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Syntheses, Structural Analyses, and Magneto-Structural Correlations of Three Polymeric Fe(II) Complexes with Azide Ligand

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Three new metal–organic polymeric complexes, $[Fe(N_3)_2(bpp)_2]$ (**1**), $[Fe(N_3)_2(bpe)]$ (**2**), and $[Fe(N_3)_2(phen)]$ (**3**) [bpp = (1,3-bis(4-pyridyl)-propane), bpe = (1,2-bis(4-pyridyl)-ethane), phen = 1,10-phenanthroline], have been synthesized and characterized by single-crystal X-ray diffraction studies and low-temperature magnetic measurements in the range 300–2 K. Complexes **1** and **2** crystallize in the monoclinic system, space group *C*2/*c*, with the following cell parameters: $a = 19.355(4)$ Å, $b = 7.076(2)$ Å, $c = 22.549(4)$ Å, $\beta = 119.50(3)°$, $Z = 4$, and $a = 10.007(14)$ Å, $b = 13.789(18)$ Å, $c = 10.377(14)$ Å, $\beta = 103.50(1)°$, $Z = 4$, respectively. Complex **3** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 7.155(12)$ Å, $b = 10.066(14)$ Å, $c = 10.508(14)$ Å, $\alpha = 109.57(1)°$, $\beta = 104.57(1)°$, $\gamma = 105.10(1)°$, and $Z = 2$. All coordination polymers exhibit octahedral Fe(II) nodes. The structural determination of **1** reveals a parallel interpenetrated structure of 2D layers of (4,4) topology, formed by Fe(II) nodes linked through bpp ligands, while mono-coordinated azide anions are pendant from the corrugated sheet. Complex **2** has a 2D arrangement constructed through 1D double end-to-end azide bridged iron(II) chains interconnected through bpe ligands. Complex **3** shows a polymeric arrangement where the metal ions are interlinked through pairs of end-on and end-to-end azide ligands exhibiting a zigzag arrangement of metals (Fe–Fe–Fe angle of 111.18°) and an intermetallic separation of 3.347 Å (through the EO azide) and of 5.229 Å (EE azide). Variable-temperature magnetic susceptibility data suggest that there is no magnetic interaction between the metal centers in **1**, whereas in **2** there is an antiferromagnetic interaction through the end-to-end azide bridge. Complex **3** shows ferro- as well as anti-ferromagnetic interactions between the metal centers generated through the alternating end-on and end-to-end azide bridges. Complex **1** has been modeled using the *D* parameter (considering distorted octahedral Fe(II) geometry and with any possible *J* value equal to zero) and complex **2** has been modeled as a one-dimensional system with classical and/or quantum spin where we have used two possible full diagonalization processes: without and with the *D* parameter, considering the important distortions of the Fe(II) ions. For complex **3**, the alternating coupling model impedes a mathematical solution for the modeling as classical spins. With quantum spin, the modeling has been made as in **2**.

Introduction

A significant amount of research has been dedicated to the study of the magnetic behavior of polynuclear metal complexes, the structures of which are built upon inorganic motifs bridged by organic components. One of the points to be seriously considered for the preparation of these systems is the choice of appropriate bridging ligands, an aspect that is specially relevant because they influence the magnetic properties and behavior of the molecules. The pseudohalide azide has been demonstrated to be an extremely versatile ligand and also an excellent magnetic coupler. Thus, a large number of azide-bridged systems, from dimers to 3D-

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compounds, have been synthesized and magnetically characterized[1−4] to date. This is primarily due to the versatility of the azide ligand in the self-assembly of extended networks and interesting magnetic properties exhibited by these compounds. Among the various coordination modes of the azide ligand $\mu-(1,1)$ (EO),[1b,c] $\mu-(1,3)$ (EE),[1d,e] $\mu-(1,1,1)$,[1f] $\mu-(1,1,3)$,[1g] alternating $\mu-(1,1)$ and $\mu-(1,3)$ in the same structure,[1h,i] and monodentate $\mu-(1)$[1j] have been reported. In general, the coordination modes observed for the bridging azide group are $\mu-(1,3)$(EE) with antiferromagnetic interaction and $\mu-(1,1)$(EO) with ferromagnetic interaction. Moreover, the magnetic properties for the $\mu-(1,1)$ (EO) bridged metal complexes are dependent on the M−N−M angle,[4] and for the $\mu-(1,3)$(EE) bridged metal complexes it is dependent on the M−N−N angle and the M−N_3−M dihedral angle.[1a]

The magnetism of transition metal ions having an orbitally degenerate ground-state such as iron(II) is very complicated and a challenging problem to physicists as well as chemists. The analysis would require complicated theoretical treatment considering spin−orbit coupling and the orbitally dependent magnetic exchange. For strongly distorted systems (the most frequent cases) the orbital contributions to the exchange as well as the first-order spin−orbital interactions are suppressed. In these cases, the zero-field splitting (D tensor considered usually as a parameter) plays a major role. Taking into account the above-mentioned aspects, in this work our goal is to explore the possibility of extending poly-iron(II) chemistry in a controlled fashion, i.e., by using polynucleating and pseudohalide (mainly azide) bridging ligands. Actually, azide bridging anisotropic iron(II) ions in a controlled manner would delineate a new class of poly-iron species that may possess interesting magnetic properties. In this contribution we report syntheses, crystal structures, and low-temperature magnetic behaviors of three extended iron(II) systems using azide and N-donor chelating/bridging ligands.

Experimental Section

Materials. High purity (98%) 1,2-bis(4-pyridyl)ethane and 1,3-bis(4-pyridyl)propane were purchased from Aldrich and were used as received. 1,10-Phenanthroline (99.5%) was purchased from E-Merck India Ltd. All other chemicals were of AR grade.

Physical Measurements. Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra were measured from KBr pellets on a Nicolet 520 FTIR spectrometer. The magnetic measurements were carried out on polycrystalline samples using a Quantum Design MPMS SQUID magnetometer (applied field = 0.1 T) working in the temperature region 300−2 K. Diamagnetic corrections were estimated from Pascal's table.[5]

Synthesis of [Fe(N_3)$_2$(bpp)$_2$] (1). Diffusion reaction in a U-tube with ethylene glycol as diffusion mediate yielded yellowish brown crystals. An aqueous solution (4 mL) of Mohr salt (0.0981 g, 0.25 mmol) was disposed at one side of the diffusion tube, and a solution of bpp (0.0496 g, 0.25 mmol) in methanol (4 mL) and NaN_3 (0.0162 g, 0.25 mmol) in water was added to the other side. The U tube was gently kept at room temperature for several weeks. Pure powder sample of **1** was synthesized by mixing bpp in methanol (10 mL, 0.5 mmol) with Mohr salt (0.5 mmol) in water (10 mL), followed by addition of an aqueous solution of NaN_3 (10 mL, 1 mmol). Yield: 62%. Anal. Calcd for $C_{26}H_{28}FeN_{10}$: C, 58.16; H, 5.20; N, 26.09 (%). Found: C, 58.10; H, 5.09; N, 26.16 (%). IR spectra: 2057 (vs), 1613 (s), 1422 (w), 1340 (vw) cm^{-1}.

Syntheses of [Fe(N_3)$_2$(bpe)] (2) and [Fe(N_3)$_2$(phen)] (3). Compounds **2** and **3** were synthesized following the procedure adopted for complex **1** using bpe (0.046 g, 0.25 mmol) and phen (0.0496 g, 0.25 mmol) for **2** and **3**, respectively, instead of bpp. Deep brown crystals of **2** and reddish brown crystals of **3** suitable for X-ray diffraction were obtained by diffusion technique as for complex **1**. The yields were 72% and 78% for **2** and **3**, respectively. Elemental analyses are in good agreement with the calculated values. (**2**) Anal. Calcd for $C_{12}H_{12}FeN_8$: C, 44.42; H, 3.70; N, 34.55 (%). Found: C, 44.64; H, 3.62; N 35.30 (%). IR spectra: 2117 (s), 2074 (vs), 1068 (m) cm^{-1}. (**3**) Anal. Calcd for $C_{12}H_8FeN_8$: C, 44.98; H, 2.50; N, 34.98 (%). Found: C, 44.76; H, 2.35; N, 34.59 (%). IR spectra: 2079 (vs), 2053 (vs), 1425 (w) cm^{-1}.

Crystallographic Data Collection and Refinement. Crystal data and details of data collections and refinements for the structures reported are summarized in Table 1. Diffraction data of **1** were collected on a Nonius DIP-1030H system with Mo Kα radiation. A total of 30 frames were collected, each with an exposure time of 15 min, with a rotation angle of 6° about φ, and the detector at a distance of 90 mm from the crystal. Cell refinement, indexing, and scaling of the data sets were carried out using Mosflm[6] and Scala.[6] For **2** and **3**, reflections were collected on a STOE four-circle diffractometer equipped with an MAR-research image plate system and Mo Kα radiation. The crystals (**2** and **3**) were positioned at 70 mm from the image plate. A total of 100 frames for **2** and 95 frames for **3** were measured at 2° intervals with a counting time of 2 min. For **2**, the structure was found to be disordered and refined in space group $C2/c$. Attempts to refine an ordered model in space group Cc were unsuccessful. In space group $C2/c$ the Fe ion and bridging ligand possess a C_2 symmetry. This implies a disorder in the bridging ethane linkage and slightly also in the two pyridine rings. The two bridgehead carbons were refined slightly off the 2-fold axis but constrained the other five atoms in the two pyridine

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Table 1. Crystallographic Data and Details of Structure Refinements for Complexes **1**, **2**, and **3**

	1	**2**	**3**
formula	$C_{26}H_{28}FeN_{10}$	$C_{12}H_{12}FeN_8$	$C_{12}H_8FeN_8$
M_r	536.43	324.15	320.12
crystal system	monoclinic	monoclinic	triclinic
space group	$C\,2/c$	$C\,2/c$	$P\bar{1}$
a (Å)	19.355(4)	10.007(14)	7.155(12)
b (Å)	7.076(2)	13.789(18)	10.066(14)
c (Å)	22.549(4)	10.377(14)	10.508(14)
α (°)	90.00	90.00	109.57(1)
β (°)	119.50(3)	103.50(1)	104.57(1)
γ (°)	90.00	90.00	105.10(1)
volume (Å^3)	2687.7(11)	1392(3)	638.9(16)
Z	4	4	2
D_{calcd} (g cm^{-3})	1.326	1.546	1.664
μ (Mo Kα) (mm^{-1})	0.596	1.089	1.186
F(000)	1120	664	324
θ_{max} (°)	29.04	26.00	25.98
reflections collected	6478	1321	3859
unique reflections	3590	1321	2279
R_{int}	0.0309	0.043	0.1201
observed $I > 2\sigma(I)$	2769	990	1827
parameters	169	116	190
goodness of fit (F^2)	1.051	0.854	0.805
$R1$ ($I > 2\sigma(I)$) [a]	0.0453	0.0586	0.0793
$wR2$ [a]	0.1158	0.1707	0.2107
$\Delta\,\rho$ (e/Å^3)	0.454, −0.271	0.612, −0.532	0.624, −0.594

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(F_o{}^2)^2]^{1/2}$.

rings with C_2 symmetry. The azide groups were unaffected by the disorder. An empirical absorption correction was carried out for both data sets using the DIFABS program.[7]

All the structures were solved by Patterson and Fourier analyses[8] and refined by the full-matrix least-squares method based on F^2 with all observed reflections with anisotropic thermal parameter for non-hydrogen atoms.[8] The contributions of H atoms at calculated positions were included in the final cycles of refinement. All the calculations were performed using the WinGX System, Ver 1.64.02.[9]

Results and Discussion

Structure Description of Complex 1. The complex **1** exhibits a parallel interpenetration of 2D layers of (4,4) topology. These are formed by octahedral Fe(II) nodes connected by bpp ligands, while N_3 anions are end-on coordinated and pendant from the corrugated sheet, as depicted in Figure 1. The Fe atoms in one sheet occupy the exact centers of the rombohedral grid of the other, and the shortest Fe−Fe separation measured between metals pertaining to the two interpenetrated layers is 7.076 Å. The complex, which is isomorphous with the polymeric structure containing Mn,[10] represents one of the possible modes of parallel interpenetration of layers reported by Batten and Robson.[11]

The iron, positioned on a center of symmetry, (Figure 2) displays an octahedral coordination with bond distances involving bpp nitrogens that are slightly longer (2.229(16) and 2.286(15) Å) with respect to the Fe−N(azide) distances of 2.106(16) Å. The latter, which refers to a terminal N_3 ligand, is the shortest Fe−N(azide) distance among those reported in the present paper. Correspondingly, the N(5)−N(6) bond length appears slightly longer than the N(6)−N(7) (1.172(2) vs. 1.152(3) Å) with a coordination bond angle N(6)−N(5)−Fe of 137.6(14)°. The bpp linker adopts a TG (*trans-gauche*) conformation, with torsion angles about the propane chain of 168.7 and 60.9°, which leads to a metal−metal separation of 12.782 Å. Thus, the entangled structure is achieved through the flexibility of the bpp ligand because it can assume different conformations and consequently different N−N distances ranging from 3.9 to 10.1 Å,[12] the present being 9.11 Å.

Structure Description of Complex 2. The structure of **2** consists of a 2D arrangement in which double azide bridged iron(II) chains are connected through bpe ligands. These layers extend parallel to the crystallographic *bc* plane (Figure 3). The choice of space group *C*2/*c*, which locates the metal and py N donors on crystallographic 2-fold axes, infers a disordered arrangement for py rings (see Experimental Section), as already reported for isostructural compounds containing Mn, Co, and Ni as metal.[13]

The octahedral coordination bond angles do not exceed ±1.0° from ideal values, with four azides in the equatorial positions, and bpe nitrogen donors occupying the axial ones. All the Fe−N bond distances are comparable in length, ranging from 2.173(5) to 2.193(7) Å. The bpe ligands, spanning the metals at 13.786 Å, exhibit an anti conformation, and the almost linear azide (N−N−N of 177.2(5)°) bridges the Fe iron with bond angles of 121.2(3) and 136.3(4)°. In the 2D net the intermetallic separation through azide is 5.271 Å, while the shortest interlayer Fe−Fe distance is 8.519 Å.

Structure Description of Complex 3. Complex **3** discloses a polymeric arrangement (Figure 4) where the metal ions are connected by pairs of EO and EE azide ligands with an intermetallic separation of 3.347 and 5.229 Å, respectively. Along the chain the zigzag arrangement of metals shows an Fe−Fe−Fe angle of 111.18°. The distorted octahedral coordination geometry has equatorial Fe−N distances ranging from 2.152(6) to 2.195(5) Å, while the axial ones, correspondent to bond lengths Fe−N(11″) and Fe−N(23), are slightly longer (2.217(5) and 2.236(6) Å, see Figure 5). The azide anions are essentially linear and the end-on connected one shows, as expected, a shorter N(12)−N(13) of 1.158(8) Å for the pendant edge. As a comparison, the other N−N distances are within 1.176(7)−1.197(7) Å, which correspond to Fe−N−N bond angles in a range from 118.9(4) to 129.6(4)°. Adjacent chains exhibit interlocked phenantholines at about 3.5 Å to originate $\pi-\pi$ interactions among the piled planar ligands. The shortest interchain metal separation in the crystal packing is 8.677 Å. The structural features are similar to those containing chelating 2,2′-bipyridine instead of phenanthroline, where M = Co, Ni, and Fe[1i] and Mn.[14]

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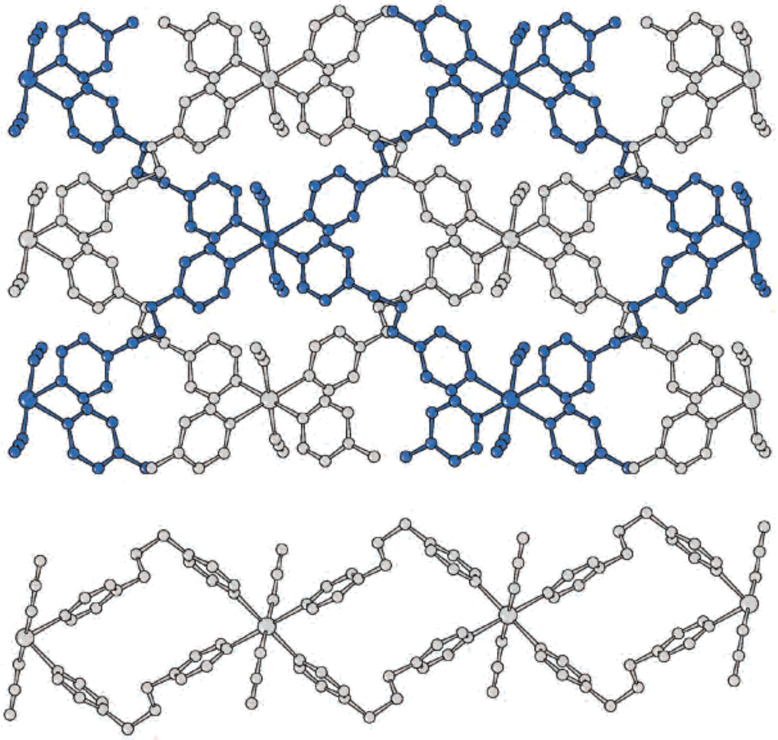

Figure 1. Top: View of the interpenetrated parallel nets (4,4 topology) in complex **1**. Bottom: A side view of one layer.

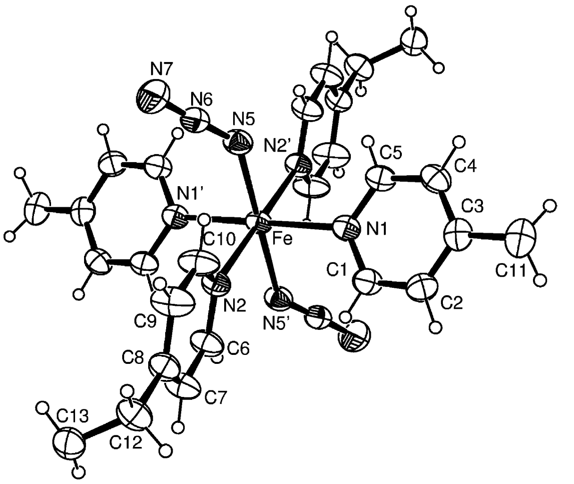

Figure 2. Metal coordination sphere in **1** (ORTEP drawing at 40% probability level) with labeling scheme of the independent unit. Selected bond distances (Å) and angles (°): Fe−N(1) 2.229(16); Fe−N(2) 2.286(15); Fe−N(5) 2.106(16); N(6)−N(5)−Fe, 137.64(14); N(7)−N(6)−N(5), 177.4(3).

Magnetic Properties. The electronic ground state of octahedral iron(II) complexes is orbitally degenerate ($^5T_2$). For mononuclear complexes, the presence of λ (spin−orbit parameter, which is about -100 cm^{-1} for isolated Fe(II) ion) and the strong orbital contribution to the exchange impede the possibility to apply the formula for a spin-only $S = 2$ system.[5,15] On the other hand, the presence of four unpaired electrons ($S = 2$) together with the usual distortion with regard to the octahedral symmetry, creates a zero-field splitting parameter (D), whose magnitude is very high for strongly distorted iron(II) complexes. Carlin, for example, reported some values close to 20 cm^{-1},[16] but currently this value lies close to ca. 6−10 cm^{-1}, as commented below. Taking into account that λ is operative for regular octahedral complexes and D works when there is an important distortion in the regular geometry, the magnetic behavior for real mononuclear Fe(II) complexes will depend on the geometry, and, thus, must be interpreted assuming λ and/or the D parameter in the corresponding formulas. Only, when the distortion is low, the theoretical possibility to use simultaneously the D and λ parameter will be interesting to prove, but, so far, it is impossible to carry out. Mabbs and Machin calculated and reported[15] the formula of the molar susceptibility for an ideal octahedral Fe(II) ion with λ parameter; O'Connor et al., reported the theoretical formula for an octahedral $S = 2$ system, with D and isotropic g value.[17] If the treatment of the magnetic behavior is difficult for a mononuclear Fe(II) complex, we can imagine that the magnetism of exchange-coupled transition-metal ions with this type of ground state is also extremely complicated, and it represents an open problem for which no general solution is yet available.[18] To study these systems it is usually assumed that a simple Hamiltonian with isotropic exchange interactions between the spins *without* or *with* single-ion anisotropy associated with the spin of each center ($S = 2$) is valid.

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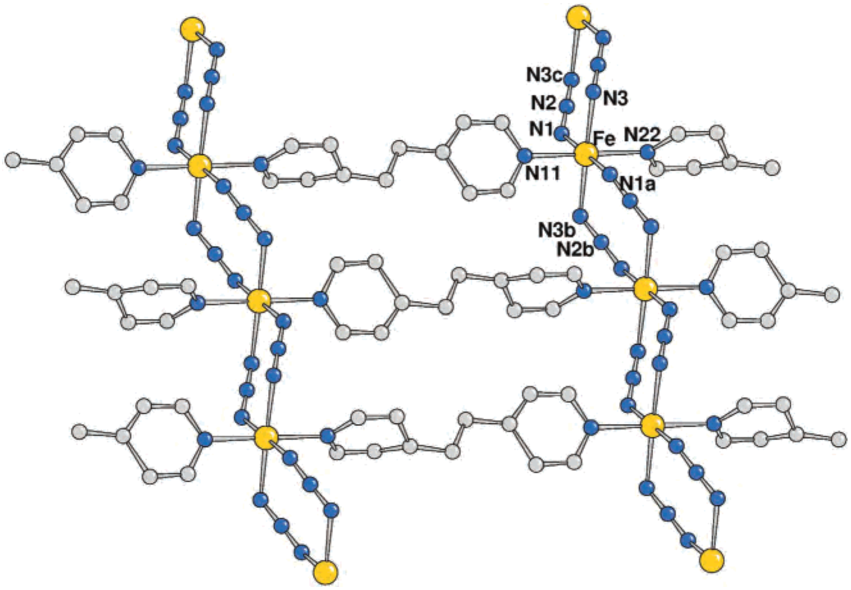

Figure 3. Layered arrangement of complex **2**. Of the disordered py rings, only one conformation is shown. Selected coordination bond distances (Å) and angles (°): Fe−N(1), 2.173(5). Fe−N(3), 2.183(5); Fe−N(11), 2.188(6); Fe−N(22), 2.193(7); N(1)−Fe−N(1a), 179.5(2); N(3)−Fe−N(3b), 178.5(2); N(11)−Fe−N(22), 180.0; N(1)−N(2)−N(3c), 177.2(5); N(2)−N(1)−Fe, 136.3(4); N(2b)−N(3b)−Fe, 121.2(3). Symmetry codes: (a) at $-x$, y, $^1/_2 - z$; (b) x, $^1/_2 - y$, $z - {}^1/_2$; (c) $-x$, $-y$, $-z$.

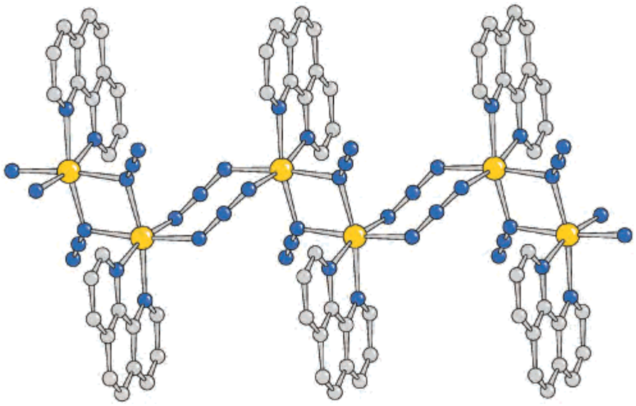

Figure 4. View of the polymeric chain for complex **3**.

Complex 1. The temperature dependence of $\chi_M T$ and χ_M for complex **1** is plotted in Figure 6 (for one Fe(II) ion). The $\chi_M T$ product measured under a magnetic field of 0.1 T decreases with decreasing temperature from 3.48 cm^3 mol^{-1} K at 300 K to ca. 1.70 cm^3 mol^{-1} K at 2.01 K. The value at room temperature is typical for Fe(II) ions with $g > 2.0$, due to the contribution of the spin−orbit coupling. The χ_M vs T curve starts from 0.01126 cm^3 mol^{-1} at 300 K and increases monotonically to 0.846 cm^3 mol^{-1} at 2.01 K. The shape of the $\chi_M T$ curve (300−30 K) is clearly indicative of no magnetic interaction. Significant zero-field splitting of the single ion ground-state quintet is evident in the low-temperature data. To evaluate the D parameter, the experimental $\chi_M T$ data have been fitted to the formula for a $S = 2$ mononuclear system with D parameter:[17]

$$\chi_{||} = C(2e^{-x} + 8e^{-4x})/(1 + 2e^{-x} + 2e^{-4x})$$

$$\chi_{\perp} = C[(6/x)(1 - e^{-x}) + 4/3x(e^{-x} - e^{-4x})]/(1 + 2e^{-x} + 2e^{-4x}) \quad (1)$$

with $\chi = (\chi_{||} + 2\chi_{\perp})/3$, $C = Ng^2\beta^2/kT$ and $x = D/kT$.

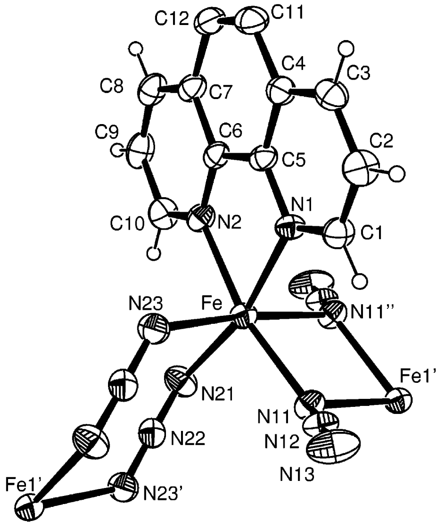

Figure 5. Coordination sphere of iron in **3** (ORTEP drawing at 40% probability level). Selected bond distances (Å) and angles (°): Fe−N(1), 2.195(5); Fe−N(2), 2.181(5); Fe−N(11), 2.152(6); Fe−N(21), 2.168(6); Fe−N(11″), 2.217(5); Fe−N(23), 2.236(6); N(1)−Fe−N(2), 76.0(2); N(1)−Fe−N(21), 167.1(2); N(2)−Fe−N(11), 167.8(2); N(11″)−Fe−N(23), 173.1(2); N(13)−N(12)−N(11), 177.8(6); N(21)−N(22)−N(23′), 178.1(6). Symmetry codes: (′) at $2 - x$, $2 - y$, $2 - z$; (″) $1 - x$, $2 - y$, $2 - z$.

According to eq 1, the best fit parameters for complex **1** have been determined to be $|D| = 5.54 \pm 0.2$ cm^{-1} and $g = 2.12 \pm 0.02$, consistent with data of the literature for Fe(II) complexes.[16] The final R value of the fit is very good ($R \approx 10^{-5}$). The reduced magnetization data ($M/N\beta$) at 2 K has been simulated using the so-obtained D and g parameters, and the simulation gave very good result, as can be seen in Figure 6 (bottom). For this simulation the MAGPACK program has been used.[26]

Complex 2. In general, the fit without the employment of the D parameter for Fe(II) ions has been used in several studies of the magnetic coupling of polynuclear iron com-

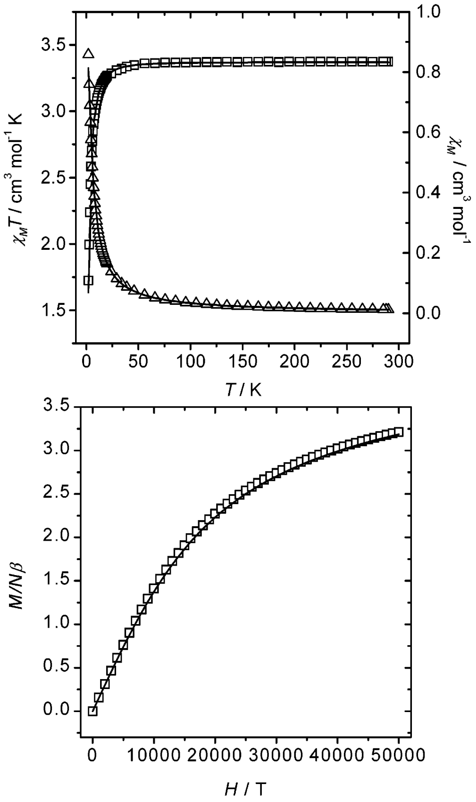

Figure 6. Top: Plots of χ_M and $\chi_M T$ vs T for **1**. Straight lines in both curves correspond to the best fit with the D parameter for a $S = 2$ mononuclear system. Bottom: Reduced magnetization of **1** at 2 K. Straight line corresponds to the simulation with the parameters obtained from the susceptibility curves.

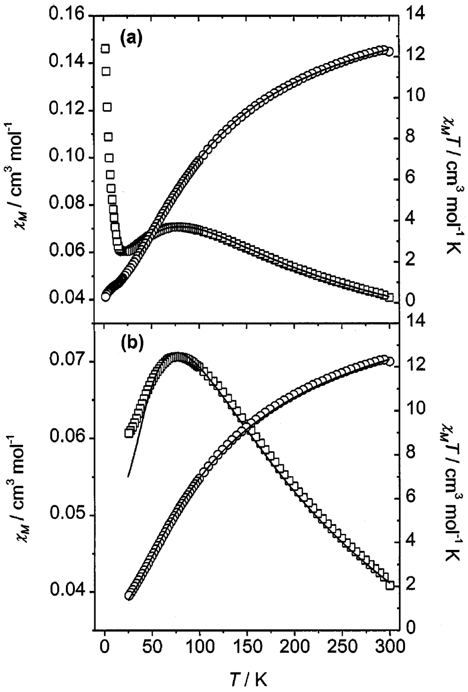

Figure 7. (a) Plots of χ_M and $\chi_M T$ vs T for **2**. Straight lines in both curves correspond to the best fit with the Fisher formula for $S = 2$ of using the CLUMAG program (see text for the results). (b) Plots of χ_M and $\chi_M T$ vs T for **2**, from 300 to 25 K. Straight lines in both curves correspond to the best fit with the MAGPACK program introducing the D parameter (see text for the results).

plexes. The results are relatively good when the J coupling parameter is appreciable.[19] Whereas in the scarce previously reported azido-bridged Fe(II) systems, either no study of the coupling was made,[20,2b] or the coupling was derived through the isotropic Hamiltonian. For example, using the Fisher formula for an one-dimensional chain with $S = 2$ (classical-like), the J parameter has been recently calculated for $[Fe(II)(N_3)_2(pyz)]$ (pyz = pyrazine).[21] This simplified model of exchange coupling applied in these studies assumes Heisenberg exchange between all spins and, thus, does not take into account the single-ion anisotropy or the spin−orbit coupling of the iron(II) centers. A more detailed analysis, including a term for the zero-field splitting, would require a considerably more complex theoretical treatment. Thus, although at a first approximation satisfactory fit of the experimental data with the simplified model can be obtained with Fe(II), new approaches are necessary including at least the D parameter of Fe(II). With this purpose, first Lippard et al. developed a theoretical computing model, incorporating isotropic exchange coupling, single-ion zero-field splitting, and g tensor anisotropy for the study of some trinuclear ferrous complexes.[22] More recently, Clemente-Juan et al., developed a new systematic study of several tetranuclear iron(II) complexes in which the study of the magnetic coupling was done considering the zero-field splitting parameter, D, of each individual Fe(II) ion.[23]

In the present case, the temperature dependence of $\chi_M T$ and χ_M for complex **2** is plotted in Figure 7 (for 4 Fe(II) ions). The $\chi_M T$ product measured under a magnetic field of 0.1 T decreases with decreasing temperature from 12.24 cm^3 mol^{-1} K at 300 K to ca. 0.28 cm^3 mol^{-1} K at 2.01 K. Whereas the χ_M curve is more indicative of the magnetic coupling: it starts at 0.0408 cm^3 mol^{-1} at 300 K, increases to give a round maximum at 78 K ($\chi_M = 0.0706$ cm^3 mol^{-1}), then decreases to 0.060 cm^3 mol^{-1} at 22 K and, finally, increases again to 0.14 cm^3 mol^{-1} at 2.01 K. Without considering this increasing at very low temperature (which can be due to some small percentage of mononuclear iron(II) impurities or to some features due to small ordering effect), the shape of the curve from 300 to 20 K is clearly indicative of antiferromagnetic coupling, in agreement with the presence of azide bridging ligands in end-to-end (1,3) coordination. Effectively, the EE coordination usually gives antiferromagnetic coupling for any metal.[1a] To evaluate the coupling constant, J, several approaches have been made. The simplest, but least accurate, is the hypothesis that

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complex **2** is a chain of classical $S = 2$ spins for which it is possible to apply the Fisher formula (eq 2).[24] In this expression, χ_M is a function of the J parameter due to exchange coupling along an infinite-spin, linear chain with $S = 2$, assuming that this large spin can be considered like classical:

$$\chi_M = 6Ng^2\beta^2/3kT\,[(1-u)/(1+u)] \qquad (2)$$

where $u = kT/12J - \coth(kT/12J)$.

According to eq 2, the best fit parameters for complex **2** have been determined to be $J = -17.9 \pm 0.2$ cm^{-1} and $g = 2.44 \pm 0.01$. For this calculation the curve has been taken from 300 to 30 K to avoid the effects at low temperature (vide infra) (Figure 7). The calculated value of g lies among the usual ones for octahedral Fe(II) (2.08−2.5).[23] The J value is consistent with the good magnetic mediating nature of the azide ligand. Another approach makes use of a full-diagonalization method, considering not classic (infinite) but quantum ($S = 2$) spins. To evaluate the exchange constant, J, a cyclic ring of four Fe(II) ions has been considered, using the following Hamiltonian

$$H = -J\,\Sigma\, S_iS_{i+1}\ (i = 1 \text{ to } 4)$$

Instead of infinite chain this cyclic ring of four iron(II) ions is not an excellent number to consider but a good approximation, because a greater number of iron(II) ions (8, for example) would complicate the calculation and the time of the calculation would increase exponentially. We have employed the CLUMAG program for this calculation, which uses the irreducible tensor operator (ITO) formalism,[25] and the curve has been taken from 300 to 30 K to avoid the effects at very low temperature, (vide infra) (Figure 7a). The best fit parameter varies slightly if the final temperature is 30 or 50 or 70 K, but the determined J values are close to $J_{AF} = -14.5 \pm 1$ cm^{-1} and $g = 2.34 \pm 0.01$. Once again, the calculated value of g lies among the usual ones for octahedral Fe(II) (2.08−2.5),[23] and the J value is consistent with the magnetic mediating nature of the azide bridging ligands. In all these fits the final R value is very good ($R \approx 10^{-5}$). Nevertheless, attempts to fit a one-dimensional complex of Fe(II) (Fisher formula or CLUMAG program) without considering the D term of the single ion, seem to be very unrealistic. Thus, to take into consideration this D parameter (zero-field splitting of the $S = 2$ ground state of each Fe(II) ions), we have tried to simulate the best results obtained with CLUMAG, using the MAGPACK program,[26,27] which allows introduction of the D parameter, very important, undoubtedly, at low temperature. The temperature dependence of χ_M for **2** has been simulated using the following Hamiltonian:

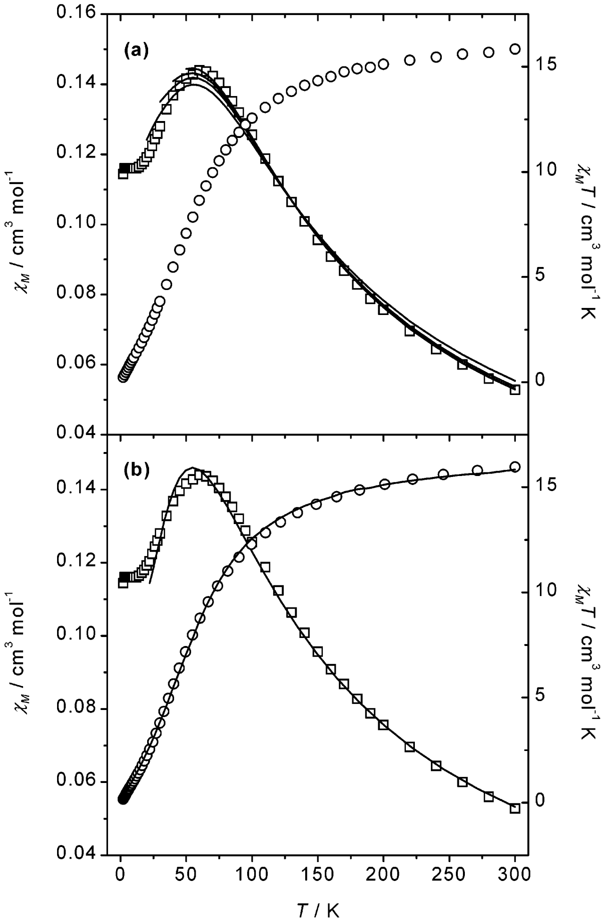

Figure 8. (a) Plots of χ_M and χ_MT vs T for **3**. Straight lines in both curves correspond to the best fit using the CLUMAG program (see text for the results). (b) Plots of χ_M and χ_MT vs T for **3**. Straight lines in both curves correspond to the best fit with the MAGPACK program introducing the D parameter (see text for the results).

$$H = -2J(S_1S_2 + S_2S_3 + S_3S_4 + S_4S_1) + D(S_{z1}^2 + S_{z2}^2 + S_{z3}^2 + S_{z3}^2)$$

Analytical expressions for eigenvalues and susceptibility cannot be derived because of the ZFS term. To calculate the energy levels and magnetic properties, diagonalization of the full matrix has been carried out.[26] With this assumption the best results have been obtained with the following parameters: $J = -15.6 \pm 1$ cm^{-1}; $g = 2.36$; and $|D| = 9 \pm 1$ cm^{-1} (Figure 7b). The J parameter is similar to that obtained without introducing the D parameter and the value of D is consistent with that reported earlier for other Fe(II) complexes.[23]

Complex 3. For **3** we have used approximately the same approach as that adopted for complex **2**. The temperature dependence of χ_MT and χ_M for complex **3** are plotted in Figure 8 (for 4 Fe(II) ions). The χ_MT decreases with decreasing temperature from 15.8 cm^3 mol^{-1} K at 300 K to 0.228 cm^3 mol^{-1} K at 2.0 K. The χ_M curve is more indicative of the magnetic coupling: it starts at 0.0526 cm^3 mol^{-1} at 300 K, increases to give a round maximum at 60 K ($\chi_M =$

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[27] As indicated in the text, the Hamiltonians used in the standard CLUMAG and MAGPACK programs are $H = -J\Sigma S_{ij}$ and $= -2\,J\Sigma S_{ij}$, respectively. Thus, for a comparison of calculated J values, all parameters simulated by the latter were multiplied by 2.

0.144 cm^3 mol^{-1}), then decreases to 0.120 cm^3 mol^{-1} at 20 K and, finally, there is a plateau of ca. 0.114 cm^3 mol^{-1} at 2.0 K. Without considering this plateau at very low temperature, the shape of the curve from room temperature to 20 K is clearly indicative of global antiferromagnetic coupling. The presence of azide bridging ligands alternated in end-to-end (1,3) and end-on (1,1) coordination modes suggests the presence of alternating ferro- and antiferromagnetic interactions. In this case, the application of Fisher formula was not possible, because this is valid only for homogeneous and not for alternating chains. Thus, to evaluate the exchange constant, J, a cyclic ring of four Fe(II) ions has been considered, using the following Hamiltonian

$$H = -J_1(S_1S_2 + S_3S_4) - J_2(S_2S_3 + S_4S_1)$$

In this case, we have assumed that the J parameters are alternately ferro- and antiferromagnetic. As for complex **2**, we have employed the CLUMAG program,[25] and for these calculations the curves have been taken from 300 to 20 K, 30K, 40 K, 50 K to avoid the effects at very low temperature (vide supra) (Figure 8a). The best fit parameters have been determined by varying the temperature (20−50 K). The best coupling parameters lie in the following range: J_F (EO) = 11.0 ± 1 cm^{-1}; J_{AF} (EE) = −13.0 ± 1 cm^{-1}, and g = 2.35 ± 0.01. As for complexes **1** and **2** the calculated values of g are among the usual ones for octahedral Fe(II) (2.08−2.5).[16,23] The J values are consistent with the good magnetic coupling behavior of the azide bridge. As for complex **2**, again we tried to improve the fit by adding the D parameter (zero-field splitting of the $S = 2$ ground state of each Fe(II) ion), using the MAGPACK program,[26,27] starting from the CLUMAG outcome. In this case, the temperature dependence of χ_M for **3** has been adjusted using the following Hamiltonian:

$$H = -2J_1(S_1S_2 + S_3S_4) - 2J_2(S_2S_3 + S_4S_1) + D(S_{z1}^2 + S_{z2}^2 + S_{z3}^2 + S_{z3}^2)$$

The best results correspond to the following parameters: $J_F = 12.6 \pm 0.5$ cm^{-1}, $J_{AF} = -12.5 \pm 0.5$ cm^{-1}, $|D| = 10 \pm 1$ cm^{-1}, and $g = 2.40 \pm 0.02$ (Figure 8b). From several simulations, the influence of parameter D is important only in the zone of the maximum of χ_M; from 300 to 100 K its influence is practically negligible.

From a structural point of view, the two $Fe(N_3)_2Fe$ (end-to-end) units in complexes **2** and **3** are too similar in distances and angles to allow a possible explanation for the differences between the J_{AF} parameters (limits are from −13 cm^{-1} in **2** to −19 cm^{-1} in **3**). The distortion of the octahedral geometry is different in all three cases (**1**, **2**, and **3**): complex **1** is the most symmetric. Although the three Fe−N1, Fe−N2, and Fe−N5 distances are slightly different, all trans N−Fe−N angles are 180°. This feature can explain why the calculated D parameter is only 5.5 cm^{-1}. On the contrary, complexes **2** and **3** are less symmetric (mainly complex **3**, owing to the bite created by phen ligand). In the last case, the trans N−Fe−N angles are less than 170°. Thus the D values (close to 10 cm^{-1} for both complexes) agree with the greater distortion, mainly for complex **3**. For rationalization of the present system, the syntheses of new Fe(II) complexes, containing azide bridges with comparable features, are necessary in order to study the magneto−structural correlations, like those reported for Ni^{II} or Mn^{II} systems.[1a]

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Supporting Information Available: X-ray crystallographic data in CIF format, and bond lengths and angles, atomic and hydrogen coordinates, and anisotropic displacement parameters (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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