

Enantiopure Tetranuclear Iron(III) Complexes Using Chiral Reduced Schiff Base Ligands: Synthesis, Structure, Spectroscopy, Magnetic Properties, and DFT Studies

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Four new tetranuclear iron(III) complexes of formula $[\{\text{Fe}(\text{L})_2\}_3\text{Fe}]$, **1–4**, have been prepared by reacting $[\text{Fe}(\text{ClO}_4)_3] \cdot 6\text{H}_2\text{O}$ with H_2L in methanol. Here, L^{2-} is the deprotonated form of *N*-(2-hydroxybenzyl)-*L*-valinol (H_2L^1), *N*-(2-hydroxybenzyl)-*L*-leucinol (H_2L^2), *N*-(5-chloro-2-hydroxybenzyl)-*L*-leucinol (H_2L^3), and *N*-(2-hydroxybenzyl)-*L*-phenylalaninol (H_2L^4). The complexes are prepared in an enantiomeric pure form. The complexes have been characterized with the help of IR, UV–vis, circular dichroism (CD), ^1H , and elemental analyses. The complex $[\{\text{Fe}(\text{L}^2)_2\}_3\text{Fe}] \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O} \cdot 2 \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$, crystallizes in enantiomeric pure form containing a propeller-like Fe_4O_6 core. ^1H and CD spectral studies of the four species are consistent with the structural similarities of the complexes in solution. Variable-temperature magnetic susceptibility of one case shows an intramolecular antiferromagnetic coupling between the Fe(III) ions. Magnetic measurements are in accord with the $S = 5$ ground state and suggest single molecular magnet behavior. The magnetic exchange coupling constant between the iron centers within the molecule is interpreted using broken-symmetry density functional theory calculation.

Introduction

Polynuclear chiral metal complexes have diverse applications in the area of transition metal catalysis^{1–4} and metallo-supramolecular^{5–8} chemistry as well as in bioinorganic^{9–12} chemistry. In this connection, the use of chiral ligands in the stereoselective synthesis^{13,14} of coordination compounds has been a burgeoning field in chemistry for the past few decades, as the combination of multiple stereogenic metal centers in polynuclear complexes leads to the formation of a large number of possible diastereomers. Moreover, there has

been considerable interest in recent years in the synthesis of polynuclear complexes that have ground electronic states with a large number of unpaired electrons in the context of preparation of molecular-based magnetic materials.^{15–23} In addition, they can act as single-molecular magnets (SMM).^{24–27} One research theme which plays a pivotal role in this field is the exploration of the synthesis of polynuclear complexes using suitable conformationally labile ligands,^{28,29}

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which may act simultaneously as bridging and terminal ligands to the metal ions. This has prompted us to initiate the search for polynuclear iron(III) complexes using chiral flexible ligands.

In this paper, we wish to report the synthesis of enantiomerically pure alkoxide bridged starlike iron(III) complexes. Although there are reports^{30–37} on the synthesis of star-shaped tetranuclear iron(III) complexes, none was incorporated using chiral ligands. In addition, stereoselective synthesis of such complexes is a challenging area to explore. The present work concerns the choice of dianionic O₂N-coordinating reduced Schiff base ligands derived from chiral L-amino alcohols and their complexation with iron(III). The X-ray structure of a representative case is studied. The complexes are characterized by UV–vis, circular dichroism (CD), and NMR spectroscopic techniques. The electrochemical behavior is also scrutinized. Static and dynamic magnetic measurements reveal that the compound has an *S* = 5 ground state. The theoretical interpretation of magnetic properties of the polynuclear complexes using density functional theory (DFT) methods^{21,38–40} is an emerging field of research aimed at gaining knowledge of the pathways of magnetic exchange interactions among the two paramagnetic ions. In the present article, the exchange coupling constants between the two adjacent iron centers are correlated by broken-symmetry density functional theory (BS-DFT) calculation.

Experimental Section

Materials. The reduced Schiff base ligands were prepared applying the general procedure as reported in the literature.⁴¹ All of the solvents were purified by standard procedures. All other chemicals were analytically pure and were used without further purification.

Caution! Perchlorate salts are highly explosive and should be handled with care and in small amounts.

Physical Measurements. UV–vis spectra were measured on a Perkin-Elmer LAMBDA 25 spectrophotometer. IR spectra were recorded with a Perkin-Elmer L-0100 spectrophotometer. ¹H NMR spectral measurements were carried out on a Bruker FT 300 MHz spectrometer with TMS as an internal reference.

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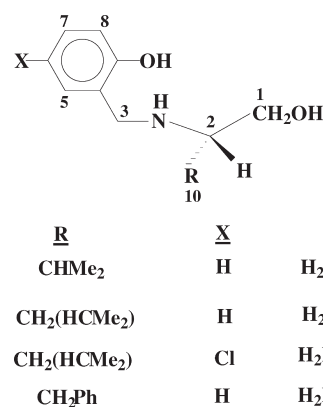
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Chart 1



The atom-numbering scheme used for ¹H NMR is the same as that used in crystallography and is given in Chart 1. Electrochemical measurements were performed (acetonitrile solution) on a CHI 620A electrochemical analyzer using a platinum electrode under a dinitrogen atmosphere. Tetraethylammonium perchlorate was used as a supporting electrolyte, and the potentials are referenced to the standard calomel electrode without junction correction. The cyclic voltammograms were recorded using a scan rate of 50 mV/sec with *iR* compensation in all cases. Magnetic measurements were carried out on polycrystalline samples with a Quantum Design MPMS XL SQUID susceptometer operating at a magnetic field of 0.1 T between 2 and 300 K. The diamagnetic corrections were evaluated from Pascal's constants. Microanalyses (C, H, N) were obtained from a Perkin-Elmer 2400 Series II elemental analyzer. CD spectra were recorded on a JASCO-815 polarimeter.

Crystallographic Studies. Single crystals of suitable quality for the X-ray diffraction study of the complex $[\{\text{Fe}(\text{L}^2)_2\}_3\text{Fe}] \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$, $2 \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$, were grown by diffusion of methanol into dichloromethane solution. The crystal loses solvent in the air, and hence, the data were collected in the presence of mother liquor taken in a capillary. The X-ray intensity data were measured at 100 K on a Bruker-Nonius SMART APEX CCD diffractometer (Mo K α , $\lambda = 0.71073$ Å). The detector was placed at a distance 6.0 cm from the crystal. A total of 606 frames were collected with a scan width of 0.3° at different settings of ϕ . The data were reduced in SAINTPLUS,⁴² and empirical absorption correction was applied using the SADABS package.⁴² Metal atoms were located using direct methods, and the rest of the non-hydrogen atoms emerged from successive Fourier synthesis. The structures were refined using the full matrix least-squares procedure on F^2 . All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions. Calculations were performed using the SHELXTL v.6.14 program package.⁴⁴ Molecular structure plots were drawn using ORTEP.⁴⁴ Relevant crystal data are given in Table 1.

DFT Study and Computational Details. The exchange coupling constant between the paramagnetic centers is studied on the basis of density functional theory coupling with the broken-symmetry approach (BS-DFT) proposed by Noodleman.^{46–48} The *J* values of the dinuclear complexes using the

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Table 1. Crystal Data and Structure Refinement Parameters for $[\{\text{Fe}(\text{L}^2)_2\}_3\text{Fe}] \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$

$[\{\text{Fe}(\text{L}^2)_2\}_3\text{Fe}] \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$	
formula	$\text{C}_{79}\text{H}_{122}\text{N}_6\text{O}_{15}\text{Fe}_4$
fw	1619.23
cryst system	orthorhombic
space group	$P2_12_12$
a (Å)	22.704(5)
b (Å)	28.963(6)
c (Å)	12.929(3)
α (deg)	90.00
β (deg)	90.00
γ (deg)	90.00
V (Å ³)	8502(3)
Z	4
D_{calcd} (Mg/m ³)	1.265
μ (mm ⁻¹)	0.732
θ (deg)	1.14 – 25.00
T (K)	100(2)
$R1, {}^a wR2^b [I > 2\sigma(I)]$	0.0490, 0.1369
GOF on F^2	1.076
Flack x^{45}	-0.011(15)

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

method given by Noodleman have been determined by calculating the energy difference between the high-spin state (E_{HS}) and the broken-symmetry state (E_{BS}), according to the following equation:

$$E_{\text{HS}} - E_{\text{BS}} = -2S_1S_2J$$

while with the nonprojected approach^{40,49} by Ruiz et al.

$$E_{\text{HS}} - E_{\text{BS}} = -(2S_1S_2 + S_2)J$$

using the Heisenberg Hamiltonian $\hat{H} = -J\hat{S}_1\hat{S}_2$. The term E_{HS} corresponds to the energy of the high-spin state and that of E_{BS} to the broken-symmetry state. Here, S_1 and S_2 are the spins of the paramagnetic centers, and in the present case $S_1 = S_2 = 5/2$ and $E_{\text{HS}} - E_{\text{BS}} = -12.5J$ and $E_{\text{HS}} - E_{\text{BS}} = -15J$ for the projected and nonprojected approaches, respectively.

The positive value of J indicates the high-spin ground state with parallel spin, that is, ferromagnetic character. The antiferromagnetic character is associated with the broken-symmetry state as the ground state with negative J values. Ground-state electronic structure calculations of the complexes have been carried out using DFT⁵⁰ methods with the Gaussian 03 program.⁵¹ Becke's hybrid

function⁵² with the LYP correlation function⁵³ was used throughout the study. We employed a double- ζ basis set⁵⁴ for C, N, O, and H, and LANL2DZ⁵⁵ valence and effective core potential functions⁵⁶ were used for iron and zinc atoms. All energy calculations were performed using the $SCF = \text{Tight}$ option of Gaussian to ensure sufficiently well-converged values for the state energies.

For simplification of the calculations, the atomic coordinates obtained from the crystal structure determination at room temperature (in $P6_522$ containing C_2 symmetry, Tables S1 and S2, Supporting Information) were used for the evaluation of coupling constant values. In all calculations, we have replaced the $-\text{CH}_2-\text{CH}(\text{CH}_3)_2$ group with the $-\text{CH}_3$ group in the ligand framework to reduce the considerable amount of computational expense.

Synthesis of Complexes. The complexes $[\{\text{Fe}(\text{L})_2\}_3\text{Fe}]$ were prepared using a general method with $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ and H_2L as starting materials. Details are given below for the complex **2**.

$[\{\text{Fe}(\text{L}^2)_2\}_3\text{Fe}]$, **2.** To 231 mg (0.5 mmol) of $[\text{Fe}(\text{ClO}_4)_3] \cdot 6\text{H}_2\text{O}$ in 15 mL of methanol was added 223 mg (1.0 mmol) of the ligand (HL^2) followed by 404 mg (4.0 mmol) of triethylamine. The resulting solution was stirred for 1 h, and a brick-red crystalline solid was obtained slowly over the course of the reaction. The solid was isolated by filtration and washed with methanol. Yield: 0.203 g (77%). Anal. calcd: C, 60.39; H, 7.40; N, 5.41. Found: C, 60.58; H, 7.52; N, 5.32. IR (KBr, cm^{-1}): $\nu(\text{Fe}-\text{O}_{\text{alkoxide}}-\text{Fe})$ 756; $\nu(\text{C}-\text{O}_{\text{phenolato}})$ 1286; $\nu(\text{C}-\text{O}_{\text{alkoxide}})$ 1060; $\nu(\text{NH})$ 3262. UV-vis ($\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) CH_2Cl_2): 240 (62 777); 280 (60 034); 443 (8313). CD ($\lambda_{\text{max}}/\text{nm}$ ($\Delta\epsilon/\text{M}^{-1}\text{cm}^{-1}$) CH_2Cl_2): 472 (-3.5); 315 (-29.00). ¹H NMR (δ (ppm), CDCl_3): 61.50 (2-CH, 1H); 36.10 (3-CH₂, 2H); 0.2 (5-CH, 7-CH) 6.8 and -8.11 (10-R, 9H); -38.20 (6-CH, 1H); -49.24 (8-CH, 1H). E_{pc} ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple): 1.11 V (irr).

Complex 1. Yield: 0.197 g (78%). Anal. calcd: C, 58.94; H, 7.00; N, 5.73. Found: C, 59.08; H, 6.95; N, 5.70. IR (KBr, cm^{-1}): $\nu(\text{Fe}-\text{O}_{\text{alkoxide}}-\text{Fe})$ 756; $\nu(\text{C}-\text{O}_{\text{phenolato}})$ 1286; $\nu(\text{C}-\text{O}_{\text{alkoxide}})$ 1060; $\nu(\text{NH})$ 3262. UV-vis ($\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) CH_2Cl_2): 240 (38675); 280 (32830); 450 (5866). CD ($\lambda_{\text{max}}/\text{nm}$ ($\Delta\epsilon/\text{M}^{-1}\text{cm}^{-1}$) CH_2Cl_2): 474 (-5.45); 313 (-22.60). ¹H NMR (δ (ppm), CDCl_3): 62.28 (2-CH, 1H); 36.43 (3-CH₂, 2H); 0.74 (5-CH, 7-CH) 7.8 and -7.51 (10-R, 7H); -38.32 (6-CH, 1H); -47.41 (8-CH, 1H). E_{pc} ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple): 1.07 V (irr).

Complex 3. Yield: 0.190 g (70%). Anal. calcd: C, 53.29; H, 6.19; N, 4.78. Found: C, 53.12; H, 6.32; N, 4.69. IR (KBr, cm^{-1}): $\nu(\text{Fe}-\text{O}_{\text{alkoxide}}-\text{Fe})$ 756; $\nu(\text{C}-\text{O}_{\text{phenolato}})$ 1286; $\nu(\text{C}-\text{O}_{\text{alkoxide}})$ 1060; $\nu(\text{NH})$ 3262. UV-vis ($\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) CH_2Cl_2): 240 (47 604); 290 (36 408); 450 (6139). CD ($\lambda_{\text{max}}/\text{nm}$ ($\Delta\epsilon/\text{M}^{-1}\text{cm}^{-1}$) CH_2Cl_2): 472 (-3.5); 315 (-29.00). ¹H NMR (δ (ppm), CDCl_3): 60.32 (2-CH, 1H); 37.24 (3-CH₂, 2H); 0.05 (5-CH, 7-CH); 8.82 and -8.79 (10-R, 9H); -47.14 (8-CH, 1H). E_{pc} ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple): 1.10 V (irr).

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Complex 4. Yield: 0.215 g (72%). Anal. calcd: C, 65.69; H, 5.85; N, 4.78. Found: C, 65.79; H, 5.92; N, 4.70. IR (KBr, cm^{-1}): $\nu(\text{Fe}-\text{O}_{\text{alkoxide}}-\text{Fe})$ 756; $\nu(\text{C}-\text{O}_{\text{phenolato}})$ 1286; $\nu(\text{C}-\text{O}_{\text{alkoxide}})$ 1060; $\nu(\text{NH})$ 3262. UV-vis ($\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) CH_2Cl_2): 240 (32978); 280 (26946); 446 (4764). CD ($\lambda_{\text{max}}/\text{nm}$ ($\Delta\epsilon/\text{M}^{-1}\text{cm}^{-1}$) CH_2Cl_2): 470 (-4.12); 302 (-31.30). $^1\text{H NMR}$ (δ (ppm), CDCl_3): 62.43 (2-CH, 1H); 35.24 (3-CH₂, 2H); 1.04 (5-CH, 7-CH); 10.48 and -7.84 (10-R, 7H); -39.88 (6-CH, 1H); -50.14 (8-CH, 1H). E_{pc} ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple): 1.10 V (irr).

Results and Discussion

Four dianionic tridentate reduced Schiff base ligands, $\text{H}_2\text{L}^1-\text{H}_2\text{L}^4$ (general abbreviation H_2L) are used in the present work (Chart 1), and the ligands have been synthesized using a reported procedure.⁴¹

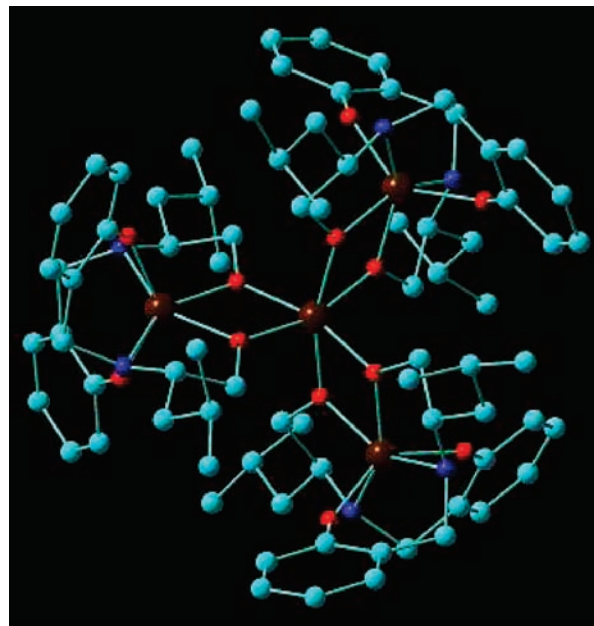
The reaction of $[\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}]$ with H_2L in a ratio of 2:3 in methanol followed by triethylamine addition at ambient conditions afforded brick-red-colored complexes of general formula $[\{\text{Fe}(\text{L})_2\}_3\text{Fe}]$ in good yields.

The new tetranuclear complexes were obtained in enantiomerically pure form. The ligands possess both terminal and bridging donor sites, and the choice of such conformationally labile chiral ligands helps us to achieve our goal in the context of synthesis of enantiopure alkoxide-bridged tetranuclear starlike iron(III) complexes. It is to be noted that elemental analyses reported in the Experimental Section are in agreement with the proposed chemical formulations.

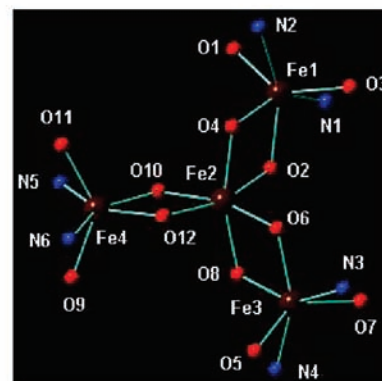
The NH stretch is observed at $\sim 3200\text{ cm}^{-1}$. The $\text{Fe}-\text{O}(\text{alkoxide})-\text{Fe}$ vibration occurs at a frequency of about 750 cm^{-1} .⁵⁷ The $\nu_{\text{C}-\text{O}(\text{phenolato})}$ and $\nu_{\text{C}-\text{O}(\text{alkoxide})}$ were obtained at 1286 and 1060 cm^{-1} , respectively.⁵⁷

Crystal Structure. The complex $[\{\text{Fe}(\text{L}^2)_2\}_3\text{Fe}]$ afforded single crystals as the solvate $[\{\text{Fe}(\text{L}^2)_2\}_3\text{Fe}] \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ in space group $P2_12_12$ with four formula units present per unit cell.⁵⁸ The choice of the coordinate was such as to conform to the L configuration of amino alcohol residue of the ligand and is assumed to be conserved during synthesis. A view of the tetranuclear entity is shown in Figure 1. Selected parameters of $[\text{Fe}(\text{L}^2)_2]^-$ and the FeO_6 core are listed in Table 2.

The tetranuclear entity consists of three $[\text{Fe}(\text{L}^2)_2]^-$ crystallographically distinct moieties. Each $[\text{Fe}(\text{L}^2)_2]^-$ unit acts as a monoanionic bidentate ligand through alkoxide oxygen for the central iron atom. This situation leads to the formation of star-shaped tetranuclear $\text{Fe}(\text{III})$ species containing the central FeO_6 core. The four iron centers in the molecule are placed on a plane in which the $\text{Fe} \cdots \text{Fe}$ distance is $\sim 3.22\text{ \AA}$ and the $\text{Fe}-\text{Fe}-\text{Fe}$ falls in the range $119.25-120.74^\circ$. The central iron atom is surrounded by six bridging alkoxide groups forming a distorted octahedral geometry. In the distorted octahedral geometry, the $\text{Fe}-\text{O}(\text{alkoxide})$ bond distances and $\text{O}-\text{Fe}-\text{O}$ angles vary between 1.922 and 2.003 \AA and



(a)



(b)

Figure 1. (a) Perspective view and atom labeling of $[\{\text{Fe}(\text{L}^2)_2\}_3\text{Fe}]$ (solvent molecules excluded). The iron, oxygen, nitrogen, and carbon atoms are emphasized in brown, red, blue, and cyan, respectively. (b) The view of $\text{Fe}_4\text{N}_6\text{O}_{12}$ core.

72.01 and 163.60° , respectively. The structural parameters of the $[\text{Fe}(\text{L}^2)_2]^-$ units are comparable where the coordination site of iron is occupied by two amine nitrogen, two phenolato oxygen, and two alkoxide oxygen atoms. The $\text{Fe}-\text{N}$ lengths, as expected, are larger than the $\text{Fe}-\text{O}$ distances, and on the other hand, the $\text{Fe}-\text{O}(\text{alkoxide})$ distances are larger than the $\text{Fe}-\text{O}(\text{phenolato})$ ones.

It is noted that, besides the L configuration of the amino alcohol residue, the amine nitrogen atom becomes stereogenic through the complexation with the iron center. Thus, several isomers are to be expected, depending on relative disposition of the amine hydrogen atom, but in the present case, only the (R)- configuration is observed in the lattice. Moreover the chelation of six bridging alkoxide groups also generates a stereogenic center on the central iron. Therefore, at least the Δ and Λ isomers are expected in the lattice with an L configuration of the amino alcohol residue. However, interestingly, the molecule crystallizes exclusively in the

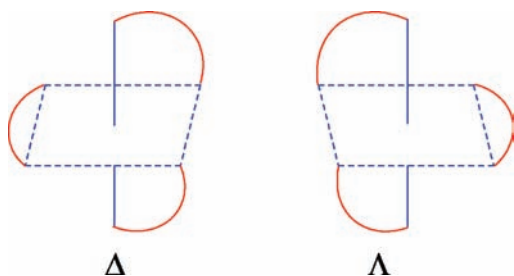
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(58) Following the suggestion made by one of the reviewers, we have performed the X-ray structure at 100 K for better refinement of the structure. Previously, we had collected the data at room temperature, and the crystal system was $P6_522$, having C_2 symmetry. The bond distances and angles for both of the cases are comparable. The relevant crystal data and selected parameters for room-temperature data collection are given in the Supporting Information (Tables S1 and S2).

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[\text{Fe}(\text{L}^2)]^-$ and FeO_6 Core

Distances			
Fe1–O1	1.932(3)	Fe3–O6	1.996(3)
Fe1–O2	2.007(3)	Fe3–O7	1.944(3)
Fe1–O3	1.915(3)	Fe3–O8	2.003(3)
Fe1–O4	2.003(3)	Fe4–O9	1.936(3)
Fe1–N1	2.276(4)	Fe3–N3	2.266(4)
Fe1–N2	2.248(4)	Fe3–N4	2.283(4)
Fe2–O2	1.975(3)	Fe4–O10	2.009(3)
Fe2–O4	1.973(3)	Fe4–O11	1.922(3)
Fe2–O6	1.981(3)	Fe4–O12	2.002(3)
Fe2–O8	1.982(3)	Fe4–N5	2.254(4)
Fe2–O10	1.972(3)	Fe4–N6	2.268(4)
Fe2–O12	1.970(3)	Fe1...Fe2	3.206(5)
Fe3–O5	1.913(3)	Fe2...Fe3	3.211(4)
		Fe2...Fe4	3.223(4)
Angles			
O1–Fe1–O2	109.79(14)	O5–Fe3–N4	78.35(14)
O1–Fe1–O3	135.63(15)	O6–Fe3–O7	105.63(14)
O1–Fe1–O4	105.98(14)	O6–Fe3–O8	72.12(12)
O1–Fe1–N1	84.29(15)	O6–Fe3–N3	75.87(13)
O1–Fe1–N2	79.58(15)	O6–Fe3–N4	146.97(13)
O2–Fe1–O3	104.97(14)	O7–Fe3–O8	109.00(14)
O2–Fe1–O4	72.01(12)	O7–Fe3–N3	80.64(14)
O2–Fe1–N1	75.12(12)	O7–Fe3–N4	84.55(14)
O2–Fe1–N2	147.81(13)	O8–Fe3–N3	147.97(13)
O3–Fe1–O4	110.44(14)	O8–Fe3–N4	74.85(13)
O3–Fe1–N1	78.79(14)	N3–Fe3–N4	137.16(14)
O3–Fe1–N2	85.55(15)	O9–Fe4–O10	107.71(14)
O4–Fe1–N1	147.12(13)	O9–Fe4–O11	134.14(16)
O4–Fe1–N2	75.81(13)	O9–Fe4–O12	109.88(15)
N1–Fe1–N2	137.07(14)	O9–Fe4–N5	83.99(15)
O2–Fe2–O4	73.31(12)	O9–Fe4–N6	80.34(14)
O2–Fe2–O6	99.18(13)	O10–Fe4–O11	109.22(14)
O2–Fe2–O8	95.33(13)	O10–Fe4–O12	70.94(12)
O2–Fe2–O10	94.99(13)	O10–Fe4–N5	75.09(13)
O2–Fe2–O12	163.60(13)	O10–Fe4–N6	145.73(13)
O4–Fe2–O6	95.22(13)	O11–Fe4–O12	107.21(14)
O4–Fe2–O8	162.37(13)	O11–Fe4–N5	80.19(14)
O4–Fe2–O10	97.64(13)	O11–Fe4–N6	84.18(14)
O4–Fe2–O12	97.54(13)	O12–Fe4–N5	145.79(13)
O6–Fe2–O8	72.90(12)	O12–Fe4–N6	75.00(13)
O6–Fe2–O10	163.10(13)	N5–Fe4–N6	139.14(14)
O6–Fe2–O12	95.13(12)	Fe1–O2–Fe2	107.22(13)
O8–Fe2–O10	96.74(13)	Fe1–O4–Fe2	107.46(14)
O8–Fe2–O12	96.50(13)	Fe1–O6–Fe2	107.65(13)
O10–Fe2–O12	72.38(12)	Fe2–O8–Fe3	107.32(13)
O5–Fe3–O6	110.94(13)	Fe2–O10–Fe4	108.12(14)
O5–Fe3–O7	135.69(15)	Fe2–O12–Fe4	108.50(13)
O5–Fe3–O8	105.44(14)	Fe1...Fe2...Fe3	120.74(6)
O5–Fe3–N3	84.78(14)	Fe1...Fe2...Fe4	119.25(4)
		Fe3...Fe2...Fe4	120.01(7)

Δ form. The isolation of a homochiral Fe_4O_6 propeller containing achiral ligands was also reported.³⁵



To get better insight into the stability of the isomers, we have performed single-point energy calculations in

the gas phase of different optical antipodes in which the $-\text{CH}_2-\text{CH}(\text{CH}_3)_2$ group is replaced by a $-\text{CH}_3$ group in the model systems (Figure 2). It has been found from the energy calculation that the Δ form having an L configuration of the amino alcohol residue of H_2L (**L- Δ**) and its optical antipode, **D- Δ** , exhibit identical energy. Similarly, Λ with a D configuration (**D- Λ**) and the corresponding antipode, **L- Λ** , are of the same energy. However, in the present case, Δ with an L configuration (**L- Δ**) is energetically more stable by 270 kcal/mol than Λ with an L configuration (**L- Λ**). The stability of one isomer can be attributed to the steric effect of the ligand moiety, and it is believed that the R group of the L-amino alcohol residue of H_2L gets more open space (Figure 2) and exerts minimum steric repulsion with the remaining ligand part in the isomer **L- Δ** compared to **L- Λ** , which favors the formation of the observed isomer.

UV–Vis and CD Spectra. The electronic and CD spectra of the complexes are measured in methylene chloride solution, and the corresponding spectral data are given in the Experimental Section. The complexes exhibit intense bands near 240 and 280 nm, and these bands are attributed to the $\pi-\pi^*$ transition of the organic moiety. The relatively broad absorption bands at 320 and 440 nm can be assigned to $\text{O}_{(\text{phenolato/alkoxide})}^- \rightarrow \text{Fe}(\text{III})$ charge transfer transitions (LMCT)^{59,60} from p_π orbitals to d_{π^*} and d_{σ^*} orbitals, respectively. The CD spectra of the ligand (H_2L^2) and complex **2** are shown in Figure 3a and b, respectively.

The pronounced cotton effect observed for the LMCT transitions at 480 and 305 nm of complexes **1–4** demonstrates the asymmetric induction from the enantiopure organic ligands to the iron center.

All of the complexes display nearly identical features; hence, the CD spectral study of the bulk products reveals that the complexes have the same stereochemical configurations by virtue of their nearly identical CD spectra.

^1H NMR Spectra. ^1H NMR spectra are very useful for learning more about the solution state behavior of the complexes containing chiral ligands. All of the complexes are paramagnetic and display paramagnetic resonances with broad linewidths in CDCl_3 solution. The ^1H NMR spectrum of $[\{\text{Fe}(\text{L}^2)_2\}_3\text{Fe}]$ is shown in Figure 4. NMR spectral data of the complexes are given in the Experimental Section. The resonance assignments have been made on the basis of relative intensities and their width analyses.^{61–63} The numbering scheme is in accordance with that in Chart 1.

The resonances located in the crowded 10.0–0.0 ppm region can be assigned to 5-CH, 7-CH, and the proton of 10-R of the amino alcohol residue. Two other resonances at 61.5 and 36.10 are assigned as the proton attached to the chiral carbon atom (2-CH) and as the 3- CH_2 protons, respectively. The remaining proton resonances are observed

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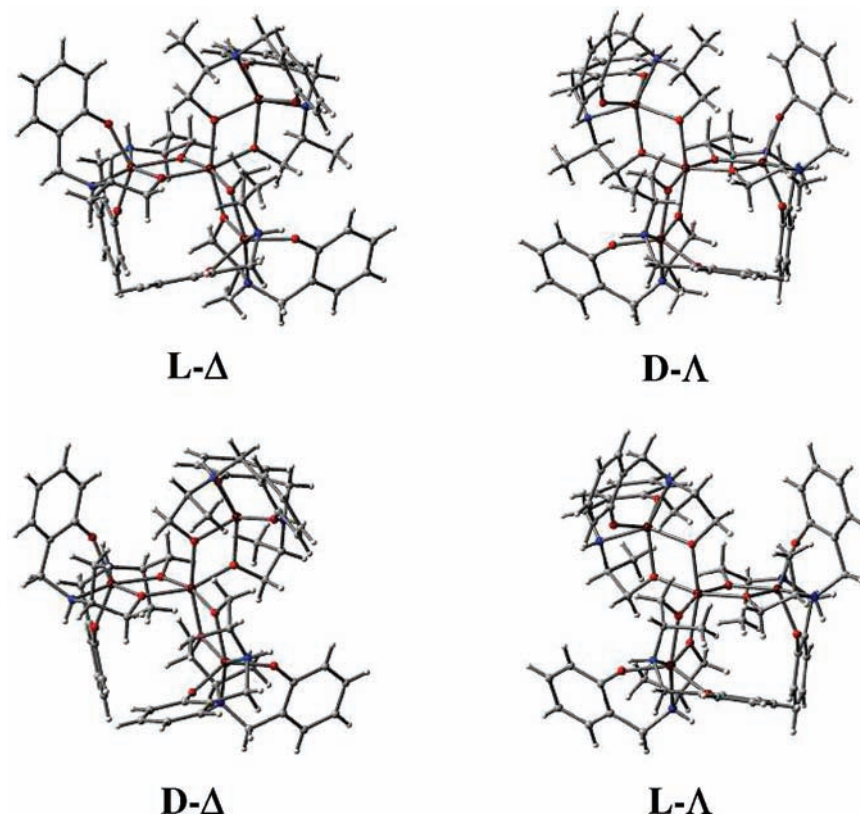


Figure 2. Optical antipode of model systems.

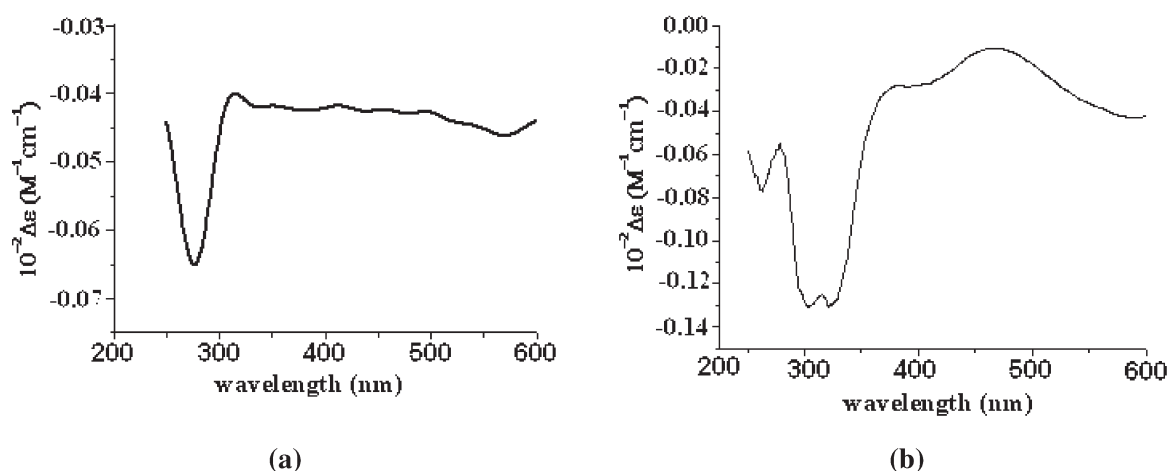


Figure 3. CD spectra of (a) H_2L^2 (b) $[{Fe(L^2)_2}_3Fe]$.

in the region -6.0 to -50.0 ppm. The peaks near -38.0 and -49.0 ppm can be attributed to $6-CH$ (this peak is absent when $6-CH$ is replaced by $6-CCl$, H_2L^3) and $8-CH$ protons, respectively. The $1-CH_2$ resonance has been presumed to be simply broadened and paramagnetically shifted beyond detection.⁶⁴ In summary, although the linewidths of the resonances are broad in nature, the 1H spectral data reveal that only one isomer is observed in solution, which is also supported from the CD spectral study.

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Magnetic Properties. The $\chi_M T$ product for **2** (χ_M being the molar magnetic susceptibility per Fe_4 unit) is given in Figure 5 in the form of a $\chi_M T$ versus T plot. $\chi_M T$ first decreases upon cooling down from room temperature, goes through a minimum around 166 K, and then reaches a maximum at around 15 K of $15.54 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. Below this temperature, $\chi_M T$ decreases to reach a value of $11.89 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K. This magnetic behavior is characteristic of “ferric stars”, where the dominant antiferromagnetic interaction between the central and peripheral high-spin iron(III) centers generates an irregular spin-state structure with an $S = 5$ ground state.^{30–37} In fact, the value at the maximum is close to the expected

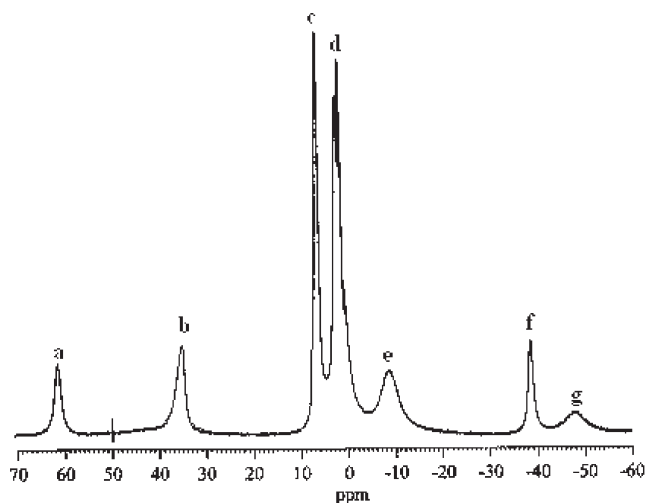
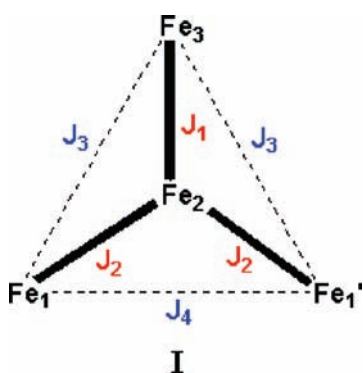


Figure 4. Proton NMR spectrum (300 MHz, +70 to -50δ) of $[\{\text{Fe}(\text{L}^2)_2\}_3\text{Fe}]$ in CDCl_3 . Resonances *a* (for 2-CH); *b* (for 3-CH₂); *c* (for 5-CH, 7-CH); *d* and *e* (protons of 10-R); *f* (for 6-CH); and *g* (for 8-CH).

value for an $S = 5$ state of $15 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ with $g = 2$. Because of the absence of significant intermolecular contacts, the decrease in $\chi_M T$ below 15 K is due to saturation and an anisotropic effect (ZFS). In keeping to the C_2 symmetry of the tetranuclear molecule of **2**, the data were quantitatively fitted using a Heisenberg spin-Hamiltonian with the two nearest neighbors (J_1 and J_2) and two next-nearest neighbors (J_3 and J_4) exchange coupling constants, as in **I**. A ZFS term common for the four iron sites was also considered. Therefore, the complete Hamiltonian is (the spin numbering follows the Fe atoms in Figure 1):

$$H = -J_1 S_2 S_3 - J_2 (S_2 S_1 + S_2 S_{1'}) - J_3 (S_3 S_1 + S_3 S_{1'}) - J_4 S_1 S_{1'} + \sum_i D_i (S_i^z)^2 + g\beta S H$$



Simulation of the $\chi_M T$ versus T data (see Figure 5) using the MAGPACK⁶⁵ program allowed for the estimation of the magnetic parameters: $J_1 = -23.6 \pm 0.2 \text{ cm}^{-1}$, $J_2 = -21.3 \pm 0.2 \text{ cm}^{-1}$, $J_3 = 2.0 \pm 0.1 \text{ cm}^{-1}$, $J_4 = 2.2 \pm 0.1 \text{ cm}^{-1}$, $g = 2.04 \pm 0.02$, and $D_{\text{Fe}} = 1.6 \text{ cm}^{-1}$ with $R = 5.6 \times 10^{-5}$ [$R = \sum (\chi_{\text{obs}} - \chi_{\text{calcd}})^2 / \sum (\chi_{\text{obs}})^2$]. However,

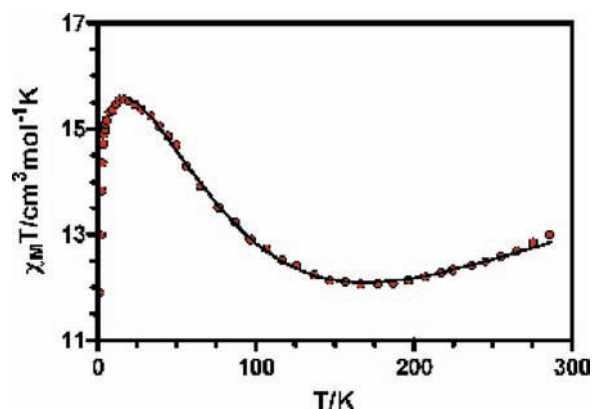


Figure 5. Temperature dependence of the $\chi_M T$ product at 1000 Oe for **2**.

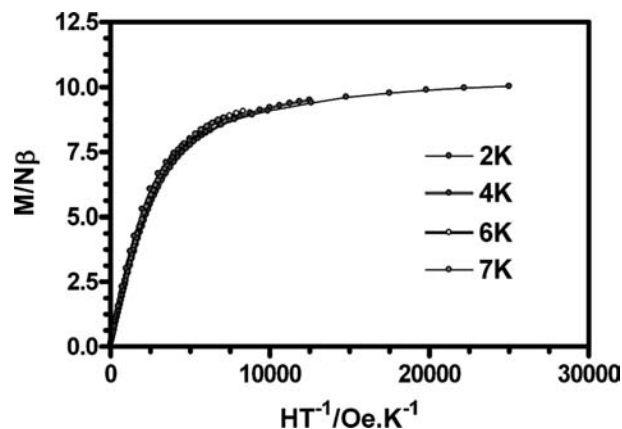


Figure 6. M vs H/T data for **2**.

these parameters do not reproduce well the maximum, and D_{Fe} is too large for iron(III) complexes.⁶⁶ In view of this, we decided to analyze the $T > 20 \text{ K}$ data, leading to the following magnetic parameters: $J_1 = -22.2 \pm 0.2 \text{ cm}^{-1}$, $J_2 = -21.7 \pm 0.2 \text{ cm}^{-1}$, $J_3 = 2.1 \pm 0.1$, $J_4 = 2.2 \text{ cm}^{-1} \pm 0.1$, and $g = 2.04 \pm 0.02$ with $R = 1.0 \times 10^{-5}$. It should be noted, as found in other similar Fe_4 complexes,^{30–37} that to obtain an accurate fit of the magnetic data it was necessary to introduce ferromagnetic exchange constants between the next-nearest neighbors (J_3 and J_4).

The mean value of J_1 and J_2 well agrees with the value of -21.9 cm^{-1} calculated using Lippard's empirical relationship between J and the average of the shortest distance between the iron(III) and the oxygen bridging atom in oxo-bridged dinuclear iron(III) complexes.⁶⁷ The isothermal magnetization at 2 K as a function of the applied field reveals a saturation under 5 T of $10.03 \text{ N}\beta$, in good agreement with the expected value for an $S = 5$ ground state ($M = 10 \text{ N}\beta$). The $S = 5$ Brillouin function rather well reproduces the experimental data with $g = 2.02$ (**2**), indicating the absence of thermally populated excited states at 2 K. In fact, if a 3-fold symmetry is assumed, the first excited state is a double-degenerated $S = 4$ state lying $\approx 71 \text{ cm}^{-1}$ above the $S = 5$ ground state.

The M versus H/T curves (Figure 6) are roughly all superimposed on a single master curve, indicating a

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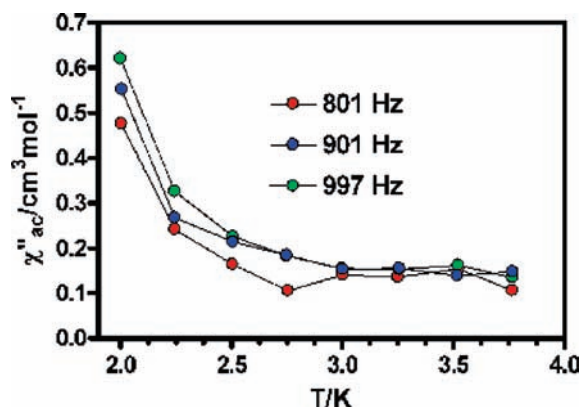


Figure 7. Temperature dependence of the out-of-phase ac susceptibility at different frequencies.

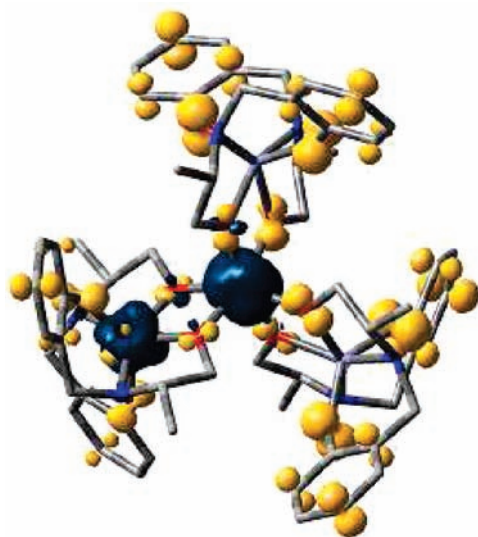


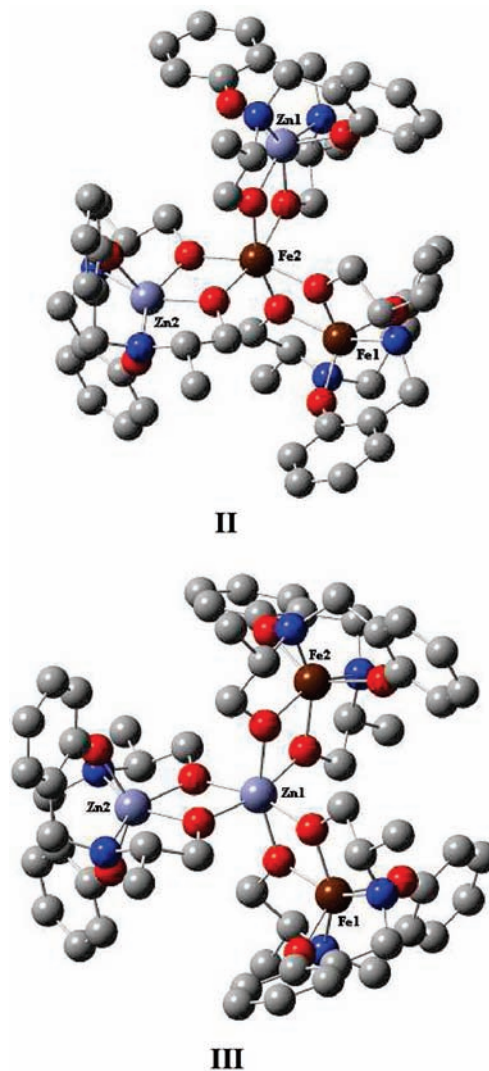
Figure 8. Spin density plot of **II**.

small magnetic anisotropy in this compound. Because other simple “ferric star” Fe_4 complexes were found to behave as SMMs,^{30–37} we have performed ac magnetic susceptibility measurements on compound **2** in the 1–5 K range, using a 3G alternating field (Figure 7). Although no maxima were observed above 2 K, the out-of-phase signals, χ''_{ac} , were clearly frequency-dependent, which may be an indication of slow relaxation of the magnetization and therefore of SMM behavior.

SMMs exhibit slow relaxation of the magnetization by a combined effect of negative axial anisotropy ($D < 0$) and a high-spin ground state (S_T). These two characteristics give rise to relaxation that is purely thermally induced by an energy barrier (equal to $|D|S_T$ for integer spins and $|D|(S_T^2 - 1/4)$ for half-integer spins) between the two equivalent configurations $m_s = \pm S_T$. Because, at equal temperatures, the out-of-phase signal in **2** appears at a higher frequency than in other Fe_4 SMMs,^{30–37} the thermally activated barrier in **2** must be of small magnitude, which probably is a consequence of its small anisotropy.

Theoretical Interpretation. The room-temperature χ_{MT} value corresponds to 10 unpaired electrons; therefore, the calculation is performed taking $S = 5$ as a high-spin

state. In order to understand the behavior of the unpaired electrons between the two iron(III) centers, the magnetic exchange constant of nearest neighbors (J_5) and equal next-nearest-neighbor (J_6) exchange coupling constants have been calculated. To evaluate J_5 , two terminal iron(III) centers are replaced by two diamagnetic Zn(II) ions,⁶⁸ and for J_6 the central and one terminal iron ion are replaced by the Zn(II) ions, and this replacement produces Fe_2Zn_2 complexes, as depicted in **II** and **III**, which become magnetically equivalent with the binuclear iron(III) complex.⁶⁹ The J values obtained (using nonprojection equation) from DFT calculation are $J_5 = -54 \text{ cm}^{-1}$ and $J_6 = 10 \text{ cm}^{-1}$ for **II** and **III**, respectively.



The antiferromagnetic interaction between the nearest-neighbor iron ions (in **II**) may be explained by considering the distribution spin density of the broken symmetry state and the nature of singly occupied molecular orbitals (SOMOs). The spin-density distribution of the broken-symmetry state provides valuable insights into the relationship between the electronic structure and exchange

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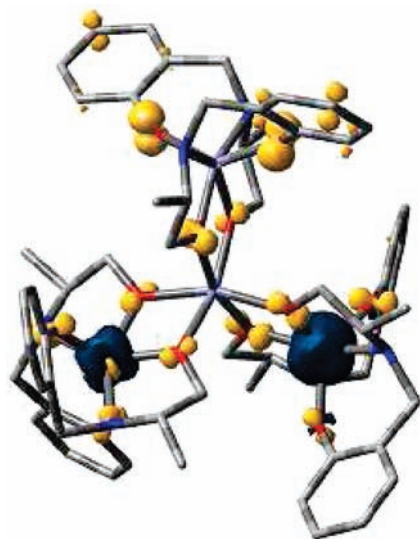


Figure 9. Spin density plot of **III**.

coupling constant between the paramagnetic ions, and hence the spin density for the $S = 0$ state of model Fe_2Zn_2 species has been calculated. The spin density plot of the Fe_2Zn_2 systems, **II** and **III**, are given in Figures 8 and 9, respectively.

The SOMOs of **II** are also depicted in Figure 10. The antiferromagnetic behavior of the paramagnetic center

is mainly governed by the degree of delocalization of unpaired electrons through the bridging ligands. It is to be noted that the extent of delocalization of unpaired electrons increases if the SOMOs are made by the participation of the coordinating atoms of the ligand, and this situation leads to the enhancement of the electron density of the donor atoms. It is clear from Figure 10 that six SOMOs (**IIa**, **IIb**, **IIc**, **IId**, **IIf**, and **IIh**) out of 10 are associated with the combination of hybrid d orbitals of iron and hybrid $p\pi$ orbitals of the alkoxy oxygen atoms. Therefore, it is evident from the plot of frontier orbitals that the superexchange phenomenon between the two iron centers in **II** is taking place through the hybrid d orbital of iron and $p\pi$ orbitals of the bridging alkoxy oxygen. Our observation is also supported from the spin density plot (Figure 8), and it is understandable that the electron density is delocalized between the metal's d orbital and the hybrid orbitals of the bridging ligand. Moreover, the calculated spin density of the bridging alkoxy oxygen atom is 0.2528, which is also reflected in the spin density plot (Figure 8), corresponding to the $S = 5$ state. The considerable amount of spin density on the bridging atom results in significant overlap between the magnetic orbital of the metal ion and the hybrid orbital of the bridging oxygen atom, resulting in anti-ferromagnetic interaction.

However, in **III**, it is believed that the through-space overlap of the magnetic orbital (Figure 9) is probably

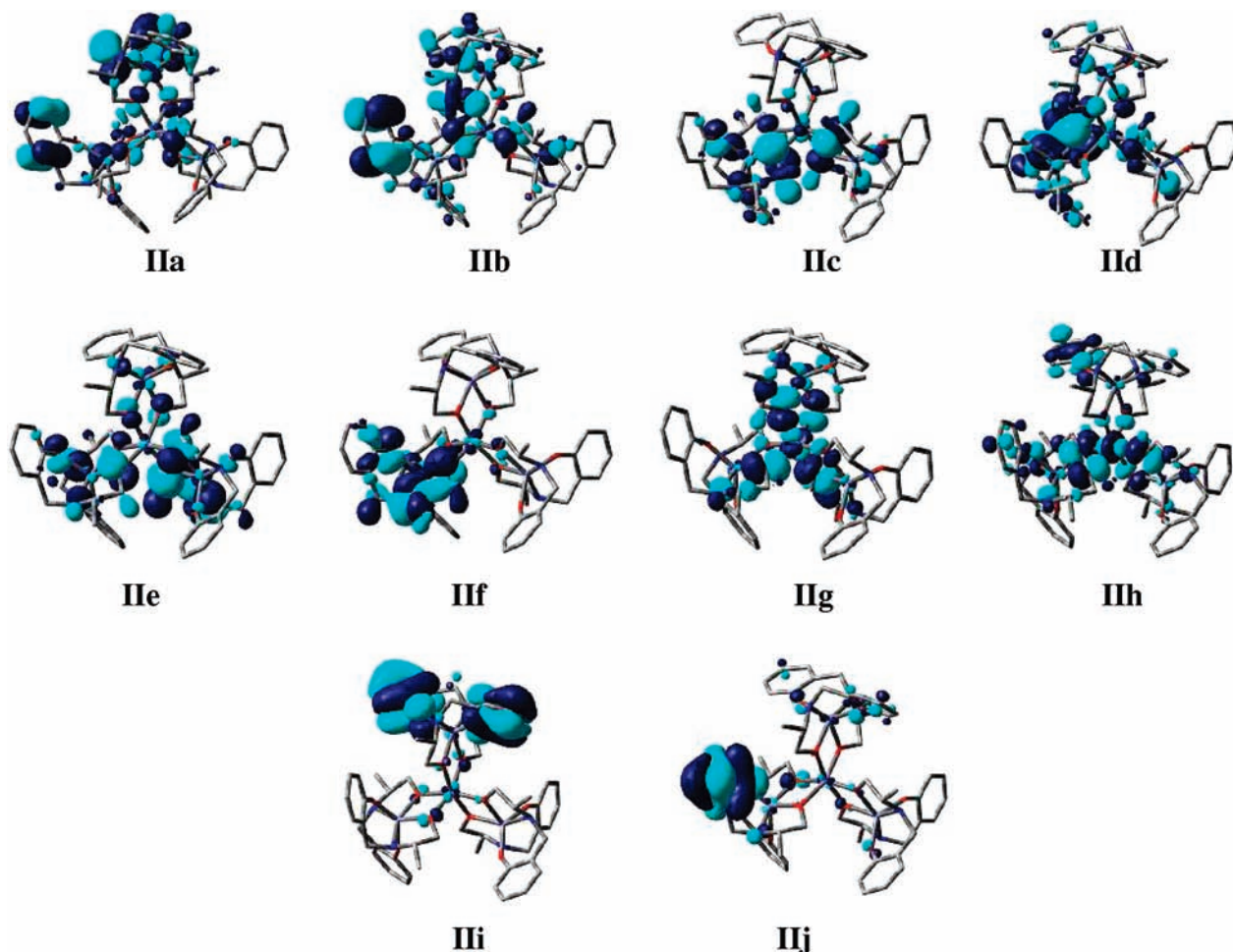


Figure 10. SOMO plots of **II**.

responsible for the ferromagnetic coupling between the two terminal iron centers.

In summary, the delocalization of unpaired electrons through the bridging atoms is attributed to the antiferromagnetic coupling of nearest neighbors (J_5), and the through-space overlap of the magnetic orbitals signals the ferromagnetic interaction of equal next-nearest neighbors (J_6). Thus, the theoretical results matched well with the experimental findings.

Conclusion

The article presented herein describes the coordination chemistry of iron(III) with the conformationally labile diacidic tridentate reduced Schiff base ligands derived from chiral α -amino alcohol. These ligands were found to react stereoselectively with $[\text{Fe}(\text{ClO}_4)_3] \cdot 6\text{H}_2\text{O}$ to give starlike tetranuclear complexes in an enantiopure Δ form in the solid-state, as confirmed by X-ray structure determination of one case. The complexes are characterized by spectroscopic techniques. ^1H and CD spectral studies also support the formation of one isomer in solution. The complexes show SMM behavior. The magnetic exchange pathways between

the iron centers have been determined using the BS-DFT method. The exploration of synthesis of polynuclear enantiopure chiral complexes using different chiral ligands of various transition metal ions and investigation of their behavior is in progress.

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Supporting Information Available: X-ray crystallographic file in CIF format for the complexes $[\{\text{Fe}(\text{L}^2)_2\}_3\text{Fe}] \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (data collected at 100 K) and $[\{\text{Fe}(\text{L}^2)_2\}_3\text{Fe}] \cdot 2\text{CH}_3\text{OH}$ (data collected at 293 K). The relevant crystal data and selected parameters for room temperature data collection are given in Tables S1 and S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.