographic Data for Complexes

	$[Fe(\mathbf{Z})_3](ClO_4)_2$	$[Fe(\mathbf{M})_3](ClO_4)_2$	$[Fe(\mathbf{M})_3](ClO_4)_2$
chemical formula	$FeC_{21}H_{18}N_{12}O_8Cl_2(H_2O)_{0.268}$	$FeC_{21}H_{18}N_{12}O_8Cl_2$	$FeC_{21}H_{18}N_{12}O_8Cl_2$
mol wt (g mol^{-1})	698.04	693.22	693.22
temperature (K)	150.0	150.0	296.0
wavelength (Å)	Μο Κα, 0.71073	Cu Ka, 1.54178	Cu Ka, 1.54178
cryst syst	monoclinic	monoclinic	monoclinic
space group	P2 ₁ /c	$P2_1/c$	$P2_1/c$
a (Å)	15.9269(18)	17.4833(6)	17.710(2)
b (Å)	9.8374(11)	12.8960(5)	13.1791(16)
c (Å)	17.1276(19)	12.0829(4)	12.1886(12)
β (deg)	101.289(2)	90.716(2)	90.569(6)
V (Å ³)	2631.6(5)	2724.05(17)	2844.7(5)
Ζ	4	4	4
$ ho_{ m calcd}~({ m g~cm^{-3}})$	1.762	1.690	1.619
F(000)	1419	1408	1408
$\mu \ (\mathrm{mm}^{-1})$	0.85	6.89	6.59
θ range (deg)	2.4-27.8	30.1-98.1	8.4-134.3
reflns coll/indep	37738/6279	38366/4976	33446/5084
$R_{\rm int}$	0.027	0.061	0.052
data/restraints/param	6279/281/578	4967/688/503	5084/509/627
$R_1 [F^2 > 2\sigma(F^2)], wR_2(F^2)$	0.051, 0.115	0.078, 0.218	0.078, 0.241
diff peak, hole (e $Å^{-3}$)	0.41, -0.54	0.54, -0.64	0.58, -0.45
GOF on $F^2(S)$	1.19	1.05	1.03
CCDC	1842589	1842593	1842592

Using the fitted molar fraction curve (Figure S6), a linear fit of eq 1 with $R^2 = 0.9996$ in the 200–300 K range results in $\Delta H_{\rm HL}^0 = 853 \pm 3 \text{ cm}^{-1} (10.21 \pm 0.03 \text{ kJ mol}^{-1}), \Delta S_{\rm HL}^0 = 3.35$ $\pm 0.01 \text{ cm}^{-1} \text{ K}^{-1}$ (40.0 $\pm 0.1 \text{ J K}^{-1} \text{ mol}^{-1}$), and $\Gamma = 0$ for the spin conversion in 2. The absence of an interaction term for the process ($\Gamma = 0$) means that it corresponds to a true spinstate equilibrium. Moreover, the enthalpy change is close to the usual values $(800-1600 \text{ cm}^{-1})$ for iron(II) SCO systems. The entropy change is comparable to the typical $4-6 \text{ cm}^{-1} \text{ K}^{-1}$ range observed for other iron(II) systems.¹⁰⁴ Because the magnetic contribution to the entropy change associated only with spin can be estimated as $\Delta S_{spin} = R[\ln(2S+1)_{HS} - \ln(2S)]$ $(+ 1)_{LS} \approx 1.1 \text{ cm}^{-1} \text{ K}^{-1,61}$ the low value found for 2 may indicate that the LS-HS conversion is in this case not accompanied by important changes in the crystal packing of the system. This interpretation is corroborated by the crystallographic data discussed in the next section. All of these observations can lead us to the conclusion that, for 2, the $\Delta H^0_{
m HL}$ value obtained from eq 1 is a good estimate for the energy difference between the ⁵HS excited state and the ¹LS ground state $(\Delta E_{\rm HL}^0)$ of the system.

Unfortunately, the lack of spin conversion for 1 in the temperature range used in the experiments prevents calculation of the thermodynamic data for this complex. However, if we consider that $\gamma_{\rm HS}$ for this sample at 300 K is close to the values observed for 2 below 20 K, one can speculate that the spin

transition in this sample would be hypothetically observed at temperatures not lower than 600 K.

Crystal Structures. Single crystals were obtained for both complexes that crystallized in the monoclinic $P2_1/c$ space group (Table 2), and data analysis confirms that only the meridional isomer is present in the samples. The molecular packing in both samples is very similar, revealing that there is no direct hydrogen bonding between cationic units, as can be seen from a comparison of Figures 3 and 4. However, perchlorate anions form hydrogen bonds with cations through the NH hydrogen atoms from the imidazole units, giving rise to a network in the crystal. Similar results were observed in the crystal structure of the ruthenium complex with ligand M, recently reported.¹⁰⁵ The absence of direct hydrogen bonding between the complexes may be related to the broad spin transition observed for the sample because the cooperative effects due to intermolecular interactions would be less pronounced in this case.⁴ Although the unit cell dimensions are not readily comparable, the cell volumes are very close to one another, yielding similar values for the calculated densities.

As a consequence of the method used to grow single crystals, the compositions of powdered samples and crystals differ in the amount of H_2O content. Because polymorphism and solvatomorphism can play a very important role on the solidstate SCO properties,^{106,107} we have performed powder XRD experiments for the samples used to obtain magnetic susceptibilities and Mössbauer spectra. A comparison of the



Figure 3. Crystal structure of **2** at two different temperatures measured from the same single crystal. Unit cell packing along the *b* axis at (a) 150 K and (b) 296 K. ORTEP diagram at 50% probability with atom numbering in which hydrogen atoms and perchlorates were omitted for clarity at (c) 150 K and (d) 296 K. (e) Overlay of the cations obtained at 150 and 296 K.



Figure 4. Crystal structure of 1 at 150 K. (a) ORTEP diagram at 50% probability with atom numbering in which hydrogen atoms were omitted for clarity and (b) unit cell packing along the b axis.

experimental and simulated diffractograms using single-crystal structures obtained at room temperature (Figure S8) reveals that powdered samples and crystals are structurally very similar. Although differences between the SCO properties of the powders and crystals cannot be ruled out, the observed similarity is strong evidence that the assessments obtained from the present crystal structures can be extended to the powdered samples used in magnetic measurements.

As expected, the complexes have distorted octahedral coordination spheres because of the bidentate nature of the ligands. The meridional configuration is the only one observed requiring that two imidazole units are trans to each other while the third is trans to a pyrimidine unit. In both cases, this results in different bond distances for similar units.

For sample 2, data collection was performed at 150 and 296 K using the same single crystal. As expected, heating of the sample yields an expansion of the cell (4.4% in volume), but

Table 3. Characteristic Geometrical Parameters (Mean Values) of the $[Fe(M)_3]^{2+}$ and $[Fe(Z)_3]^{2+}$ Complexes Obtained from Single-Crystal XRD and at the DFT/PBE0 Level in the Singlet (¹LS) and Quintet (⁵HS) States

	$[Fe(M)_3]^{2+}$				$[Fe(Z)_3]^{2+}$		
	XRD		DFT		XRD	DFT	
	150 K	296 K	¹ LS	⁵ HS	150 K	¹ LS	⁵ HS
$d(\text{Fe-N}_{\text{imidazole}})$ (Å)	1.98	2.12	1.99	2.16	1.96	1.98	2.15
$d(\text{Fe}-N_{\text{diazine}})$ (Å)	2.00	2.15	2.03	2.28	1.96	2.02	2.27
bite angle (deg)	81.2	78.2	81.2	76.3	81.5	80.9	75.6
interligand angle (deg)	93.2	94.6	93.1	95.0	92.8	93.2	95.2

apart from that, no other important differences are observed when the two unit cells are compared (Figure 3a,b). The atomic positions remain almost the same, but the thermal ellipsoids increase as expected for higher temperatures (Figure 3c,d). Considering that the two selected temperatures encompass the observed spin transition for 2, the subtle changes in the atomic positions are in very good agreement with the low value for the entropy change obtained from the magnetic data. It is important to note that the increase in the temperature does not change the overall hydrogen-bonding pattern in the unit cell. Although the intermolecular network formed by the hydrogen bonding between perchlorate anions and cations may play an important role in defining the overall temperature-dependent magnetic behavior, these results suggest that changes in the packing of the sample as a function of the temperature are not the dominant driving force for the contrasting magnetic behavior when the two isomers are compared. Another important fact is that the shortest Fe-Fe distances are too long to be considered as a mechanism for magnetic interactions. At 150 K, the distance is 7.247 Å, and it increases to 7.347 Å at room temperature. This is also in agreement with the zero value predicted for Γ using eq 1, as discussed in the previous section. A direct Fe-Fe interaction mechanism can also be ruled out for sample 1 because the metal-metal distance is even longer for this sample (8.564 Å) probably induced by the higher β angle in comparison with **2**.

The most important difference between structure 2 at low and high temperatures is the change in the iron(II) coordination sphere. With increasing temperature, the bond distances and angles change, and this can fully account for the magnetic behavior of this sample. Similar distortions were observed for other SCO complexes with N-heterocycle chelating ligands.²⁷ Parts c and d of Figure 3 show the FeN₆ distorted octahedral arrangement of the cationic $[Fe(\mathbf{M})_3]^{2+}$ species at 150 and 296 K. An overlay of the two structures is also depicted in Figure 3e. This figure reveals that upon heating the Fe–N bond distances increase accompanied by a distortion in the bond angles, with one of the ligands showing more pronounced distortions.

If we analyze the geometry of the FeN₆ octahedron on the basis of the parameters suggested by Guionneau and coworkers,¹⁰⁸ we obtain the values $d_{\rm Fe-L} = 2.135$ Å and $\Sigma = 82^{\circ}$ for the ⁵HS [Fe(**M**)₃]²⁺. SCO leads to structural modifications, yielding $\Delta r = 0.145$ Å and $\Delta \Sigma = 19^{\circ}$ (24%). Such variations are in very good agreement with other SCO iron(II) complexes for which temperature-dependent crystallographic studies were performed.^{4,108}

Geometric changes can also be clearly seen by data in Table 3, showing select mean values for the bond distances and angles. At 150 K, the different Fe–N bond distances are very similar, but, remarkably, Fe–N_{diazine} is a little bit longer than Fe–N_{imidazole}, an asymmetry that reflects the stronger bond and

stronger electron-donor character of imidazole. The same trend was observed in copper(II) complexes of the same ligands.⁶⁴ Moreover, the mean values of the Fe-N bond lengths are comparable with those reported for other related LS iron(II) complexes like $[Fe(bpz)_3]^{2+}$ and $[Fe(bpym)_3]^{2+}$ (with 2,2'-bipyrazine and 2,2'-bipyrimidine).^{109,110} Thus, the crystallographic data at 150 K and the Mössbauer spectrum of this sample at low temperatures unambiguously correspond to a LS state for this complex. The data at 296 K indicate elongation of all Fe-N bond distances, especially for one of the ligands, which is consistent with a transition from ¹LS to ⁵HS iron(II). The more distorted structure at 296 K might be caused by a Jahn–Teller effect in the ⁵HS state (corresponding to a degenerate ${}^{5}T_{2g}$ in a pure octahedron). The $[Fe(Z)_{3}]^{2+}$ complex has a coordination sphere very similar to that of $[Fe(M)_3]^{2+}$ at 150 K, indicative of the LS nature of this sample, in agreement with the magnetic and Mössbauer results. We also find that $[Fe(Z)_3]^{2+}$ has slightly shorter Fe–N bond distances, conforming with the stronger LF exerted by this ligand.

Spin-State Energetics. To obtain a reliable computational estimate of the adiabatic energy difference $\Delta E_{\rm HL}^0$ for both complexes, CASPT2 calculations were performed on structures for the different spin states obtained from DFT (PBE0 functional). As can be seen from Table 3, the bond distances and angles of the structures in silico (Tables S6–S8) properly reproduce the features observed in the XRD results. Zero-point vibrational energies were also taken from these DFT calculations. However, as is well-known, obtaining accurate spin-state energetics from DFT is problematic because the results are strongly dependent on the applied functional. Therefore, we rather revert to traditional wave-function methods for calculation of the electronic energy differences between the different spin states. Results obtained with CASPT2 and CASPT2/CC with different basis set combinations (as described in the Computations Details section) are collected in Table S9. Our "best" results, obtained with CASPT2/CC in combination with CBS(Q:5) (i.e., CBS extrapolation based on the results obtained with iron aug-ccpwCV5Z-DK versus aug-cc-pwCVQZ-DK), are $\Delta E_{\rm HL}^0 = 500$ cm^{-1} for $[Fe(\mathbf{M})_3]^{2+}$ and 2012 cm^{-1} for $[Fe(\mathbf{Z})_3]^{2+}$. As noted in our previous paper,⁶² the CBS(Q:5) extrapolation might be slightly biased (by a few hundred wavenumbers) toward the LS state compared to "full" CBS (that is, including also extrapolation of the ligand basis sets). However, this error is compensated for by the inherent bias (by about the same amount) toward HS states of valence-only CASPT2.⁶² Therefore, we believe that the CBS(Q:5) CASPT2/CC results should give a highly accurate estimate of this property in the gas phase. $\Delta E_{\text{HL}}^0 \simeq \Delta H_{\text{HL}}^0 = 500 \text{ cm}^{-1} \text{ for } [\text{Fe}(\mathbf{M})_3]^{2+} \text{ closely}$ corresponds to the crystal $\Delta H_{\rm HL}^0 = 853 \text{ cm}^{-1}$, confirming our

observation that the LS–HS conversion is not accompanied by important changes in the crystal packing of the system. Assuming that the difference in the gas phase $\Delta H_{\rm HL}^0$ may be extrapolated to the solid state, our theoretical estimate of 1 for $\Delta H_{\rm HL}^0$ is 2365 cm⁻¹.

UV/Vis Spectroscopy. Ligands **Z** and **M** are constitutional isomers ($C_7H_6N_4$) only differing in the relative position of one diazinic nitrogen atom. Because both structures are fully aromatic and because of the π system of the diazine cycle, we expect a rich spectroscopic behavior like in other coordination compounds.^{111–118}

Figure 5 shows the UV/vis absorption spectra of 2 and 1 recorded in MeOH at room temperature. The two isomers



Figure 5. UV/vis absorption spectra of 2 (red) and 1 (black) in MeOH.

show distinctive features, which might go beyond the structural differences between them and reflect the uneven presence of different spin states observed in the magnetic and Mössbauer experiments at room temperature. The spectra of both complexes are dominated by intense absorptions in the 300 nm region, originating from intraligand (IL) transitions. The change of ligand from Z to M blue-shifts the main peak of the IL band from 320 to 280 nm.

Furthermore, complex 1 has a less intense and broad band in the 400–600 nm region of the spectrum, which is completely missing for 2. On the other hand, the spectrum of the **M** complex has a very weak absorption as a shoulder of the IL band at 440 nm. The assignment of these low-energy bands is done by computational means, taking into account the presence of both ¹LS and ⁵HS species and evaluating the MLCT transitions from the occupied Fe(3d) orbitals to the Z/ $M(\pi^*)$, which we suspect to be behind those weaker bands in the spectra.

We have explored the vertical spin-allowed MLCT transitions by means of the CASPT2 method. On the basis of the magnetic and Mössbauer data, we describe the first quintet MLCT manifold of $[Fe(M)_3]^{2+}$ because the ⁵HS species should be the dominant species under the conditions of the UV/vis spectrum, whereas we calculate the MLCTs from both the ¹LS and ⁵HS states of $[Fe(Z)_3]^{2+}$ because the ¹LS state should be dominant but the presence of ⁵HS cannot be discarded. Figure 6 compares the transition energies and oscillator strengths of the MLCTs calculated for both complexes with their absorption spectra in the 300–700 nm region. The manifold of ⁵MLCTs is formed by three states, where one electron is transferred to each of the three ligands, i.e., a $[t_{2g}{}^{3}e_{g}{}^{2}\pi^{*1}]$ electronic configuration. The difference in



Figure 6. MLCT transitions from the ⁵HS state of $[Fe(\mathbf{M})_3]^{2+}$ (red) and the ⁵HS and ¹LS states of $[Fe(\mathbf{Z})_3]^{2+}$ (gray and black) compared to the experimental data (Figure 5). The absorbance of the spectra is adjusted based on the maximum of the $[Fe(\mathbf{Z})_3]^{2+}$ band at 510 nm and its most intense transition at 537 nm.

energy between these states is 300 cm⁻¹ or less for both complexes, a consequence of the small distortion from the ideal O_h coordination environment.

The ⁵MLCTs are only weakly affected by the PCM(MeOH) solvent model, being red-shifted by ~1000 cm⁻¹ for [Fe($(M)_3$]²⁺ and twice as much for [Fe($(Z)_3$]²⁺. Such a weak sensitivity to the polar solvent was observed for other iron(II) complexes with similar chelating ligands as well¹¹⁹ and justifies the use of a relatively simple solvent model without explicit solvent molecules.¹²⁰

The manifold of ¹MLCT states of $[Fe(Z)_3]^{2+}$ is broader, with nine possible states with a $[t_{2g}^5 e_g^0 \pi^{*1}]$ electronic configuration. These transitions appear around 5500 cm⁻¹ lower in energy than the ⁵MLCTs and cover a range of energies of 3552 cm⁻¹ (Tables S10-S13). Because both the ¹LS and ⁵HS states of the Z complex and their respective MLCT states have similar dipole moments, the inclusion of PCM(MeOH) induces a red shift to the ¹MLCTs similar in magnitude to the ⁵MLCTs of the same complex. The transition energies and oscillator strengths of the ¹MLCTs closely agree with the band at 510 nm of the $[Fe(Z)_3]^{2+}$ spectrum. The ⁵MLCTs are higher in energy and less intense. Nevertheless, a very weak shoulder can indeed be observed in the experimental spectrum at around 400 nm, close to the calculated ⁵MLCT band positions. This shoulder should therefore be assigned to the presence of a small but significant amount of HS complexes at room temperature, conforming with the paramagnetic behavior observed in its ¹H NMR spectrum in solution and also with the magnetic measurements in the solid state. The current approach cannot describe the large broadening of the ¹MLCT band because it depends on dynamical conformational distortions of the complex.¹²¹

Only two ⁵MLCT intense transitions at 364 and 366 nm contribute to the absorption spectrum of $[Fe(\mathbf{M})_3]^{2+}$ in very good agreement with the observed shoulder at 360 nm in the experimental spectrum (Figure 6).

LF. Given the distortion of $[Fe(M)_3]^{2+}$ and $[Fe(Z)_3]^{2+}$ from an ideal octahedral coordination, we can qualitatively evaluate their LF parameters from the LF expression for an octahedral d⁶ complex. We have performed CASPT2 calculations on spinallowed and spin-forbidden metal-centered transitions from the ^{1}LS and ^{5}HS states of both complexes to cover the $^{1}\text{A}_{1g}$ \rightarrow $^{3,1}T_{1g}$, $^{1}A_{1g} \rightarrow ^{3,1}T_{2g}$, and $^{5}T_{2g} \rightarrow ^{5}E_{g}$ transitions in O_{h} symmetry and averaged the energies of electronic states belonging to the same electronic O_h term (Table S14). For the LS complexes, the Racah parameters B and C may be obtained from the energy differences $E({}^{1}T_{1g}) - E({}^{3}T_{1g}) = 2C$ and $E({}^{1}T_{2g}) - E({}^{1}T_{1g}) = 16B$, respectively. These repulsion parameters are very similar for both complexes, i.e., $B \simeq 500$ cm^{-1} and $C \simeq 4000$ cm⁻¹. The LF strength of the LS complexes can be obtained from $E({}^{1}T_{1g}) - E({}^{1}A_{1g}) = 10 \text{ Dq} -$ C. We obtain 10 Dq = 19075 cm⁻¹ for $[Fe(Z)_3]^{2+}$ and 10 Dq = 18569 cm⁻¹ for $[Fe(M)_3]^{2+}$. The larger 10 Dq value of $[Fe(Z)_3]^{2+}$, by 506 cm⁻¹, confirms the larger stabilization of the singlet state by the Z ligand.

For a HS d⁶ complex, the value of 10 Dq is directly related to the ${}^{5}T_{2g} \rightarrow {}^{5}E_{g}$ transition energy [10 Dq = $E({}^{5}E_{g}) - E({}^{5}T_{2g})$] and diminishes to 10243 cm⁻¹ for [Fe(**Z**)₃]²⁺ and 9936 cm⁻¹ for [Fe(**M**)₃]²⁺. As expected, the stronger field of **Z** is maintained, but by only 307 cm⁻¹ in the HS state.

In order to gain insight into the role of σ donation of imidazole and diazine units in defining ligands' strengths, we

measured their pK_{aH} in H₂O. Experimental results reveal only one protonation equilibrium in the 0–11 pH range, and values are in agreement with the lower pK_{aH} expected for a 1*H*imidazol-2-yl moiety bonded to an electron-deficient group, such as a diazine, in comparison to imidazole itself with $pK_{aH} =$ 6.99.¹²² The experimental value for free ligand Z is $pK_{aH} =$ 4.51, a lower value than that for isomer **M** with $pK_{aH} =$ 5.21.

The larger pK_{aH} for **M** would imply a stronger σ donation toward coordination with iron(II), resulting in a stronger field for ligand **M**, in high contrast with the experimental and theoretical results previously described. These results confirm that σ donation from imidazole is not the major electronic effect defining the LF strength. Unfortunately, diazine protonation was not observed, but a comparison of these ligands using NMR spectroscopy shows a strong communication between the two moieties of the ligands, where the electron density of the imidazole is delocalized toward the diazine (discussion in the Supporting Information). CASSCF calculations revealed that π -back-donation is negligible in the ground and LF excited states for both complexes, suggesting that their LF strength is defined by a subtle balance between σ donation from both units.

In conclusion, the slightly stronger LF of Z with respect to M is sufficient to stabilize the ¹LS state and change the spin of the complex, causing their strikingly different room temperature macroscopic properties. This change in the σ -donor character between the complexes of M and Z provides a potential mechanism for tuning the electron density on the metal center.

CONCLUSIONS

We have shown that the different magnetic and spectroscopic properties of two iron(II) complexes obtained from two constitutional isomers of the 2-(1*H*-imidazol-2-yl)diazine ligand originate from the subtle differences in their electronic structures, in the absence of strong cooperativity. A combination of an electron-rich σ -donor imidazole moiety with an electron-poorer diazine moiety can be used to fine-tune the SCO in 2 with a spin transition at 241 K, whereas 1 shows a stable magnetic behavior in the 0–300 K range of temperatures.

The interpretation of the magnetic susceptibility data is straightforward and was corroborated by temperature-dependent Mössbauer spectra that reveal an equilibrium between the quintet and singlet species in the SCO system. Thermodynamic treatment of the magnetic data gives $\Delta H^0 = 10.21 \pm 0.03 \text{ kJ mol}^{-1}$ and $\Delta S^0 = 40.0 \pm 0.1 \text{ J K}^{-1} \text{ mol}^{-1}$ for the spin transition between these states.

The temperature-dependent single-crystal study of **2** confirmed that the changes in the unit cell packing as a consequence of the temperature are negligible, explaining the low value for the calculated ΔS^0 and pointing to a change in the coordination sphere around the iron(II) center. It revealed an expansion of the pseudooctahedral coordination sphere on the LS–HS transition in agreement with other similar SCO complexes, which was corroborated by DFT geometry optimizations, showing that the metal–ligand bonds are enlarged by ~0.1 Å as a function of the temperature and spin change.

CASPT2 calculations of the spin-state energetics in the gas phase, making use of correlation-consistent basis sets extrapolated to CBS, confirm the SCO behavior of $[Fe(\mathbf{M})_3]^{2+}$ but not $[Fe(\mathbf{Z})_3]^{2+}$, with ΔH^0_{HL} values of 5.98 and 24.05 kJ

mol⁻¹, respectively. Using CASPT2 calculations, we were also able to resolve the UV/vis spectra of the complexes in MeOH and to verify the picture drawn from the spin-state energetics. Complex 1 has a broad and relatively intense absorption band at 510 nm formed by spin-allowed transitions from the ¹LS state to the lowest ¹MLCT manifold that is almost missing in the spectrum of 2 (it appears as a very weak band in concentrated solutions). Conversely, the latter has a weak absorption at 360 nm, appearing as a shoulder of the intense IL band, that rises from spin-allowed transitions from the ⁵HS to the lowest ⁵MLCT manifold. Thus, the UV/vis spectra are composed of both ¹LS and ⁵HS species in different proportions in 1 and 2 at room temperature. The LF parameters obtained from CASPT2 confirm the stronger LF of Z with respect to M, with a 10 Dq value that is larger by $300-500 \text{ cm}^{-1}$. Hence, the change of the position of the diazinic nitrogen atom does not produce large structural distortions on the complexes but induces a weak change of the LF that explains the appearance of SCO in only one of their complexes (2).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b02278.

¹H and ¹³C NMR spectra and the corresponding assignments of **M** and **Z** in DMSO- d_6 , experimental and simulated powder XRD data for both complexes, atomic coordinates of $[Fe(\mathbf{M})_3]^{2+}$ and $[Fe(\mathbf{Z})_3]^{2+}$ in the singlet, triplet, and quintet lowest states optimized in a vacuum with DFT/PBE0, estimation of the core correlation effect for $[Fe(\mathbf{M})_3]^{2+}$ and $[Fe(\mathbf{Z})_3]^{2+}$ at the CASPT2 level, energy, dipole moment, and oscillator strength of the spin-allowed transitions to the low-lying MLCT manifold from the quintet state of $[Fe(\mathbf{M})_3]^{2+}$ and the singlet and quintet states of $[Fe(\mathbf{Z})_3]^{2+}$ in a vacuum and MeOH (PDF)

Accession Codes

CCDC 1842589 and 1842592–1842593 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/ cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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