

Macrocycle-Based Spin-Crossover Materials

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New iron(II) complexes of formula [Fe(L1)](BF₄)₂ (**1**) and [Fe(L2)](BF₄)₂·H₂O (**2**) (L1 = 1,7-bis(2'-pyridylmethyl)-1,4,7,10-tetraazacyclododecane; L2 = 1,8-bis(2'-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane) have been synthesized and characterized by infrared spectroscopy, variable-temperature single-crystal X-ray diffraction, and variable-temperature magnetic susceptibility measurements. The crystal structure determinations of **1** and **2** reveal in both cases discrete iron(II) monomeric structures in which the two functionalized tetraazamacrocycles (L1 and L2) act as hexadentate ligands; the iron(II) ions are coordinated with six nitrogen atoms: four from the macrocycle and two from two pyridine groups occupying two cis positions around the metal ion. In **1**, the N–Fe–N bond angles indicate that the Fe(II) ion adopts an unusual distorted trigonal prismatic geometry. In agreement with the observed paramagnetic behavior, the average of the six Fe–N distances at 293 K (2.218(6) Å) and at 90 K (2.209(2) Å) correspond well with distances observed for high-spin (HS) Fe(II) complexes with a coordination index of 6. For **2**, the Fe(II) ion adopts a distorted octahedral geometry for which the six Fe–N distances (average 2.197(4) Å) at room temperature are in the range expected for HS Fe(II) complexes. The crystal structure solved at 90 K showed a strong modification of the iron coordination sphere, suggesting the presence of a spin-crossover transition from HS to low spin (LS). Surprisingly, the averaged Fe–N value (2.077(4) Å) at this temperature is not in agreement with the magnetic measurements since the $\chi_m T$ product versus T showed a full LS state at 90 K. This may be explained by the presence of important distortions arising from the macrocycle constraints. To understand how the crystal and the lattice parameters were affected by the magnetic transition, the temperature dependence of the lattice parameters of **2** was determined in the range 293–90 K: the a and b parameters show essentially linear and gradual decreases, while the c and β parameters show dramatic decreases nearly similar to that observed in the magnetic behavior.

Introduction

The design of new coordination complexes exhibiting the spin-crossover phenomenon (SCO) is one of the most relevant

and challenging issues in the field of magnetic molecular materials.^{1,2} In such systems, the magnetic state can be switched from the high-spin (HS) to a low-spin (LS) configuration through external stimuli such as temperature, pressure, magnetic field, or light irradiation.^{1–6} This magnetic transition can occur in d⁴–d⁷ transition metal complexes, but the most studied examples to date are those based on Fe(II) (d⁶ configuration), for which a paramagnetic–diamagnetic transition from the HS ($S = 2$) to the LS ($S = 0$) state is

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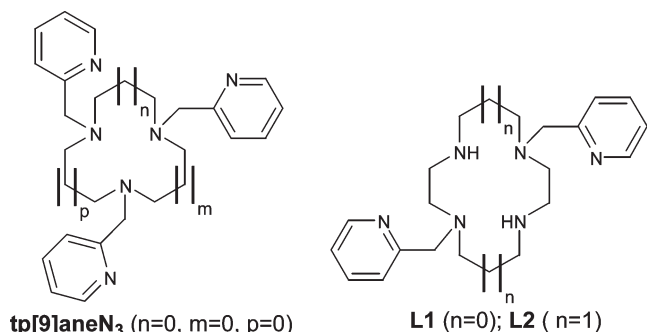
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Scheme 1. Examples of N-Functionalized Polyazamacrocycles

tp[9]aneN₃ (n=0, m=0, p=0)
tp[10]aneN₃ (n=1, m=0, p=0)
tp[11]aneN₃ (n=1, m=1, p=0)
tp[12]aneN₃ (n=1, m=1, p=1)

L1 (n=0); **L2** (n=1)

observed. In the past few years, several studies have been described related to the correlations between strong intermolecular interactions (π -stacking, hydrogen bonding, van der Waals interactions, and the nature of the covalent link between the metal active centers) and SCO characteristics such as thermal hysteresis due to cooperativity and light-induced excited spin-state trapping effects.^{3–7} However, the development of synthetic strategies to design new SCO systems based on new ligands are scarcely reported. It has been shown that most of the SCO Fe(II) complexes involve polydentate ligands combining both N-heterocyclic and amino-aliphatic groups.⁸ In this context, the use of polydentate ligands such as polyazamacrocycles derivatives (Scheme 1) could constitute an efficient way to design new SCO systems since the ligand field of the fully saturated polydentate macrocycle ligands might be fine-tuned via their N-functionalization with desirable potentially coordinating or chelating groups such as pyridine or poly-N-donating heterocyclic groups (see the selected examples depicted in Scheme 1).

Furthermore, most of the SCO complexes studied to date require two or more appropriate ligands which generally make it difficult to control the synthesis and to avoid the formation of polymorphic mixtures.⁷ Thus, the use of polydentate macrocyclic ligands, such as cyclen, cyclam, or their C-hexamethyl derivatives, involving at least six N-donor atoms

should open an original way to the design of new SCO complexes (Scheme 1).^{9–11} Still, in the case of Fe(II), most of them are either LS or HS.^{10,11} To the best of our knowledge, only two examples of SCO complexes of this kind have been reported: the [FeL(NCS)₂] complex (L = *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) with a transition temperature ($T_{1/2}$) around 350 K,¹¹ and the [Fe(Me₃[9]aneN₃)(MeCN)₃](CF₃-SO₃)₂ complex (Me₃[9]aneN₃ = 1,4,7-trimethyl-1,4,7-triazacyclonane) with a $T_{1/2}$ of ca. 320 K.¹² In the case of the unsaturated macrocycle rings, it is worth noting that Busch et al. reported in 1972 the complex [FeL'(phen)](ClO₄)₂¹³ (L' = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; phen = o-phenanthroline) as a new example exhibiting SCO behavior with a $T_{1/2}$ of around 250 K. It is expected that the total or selective partial N-functionalization of these ligands by pendant donor groups such as N-donating heterocyclic groups will yield novel and unusual coordination modes and, therefore, new coordination spheres for which the ligand field energy could be fine-tuned by varying the size of the fully saturated heterocycle, or the number and the nature of the substituting groups. In this context, Hendrickson et al.¹⁴ reported in 1986 a detailed study on the Fe(II) complexes of triazamacrocycles involving three pendant pyridylmethyl groups (Scheme 1). In the case of the nine-membered ring system (tp[9]aneN₃), the Fe(II) complex is LS, while the Fe(II) complex of the larger 12-membered ring system (tp[12]aneN₃) is HS. Using the intermediate 10-membered ring system (tp[10]aneN₃), McGarvey et al.¹⁵ prepared the complex [Fe(tp[10]aneN₃)]²⁺. In the solid state, the perchlorate salt of this complex exhibited a LS state at room temperature, while in acetonitrile solution, the complex showed a relaxation of the ¹A₁ ↔ ⁵T₂ spin equilibrium after perturbation by a pulsed laser.

In the present paper, we report the synthesis, crystal structures, and magnetic properties of two new Fe(II) complexes based on the cyclen and cyclam N₄-macrocycle rings bearing two pyridylmethyl arms. The complex based on the substituted cyclen ligand, [Fe(L1)](BF₄)₂ (**1**; L1 = 1,7-bis(2'-pyridylmethyl)-1,4,7,10-tetraazacyclododecane), shows an unusual trigonal prismatic coordination sphere with a HS state in the whole temperature range studied, whereas the cyclam derivative [Fe(L2)](BF₄)₂·H₂O (**2**; L2 = 1,8-bis(2'-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane) shows a distorted octahedral coordination and a SCO behavior with a $T_{1/2}$ of ca. 150 K. To the best of our knowledge, complex **2** is the first SCO system based on a functionalized tetraazamacrocyclic ligand.

Experimental Section

Materials. Most of the starting materials and solvents for the syntheses were obtained commercially and used without further purification. Cyclen and Fe(BF₄)₂·6H₂O were purchased from commercial sources and used without further purification. Cyclam was prepared according to the method previously reported.¹⁶ The

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L2 tetraazamacrocyclic 1,8-bis(2'-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane was prepared as previously described,¹⁷ while the L1 ligand (1,7-bis(2'-pyridylmethyl)-1,4,7,10-tetraazacyclododecane) was prepared as described below.

Synthesis of L1. Cyclen-Glyoxal Di-N-picolyl Diiodide Salt ([L¹]₂). A total of 2 g (12.2 mmol) of picolyle chloride hydrochloride was first treated by an aqueous NaOH solution (pH = 12) and extracted with CH₂Cl₂ (3 × 40 mL). The organic phases were dried with MgSO₄, and the solvent evaporated to give a red liquid which was added to 2 g (13.3 mmol) of NaI in 30 mL of dry acetone. The mixture was stirred for 6 h at room temperature. The solution was then filtered, and the solvent evaporated to give the corresponding iodo derivative used in the next step without further purification. This compound was added to a solution of 1 g (5.2 mmol) of cyclen-glyoxal¹⁸ in 20 mL of distilled acetonitrile. The solution was stirred for three days at room temperature, and the pink precipitate formed was then filtered, washed with acetonitrile, and dried under a vacuum (yield: 88%). ¹H NMR (300 MHz, D₂O, 298 K): δ 2.99–4.32 (m, 16H, CH₂α–N), 4.63 (s, 4H, N–CH₂–C₅H₄N), 4.81 (d, 1H, CH), 4.92 (d, 1H, CH), 7.57 (t, 2H, C₅H₄N), 7.67 (d, 2H, C₅H₄N), 7.97 (t, 2H, C₅H₄N), 8.66 (d, 2H, C₅H₄N). ¹³C NMR (75.47 MHz, D₂O, 298 K): δ 45.7, 49.1, 59.1, 64.0 (CH₂α), 64.3 (N–CH₂), 80.5 (CH), 128.9, 131.0, 141.8, 149.6, 153.3 (C₅H₄N). Anal. Calcd for C₂₂H₃₀N₆I₂·H₂O: C, 40.63; H, 4.96; N, 12.92%. Found: C, 40.46; H, 4.61; N, 12.79%.

1,7-Dipicolyl-1,4,7,10-tetraazacyclododecane (L1). Compound [L¹]₂ was refluxed in 15 mL of hydrazine monohydrate for 2 h. After cooling, the solution was extracted with CH₂Cl₂ (3 × 20 mL), and the organic phase was then washed with 10 mL of water to eliminate hydrazine traces. The organic layers were dried over MgSO₄, filtered, and evaporated to give L1 as a yellow oil (yield: 80%). ¹H NMR (300 MHz, CDCl₃, 298 K): δ 2.73 (m, 16H, CH₂α–N), 3.85 (s, 4H, N–CH₂–C₅H₄N), 7.19 (t, 2H, C₅H₄N), 7.54 (d, 2H, C₅H₄N), 7.70 (t, 2H, C₅H₄N), 8.56 (d, 2H, C₅H₄N). ¹³C NMR (75.47 MHz, CDCl₃, 298 K): δ 45.9 (2C), 52.0 (2C), (CH₂α), 61.6 (N–CH₂–C₅H₄N), 122.2, 123.1, 136.5, 149.1, 159.3 (C₅H₄N). Chlorhydrated form (L1·5HCl·2H₂O) ¹H NMR (300 MHz, D₂O, 298 K): δ 3.07 (m, 8H, CH₂α–N), 3.41 (m, 8H, CH₂α–N), 4.36 (s, 4H, N–CH₂–C₅H₄N), 8.05 (t, 2H, C₅H₄N), 8.11 (d, 2H, C₅H₄N), 8.61 (t, 2H, C₅H₄N), 8.85 (d, 2H, C₅H₄N). ¹³C NMR (75.47 MHz, D₂O, 298 K): δ 42.2 (2C), 46.8 (2C) (CH₂α), 53.8 (N–CH₂–C₅H₄N), 126.1, 128.0, 142.1, 146.5, 149.4 (C₅H₄N). Anal. Calcd for C₂₀H₃₀N₆·5HCl·2H₂O: C, 41.9; H, 6.9; N, 14.7; Cl, 30.9%. Found: C, 41.8; H, 6.4; N, 15.0; Cl, 30.2%.

Syntheses of the Complexes [Fe(L1)](BF₄)₂ (1) and [Fe(L2)](BF₄)₂·H₂O (2). Compounds **1** and **2** were prepared in the same way by adding progressively 3 mL of an aqueous solution of Fe(BF₄)₂·6H₂O (33.76 mg, 0.1 mmol) to 3 mL of an aqueous solution of the corresponding macrocycle ligand (35.40 mg, 0.1 mmol of L1 for compound **1**; 38.20 mg, 0.1 mmol of L2 for compound **2**) with continuous stirring. In each case, slow evaporation of the yellow resulting solutions at room temperature gave yellow prismatic single crystals of **1** (yield: 38 mg, 65%) and **2** (yield: 44 mg, 70%). Complex **1**. Anal. Calcd. for FeC₂₀H₃₀N₆B₂F₈: C, 41.1; N, 14.4; H, 5.2%. Found: C, 40.8; N, 13.9; H, 5.5%. IR data (ν/cm⁻¹) on KBr pellets: 3426(s), 3308(m), 3115(m), 2917(m), 3881(m), 1609(s), 1572(m), 1540(w), 1506(w), 1487(m), 1464(s), 1456(s), 1386(w), 1361(w), 1312(m), 1287(w), 1198(m), 1081(vs), 922(w), 844(w), 791(m), 769(m), 729(w), 633(w), 596(w), 522(m), 419(w). Complex **2**. Anal. Calcd. for FeC₂₂H₃₄N₆B₂F₈O: C, 42.1; N, 13.4; H, 5.5%.

Found: C, 41.9; N, 12.9; H, 5.6%. IR data (ν/cm⁻¹) on KBr pellets: 3630(m), 3559(m), 3433(br), 3287(m), 2930(m), 2874(m), 1604(s), 1570(m), 1466(m), 1441(m), 1358(m), 1328(w), 1295(m), 1084(vs), 1036(vs), 958(sh), 877(w), 835(w), 818(w), 777(m), 765(m), 729(m), 645(w), 572(w), 534(m), 522(m).

Physical Techniques. Infrared spectra were recorded in the range 4000–200 cm⁻¹ as KBr pellets on a FT-IR NEXUS NICOLET spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker AMX 3–400 spectrometer. Chemical shifts are reported in δ units (parts per million) downfield from the solvent resonance as an external reference. Variable-temperature magnetic susceptibility measurements were carried out in the temperature range 2–300 K with applied magnetic fields of 0.1 T on polycrystalline samples of compounds **1** and **2** (with masses of 7.47 and 13.61 mg, respectively) with a Quantum Design MPMS-XL-5 SQUID magnetometer. The susceptibility data were corrected for the sample holders previously measured under the same conditions and for the diamagnetic contributions of the salt as deduced using Pascal's constant tables (χ_{dia} = -353 × 10⁻⁶ and -383.8 × 10⁻⁶ emu mol⁻¹ for **1** and **2**, respectively). Elemental analyses were performed at the "Service de microanalyse", CNRS, 91198 Gif-sur-Yvette.

Crystallographic Data Collections and Structural Determinations. Crystallographic studies of complexes **1** and **2** were performed at 293 and 90 K using an Oxford Diffraction Xcalibur κ-CCD diffractometer with Mo Kα radiation. Small crystals of 0.06 × 0.08 × 0.16 mm³ for **1** and 0.8 × 0.15 × 0.18 mm³ for **2** were used to collect the data. The data collection was performed using 1° ω scans with an exposure time of 80 s per frame. The unit cell determination and data reduction were performed using the CrysAlis program suite¹⁹ on the full set of data. For both complexes, the crystal structures were solved using direct methods and successive Fourier difference syntheses with the Sir97 program²⁰ and refined on F² with weighted anisotropic full-matrix least-squares methods using the SHELXL97 program.²¹ Both pieces of software were used within the WINGX package.²² No absorption correction was needed owing to the low absorption coefficient of these compounds. The crystal used for compound **2** presents a pseudomerohedral twinning with a monoclinic cell having a β angle of nearly 90°, which emulates an orthorhombic cell. Both components of the twinned crystal are related by a 2-fold rotation around the *a* axis. Thus, the structure was solved and refined using the P2₁/*n* monoclinic space group and the following twinning law: 1 0 0 0 -1 0 0 0 -1. The two components were at a ratio of 0.57/0.43, which explains the pseudo-orthorhombic symmetry. This pseudomerohedral twinning was more clearly evidenced using low-temperature crystallographic data since the β angle deviates significantly from 90° at low temperatures, as clearly depicted in precession images performed at 293 and 90 K (Figure 1). The two twinned components are clearly shown separately by the precession image at 90 K where both networks are tilted from each other by ca. 5°. This observation agrees with the former twin law as the two-fold rotation around the *a* axis induces the nonsuperposition of networks when β differs from 90° with an angle of 180 - 2β = 5.8° between them. Because of the partial overlapping of diffraction patterns for both twin components, the crystal structure of **2** at 90 K was solved and refined using separate scale factors for the group of *hkl* reflections which do not present the same components overlapping. The equivalent reflections were then merged according to the crystal symmetry within the previous formed groups.

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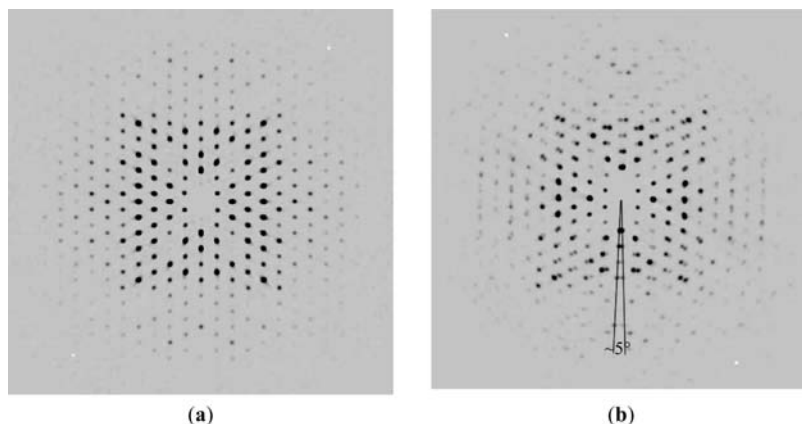
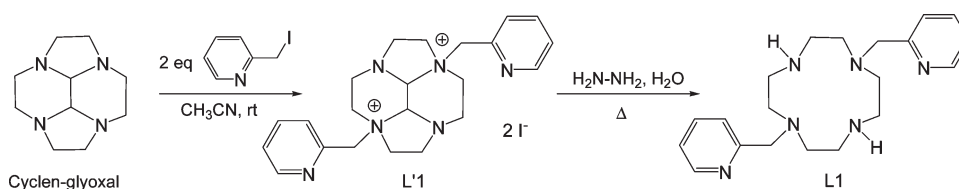


Figure 1. Precession images of the $h0l$ plane at (a) 293 K and (b) 90 K for compound **2**.

Scheme 2



CCDC 736986–736989 contain the supplementary crystallographic data for complexes **1** (293 and 90 K) and **2** (293 and 90 K), respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Syntheses and General Characterizations. Cyclen disubstituted by two methylpyridine (also named picolyle) arms grafted in the trans position on the macrocycle core, ligand L1, was synthesized using the intermediary of a bisaminal derivative (Scheme 2),¹⁸ the cyclen-glyoxal, obtained by condensation of the dicarbonylated compound with cyclen. The reaction with (2-picolyle) iodide formed the corresponding bis-iodide salt $[L'1]I_2$, which was easily isolated by filtration of the precipitate. Treatment of the salt with hydrazine monohydrate under reflux led to the free 1,7-di(2-picolyl)cyclen (L1) in good yield.

Complexes **1** and **2** were prepared in the same way by treating the aqueous solutions of the corresponding macrocycle ligand (L1 for **1** and L2 for **2**) with an aqueous solution of $Fe(BF_4)_2 \cdot 6H_2O$ in a 1:1 ratio. Single yellow crystals of compounds **1** and **2** were obtained by slow evaporation with relatively low yields. However, both compounds can be obtained quantitatively when acetonitrile solutions were used instead of the corresponding aqueous solutions. In this case, when the resulting yellow solutions were treated with diethylether, both compounds were obtained as yellow powders (yield, 85% for **1** and 90% for **2**). The IR spectra of both compounds show similar patterns. The sharp peaks around the 3300 cm^{-1} and $3000\text{--}2800\text{ cm}^{-1}$ regions are due to the symmetric and antisymmetric N–H and C–H stretching modes, respectively. The two strong absorption bands around 1450 cm^{-1} (1456 and 1464 cm^{-1} for **1**; 1441 and 1466 cm^{-1} for **2**) can be assigned to CH_2 bending modes. In each case, there are two vibration bands attributable to

the $\nu(\text{py ring})$ stretching vibrations (1609 and 1572 cm^{-1} for **1**; 1604 and 1570 cm^{-1} for **2**).^{23,24} In addition, the spectra exhibit at around 1060 cm^{-1} (1081 cm^{-1} for **1**; 1084 and 1036 cm^{-1} for **2**) the absorption due to the free $(BF_4)^-$ anions.

Crystal Structure Descriptions. $[Fe(L1)](BF_4)_2$ (**1**) and $[Fe(L2)](BF_4)_2 \cdot H_2O$ (**2**) crystallize in the monoclinic $C2/c$ and $P2_1/n$ space groups, respectively. For both complexes, there is not any structural transition within the studied temperature range (90–293 K). The unit cell parameters and crystal and refinement data are summarized in Table 1. The following general structural descriptions are given at 293 K. The pertinent structural modifications induced by cooling will be discussed further in the paragraph dealing with structural and magnetic properties correlations. Figures 2 and 3 show perspective ORTEP²⁵ drawings of the iron complexes in compounds **1** and **2**, respectively. In both cases, the structure consists of a discrete monomeric $[FeL]^{2+}$ cation ($L =$ neutral L1 (**1**) or L2 (**2**) macrocycle ligand) and two uncoordinated tetrafluoroborate anions. The discrete $[FeL1]^{2+}$ cation of **1** possesses a crystallographic two-fold axis passing through the iron atom position, and the asymmetric unit contains one-half of the above formula unit (Figure 2). The iron(II) ion is six-coordinated with four nitrogen atoms of the macrocycle [N1, N2, N1^a, and N2^a] and two of the pyridine rings [N5 and N5^a] occupying two cis positions around the metal ion. Careful examination of

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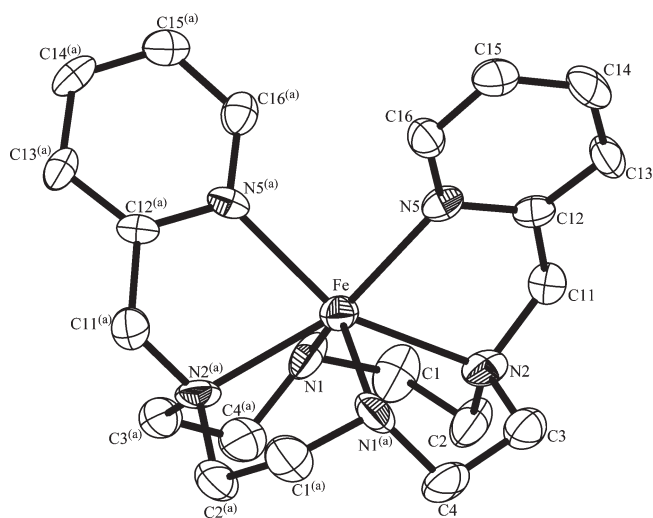
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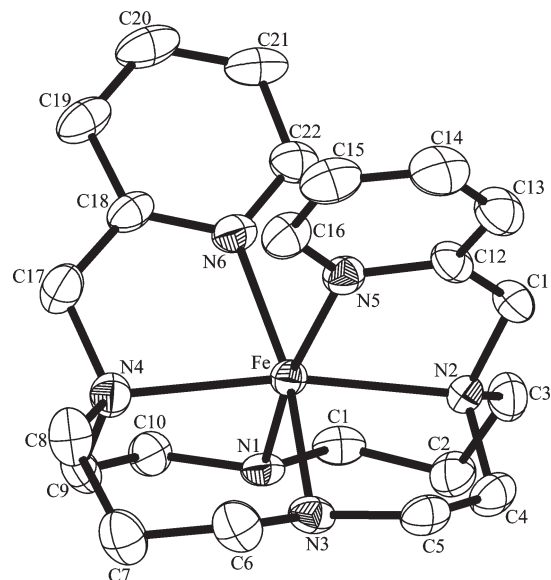
Table 1. Summary of X-Ray Data Collection and Refinement for [Fe(L1)](BF₄)₂ (1) and [Fe(L2)](BF₄)₂·H₂O (2)

	1		2	
^a Formula	C ₂₀ H ₃₀ B ₂ F ₈ FeN ₆		C ₂₂ H ₃₄ B ₂ F ₈ FeN ₆ O	
fw	583.97		628.02	
cryst syst	monoclinic		monoclinic	
space group	C2/c		P2 ₁ /n	
T (K)	293	90	293	90
a (Å)	15.3259(16)	15.1192(9)	9.8859(4)	9.6916(6)
b (Å)	13.8177(13)	13.9806(8)	14.1660(5)	13.9774(4)
c (Å)	11.8714(12)	11.4062(6)	19.7180(8)	19.3121(9)
β (deg)	90.242(10)	90.150(6)	90.058(3)	87.079(5)
V (Å ³)	2512.1(4)	2411.0(2)	2761.4(2)	2612.7(2)
^a Z	4	4	4	4
color	yellow	yellow	yellow	red
ρ (g cm ⁻³)	1.544	1.609	1.511	1.597
μ (mm ⁻¹)	0.682	0.710	0.629	0.664
^b R1	0.0677	0.0404	0.0438	0.0625
^c wR2	0.1678	0.0706	0.0968	0.1155
^d GOF	0.953	0.965	0.975	1.072

^a For complex **1**, the asymmetric unit contains 0.5 of the chemical formula. ^b R1 = $\sum |F_o - F_c| / F_o$. ^c wR2 = $\{\sum [w(F_o^2 - F_c^2)]^2 / \sum w(F_o^2)\}^{1/2}$. ^d GOF = $\{\sum [w(F_o^2 - F_c^2)] / (N_{obs} - N_{var})\}^{1/2}$.

**Figure 2.** ORTEP drawing (50% probability ellipsoids) of the cationic complex of **1** showing the asymmetric unit, the atom labeling scheme, and the coordination environment of the iron ions. Code of equivalent position: (a) $-x, y, 1/2 - z$.

the N–Fe–N bond angles depicted in Table 2 reveals that the six-coordinate geometry of the iron ion in **1** differs strongly from the distorted octahedron observed in transition metal complexes based on similar hexadentate macrocycle ligands²³ since the Fe(II) ion adopts an unusual distorted trigonal prismatic geometry. This trigonal prismatic geometry is well characterized by the very high value of the trigonal distortion parameter²⁶ of 809(4)° compared to the observed range for the octahedral geometry (0–300°). However, as observed in parent M(II) complexes based on hexadentate poly(pyridylmethyl)-cyclen ligands, the coordinated pyridyl groups are disposed on the same side of the basal macrocyclic ring. This fact results from the small size of the cyclen ring, which precludes the Fe(II) ion from entering the ring and forces it to remain well above the mean ring

**Figure 3.** ORTEP drawing (50% probability ellipsoids) of the cationic complex of **2** showing the asymmetric unit, the atom labeling scheme, and the coordination environment of the iron ions.

plane. Such geometric requirements of the ligand impose a large deviation of the metal ion (1.0 Å) from the average plane through the four nitrogen atoms of the cyclen ring.

The average Fe–N distance (2.218(6) Å; Table 2) is similar to those observed for HS Fe(II) complexes in octahedral environments. The Fe–N1 and Fe–N5 bond distances (and their equivalent Fe–N1^a and Fe–N5^a) are significantly shorter than the Fe–N2 (and Fe–N2^a) ones, indicating a weaker coordination of the two macrocycle nitrogen atoms connected to the methyl-pyridine groups than those of the two secondary amines (N1 and N1^a) of the macrocycle. This should be imposed by the position of the two methyl-pyridine groups to minimize their repulsions and the steric constraints within the two five-membered chelate rings (Fe–N2–C11–C12–N5 and Fe–N2^a–C11^a–C12^a–N5^a). The structure of **2** contains a discrete monomeric [FeL2]²⁺ cation, two BF₄⁻ anions, and a water molecule, all located on general positions (Figure 3). The Fe(II) ion adopts a distorted octahedral geometry with four nitrogen atoms of the macrocycle (N1, N2, N3, and N4) and two of the pyridine rings (N5 and N6). The four amine nitrogens span two contiguous faces of the coordination polyhedron, and the pyridine nitrogens occupy the remaining pair of cis positions, as observed in parent Ni(II) complexes based on similar macrocycle ligands (Figure 3).²⁴ As for complex **1**, the Fe(II) cation is displaced in the same direction as the methyl-pyridine groups from the mean plane of the four nitrogen atoms of the cyclam ring. However, the deviation in **2** is slightly shorter (0.91 Å) than the corresponding one observed for **1**. This difference is probably due to the higher flexibility of the cyclam ring resulting from the two additional saturated aliphatic carbon atoms.

The average value of the six Fe–N distances (2.197(4) Å, Table 3) is in good agreement with the values expected for HS Fe(II) complexes in octahedral geometry.²⁷ As for complex **1**, the bond distances involving the secondary

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Table 2. Selected Bond Length (Å) and Bond Angles (deg) for the Iron Coordination Sphere for **1**

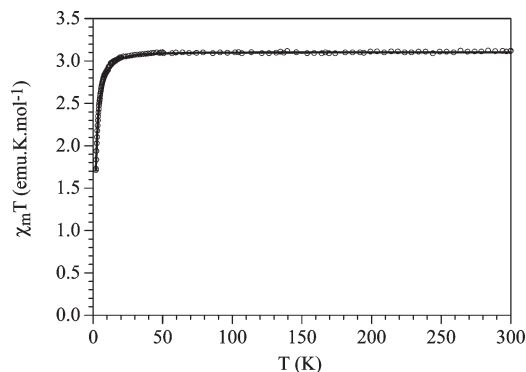
	$T = 293\text{ K}$	$T = 90\text{ K}$
Fe–N1(N1 ^a)	2.185(6)	2.172(2)
Fe–N2(N2 ^a)	2.273(6)	2.275(2)
Fe–N5(N5 ^a)	2.195(5)	2.180(2)
⟨Fe–N⟩	2.218(6)	2.209(2)
N1–Fe–N1 ^a	123.7(4)	124.71(15)
N1–Fe–N2	77.3(2)	77.41(9)
N1–Fe–N2 ^a	79.5(2)	79.90(9)
N1–Fe–N5	125.2(2)	125.38(9)
N1–Fe–N5 ^a	95.9(2)	95.31(10)
N2–Fe–N2 ^a	129.5(3)	129.85(12)
N2–Fe–N5	74.64(19)	74.92(9)
N2–Fe–N5 ^a	151.6(2)	150.86(8)
N5–Fe–N5 ^a	87.8(3)	87.31(12)

^aCode of equivalent position: $-x, y, 1/2 - z$.**Table 3.** Selected Bond Length (Å), Bond Angles (deg), and Distortion Parameters (deg) for Iron Coordination Sphere for **2**

	$T = 293\text{ K}$	$T = 90\text{ K}$
Fe–N1	2.172(3)	2.064(4)
Fe–N2	2.225(4)	2.152(4)
Fe–N3	2.180(4)	2.056(4)
Fe–N4	2.245(4)	2.135(5)
Fe–N5	2.181(3)	2.019(4)
Fe–N6	2.177(4)	2.035(4)
⟨Fe–N⟩	2.197(4)	2.077(4)
N1–Fe–N2	91.17(15)	92.43(17)
N1–Fe–N3	96.33(15)	95.26(16)
N1–Fe–N4	81.72(15)	82.20(17)
N1–Fe–N5	168.60(16)	172.92(18)
N1–Fe–N6	90.14(13)	88.92(16)
N2–Fe–N3	81.49(16)	78.19(17)
N2–Fe–N4	169.02(15)	172.10(15)
N2–Fe–N5	79.15(15)	81.95(17)
N2–Fe–N6	110.09(16)	108.33(17)
N3–Fe–N4	90.94(17)	96.46(17)
N3–Fe–N5	88.24(14)	87.84(16)
N3–Fe–N6	166.69(16)	172.15(18)
N4–Fe–N5	108.72(15)	103.82(17)
N4–Fe–N6	78.45(16)	77.49(17)
N5–Fe–N6	87.60(13)	88.77(16)
Σ	91(2)	91(2)
Θ	335(4)	221(4)

amines of the cyclam ring (Fe–N1 and Fe–N3 = 2.172(3) and 2.180(4) Å, respectively) and those involving the pyridine groups (Fe–N5 = 2.181(3) and Fe–N6 = 2.177(4) Å) are shorter than the two distances involving the nitrogen atoms (N2 and N4) connected to the methylpyridine (2.225(4) and 2.245(4) Å respectively). Careful examination of the intermolecular contacts (π -stacking, hydrogen bonding, and van der Waals contacts) in both complexes reveals an absence of significant intermolecular interactions.

Magnetic Properties. The thermal dependences of the product of the molar magnetic susceptibility times the temperature ($\chi_m T$) for the two complexes are depicted in Figures 4 and 5a. For complex **1**, the $\chi_m T$ product shows a room temperature value of 3.10 emu K mol⁻¹ that remains constant down to ca. 20 K. This value, slightly higher than the spin-only value calculated for an isolated metal ion with $S = 2$ (3.0 emu K mol⁻¹), indicates that complex **1** is essentially paramagnetic and presents the high-spin ($S = 2$) configuration over the whole temperature range. Below 20 K, the $\chi_m T$ product sharply decreases to reach a value of ca. 1.7 emu K mol⁻¹ at 2 K. This decrease at low

**Figure 4.** Thermal variation of the $\chi_m T$ product for compound **1**. Solid line represents the best fit to the model (see text).

temperatures can be attributed to the presence of a zero-field splitting (ZFS) of the $S = 2$ ground spin state rather than to an intermolecular coupling since the $[\text{FeL}]^{2+}$ cations in **1** are quite well isolated (see above).

Accordingly, we have fit the magnetic data to a simple isolated $S = 2$ ion with a ZFS using the following expression:²⁸

$$\chi_m = \frac{(2\chi_{\perp} + \chi_{\parallel})}{3}$$

$$\text{with } \chi_{\parallel} = \frac{Ng^2\beta^2}{kT} \frac{2e^{-x} + 8e^{-4x}}{1 + 2e^{-x} + 2e^{-4x}} \text{ and}$$

$$\chi_{\perp} = \frac{Ng^2\beta^2}{kT} \frac{(6/x)(1 - e^{-x}) + (4/3x)(e^{-x} - e^{-4x})}{1 + 2e^{-x} + 2e^{-4x}} \text{ and } x =$$

$|D|/kT$. This expression reproduces very satisfactorily the magnetic data in the whole temperature range with $g = 2.034(3)$ and $|D| = 4.7(2)$ cm⁻¹ (solid line in Figure 4). Note that this value is in the normal range found for other similar Fe(II) mononuclear complexes with a coordination number of 6 (where $|D|$ values in the range 3.4–10.9 cm⁻¹ have been found with powder susceptibility measurements).²⁹

As for **1**, compound **2** shows a room-temperature $\chi_m T$ value of 3.25 emu K mol⁻¹, slightly higher than the spin-only value. However, the magnetic thermal behavior is very different from that of complex **1**. Thus, the $\chi_m T$ product for **2** decreases upon cooling, first smoothly down to ca. 3.1 emu K mol⁻¹ at ca. 200 K, where the $\chi_m T$ drops more rapidly to reach a value close to zero at ca. 90 K (Figure 5a). This behavior is characteristic of a HS \leftrightarrow LS SCO conversion. The temperature of the transition, $T_{1/2}$, is estimated, from the derivative of the thermal variation of the $\chi_m T$ product, to be around 150 K (inset in Figure 5a). On increasing the temperature, a slight hysteresis of ca. 1.0 K was detected. Nevertheless, such a small hysteresis may be attributed to the thermal hysteresis of the sample (the temperature is varied at a rate of 2 K/min in the cooling and warming scans) rather than to a true hysteresis in the SCO transition. These temperatures are, within experimental error, independent of the applied magnetic field and of the number of cycles.

Discussion. The two complexes studied herein present different molecular structures and different magnetic behaviors. Compound **1** does not undergo any spin transition, remaining HS in the whole temperature range,

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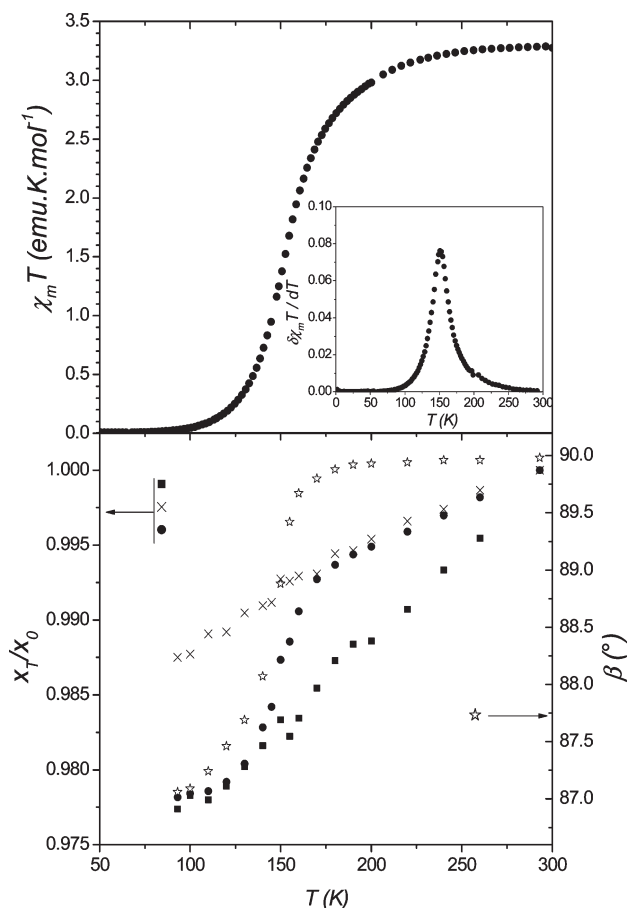


Figure 5. (a) Thermal variation of the $\chi_m T$ product for **2**. Inset shows the derivative of the $\chi_m T$ product vs temperature (top). (b) Thermal variation of the lattice parameters of complex **2**; a (■), b (×), and c (●) parameters and angular β parameter (open stars) showing the anisotropic contraction of the crystal around the SCO transition (bottom).

whereas compound **2** presents a relatively gradual spin transition between 200 and 90 K with a $T_{1/2}$ of ca. 150 K. As expected from the magnetic behavior, the crystal structures of **1** at 293 and 90 K do not show any significant structural changes (see Table 2). The HS behavior of this complex may be attributed to the nature and the geometry of the macrocycle ligand for which the cyclen ring is not sufficiently large to accommodate a normal distorted octahedron geometry, as shown by the huge value of the trigonal distortion parameter ($\Theta = 809(4)^\circ$). Indeed, this ligand imposes a distorted trigonal prismatic coordination geometry with relatively long Fe–N distances. As a consequence of this unusual geometry, the HS spin state is stabilized in the whole studied temperature range. In contrast, complex **2**, which has substituted tetraazamacrocyclic with a larger N4-macrocycle ring, displays a distorted octahedral geometry, and consequently, the SCO transition can take place.

In order to study in **2** how the structure of the iron site changes when the SCO transition occurs, variable-temperature single-crystal X-ray diffraction measurements were performed in the temperature range 293–90 K. The crystal structure solved at 90 K showed strong modifications of the iron coordination sphere. The average Fe–N distances and the trigonal distortion parameter (Θ) of the coordination

sphere decrease significantly (Table 3). This particular behavior is the structural signature of the HS \rightarrow LS transition. Surprisingly, the octahedral distortion parameter remains constant in both spin states ($\Sigma = 91(2)^\circ$). This particularity cannot be solely explained by the incomplete transition at 90 K, as the magnetic data indicate almost a 100% conversion at 90 K. Such a high distortion of the octahedron may be due to the constrained geometry induced by the macrocyclic ligand. It can be assumed that such a ligand imposes distorted geometries even in the low-spin state for Fe(II) SCO complexes. An additional proof of this distortion is the fact that the average Fe–N bond distance in the LS state (2.077(4) Å) is slightly longer than those usually observed in other LS Fe(II) complexes (ca. 1.96–2.00 Å). Furthermore, the trigonal distortion parameter, Θ , significantly decreases during the HS-to-LS transition, confirming that the spin transition process is specifically accompanied by this type of twisting distortion from O_h to D_{3h} symmetry. To understand how the crystal and the lattice parameters were affected by the magnetic transition, the temperature dependence of the lattice parameters of a single crystal of **2** were measured in the range 293–90 K. As can be seen in Figure 5b, the a and b parameters show essentially a linear and gradual decreases with a more gradual effect for the b parameter. In the temperature range 293–160 K, the c parameter shows a gradual decrease similar to that of the b axis. Below 160 K, a relatively abrupt decrease, parallel to that described above for the magnetic moment, was observed at the same temperature as that of the magnetic transition (150 K). The thermal variation of the angular β parameter depicted in Figure 5b does not show any anomaly in the thermal dependence down to 160 K, where a drop of about 2.5° occurs. This behavior corresponds very well with the SCO transition, as evidenced by the abrupt color change observed in the single crystal as the temperature is decreased from 200 to 100 K (Figure 5b). These structural data show that the single crystal of **2** contracts anisotropically on cooling since the more significant changes occur essentially along the c axis and the β angle. On heating the single crystal back to 200 K, no thermal hysteresis in lattice parameters is observed.

Conclusions

We have reported here the syntheses, structural characterizations, and magnetic properties of the two Fe(II) complexes [Fe(L1)](BF₄)₂ (**1**) and [Fe(L2)](BF₄)₂·H₂O (**2**), which are based respectively on functionalized cyclen (L1) and cyclam (L2) ligands. In both cases, the structure consists of a discrete monomeric [FeL]²⁺ cation and two uncoordinated (BF₄)[−] anions. The two complexes display different magnetic behaviors as a consequence of the different geometries around the metal ion (trigonal prismatic for **1** and distorted octahedral for **2**). Thus, **1** does not undergo any spin transition, while complex **2** presents a SCO behavior with a transition temperature of 150 K. As expected from the magnetic data, the crystal structure of **2** at 90 K shows a strong modification of the iron coordination site, which is the structural signature of the spin-state transition from HS to LS. In addition, temperature dependence of the lattice parameters shows that the crystal contracts anisotropically on cooling since the most

important structural changes occur along the c axis and the β angle and fit the SCO magnetic behavior well. From the synthetic point of view, this is the first report showing the use of such functionalized macrocycle ligands to design new SCO complexes. On the other hand, the chemical flexibility of such ligands can be viewed as an excellent starting point for the design of new parent macrocycle ligands able to create moderate or strong intermolecular interactions, which are crucial for observing SCO cooperative phenomena in such systems.

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