

Multinuclear Fe(III) Complexes with Polydentate Ligands of the Family of Dicarboxyimidazoles: Nuclearity- and Topology-Controlled Syntheses and Magneto-Structural Correlations

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Two polydentate ligands of the family of dicarboxyimidazoles, H₂MeDCBI (= 4,5-dicarboxy-1-methyl-1H-imidazole) and H₃DCBI (= 4,5-dicarboxyimidazole), have been used in reactions with the [Fe(3,5-^tBu₂salpn)]⁺ species {3,5-^tBu₂salpn = the dianion of 1,3-bis-[(3,5-di-*tert*-butylsalicylidene)amino]propane} to synthesize selectively complexes of different nuclearities. Four complexes have been synthesized: the mononuclear complex [Fe(3,5-^tBu₂salpn)-(HMeDCBI)] (**1**), the two binuclear but topologically different complexes [Fe(3,5-^tBu₂salpn)(MeDCBI)Fe(3,5-^tBu₂salpn)] (**2**) and {[Fe(3,5-^tBu₂salpn)]₂(HDCBI)} (**3**), and the trinuclear complex {[Fe(3,5-^tBu₂salpn)]₂(DCBI)Fe(3,5-^tBu₂salpn)} (**4**). The structures of these complexes have been determined by X-ray crystallography. Variable-temperature direct-current magnetic susceptibility measurements were conducted for all compounds to obtain information about their electronic structure and to investigate the extent of magnetic communication among the Fe(III) centers. The results of these measurements allowed us to correlate the different structural motifs with the possible magnetic interactions that arise in multinuclear complexes of dicarboxyimidazoles. For **1**, the room-temperature $\chi_M T$ value reveals an $S = 5/2$ ground state. The data for the binuclear but topologically different complexes **2** and **3**, and the trinuclear complex **4** suggest that weak intramolecular antiferromagnetic interactions are present, with interaction parameters ranging from -3.6 to -5.1 cm⁻¹. Differences in the extent of the magnetic communication between the metal centers through the two different interaction pathways of the ligands MeDCBI and DCBI (either through the imidazole ring or through the carboxylate groups) have been observed in complexes **2–4** that can be explained by the structural differences observed in the crystal structures of these compounds (the separation of the metal centers and the coplanarity of the metal ion orbitals with the π system of the ligands). Cyclic voltammetry measurements for the mononuclear compound **1** show an irreversible reduction wave that is attributed to Fe³⁺ + e⁻ → Fe²⁺. The electrochemical behavior of the multinuclear complexes **2–4** is more complicated; however, it indicates that there is a degree of electronic communication between the Fe(III) centers.

Introduction

During the past 3 decades, there has been great interest in polynuclear Fe(III) complexes. This can be attributed to the relevance of these compounds to a variety of research areas ranging from biological chemistry to magnetic materials. Multinuclear Fe centers are found in the active sites of several non-heme metalloproteins.¹ Examples of such proteins include hemerythrin, methane monooxygenase, and ribonucle-

otide reductase, all of which have binuclear Fe active sites,^{2,3} as well as the iron storage protein ferritin, which contains a core with as many as 4500 Fe centers.^{4,5} In addition, a large number of multinuclear Fe compounds display interesting magnetic behavior. For example, trinuclear systems frequently exhibit spin frustration,^{6,7} and other systems of higher

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nuclearity with large ground-state spin values and large degrees of anisotropy function as single-molecule magnets.^{8–12}

The majority of the multinuclear Fe complexes that have been synthesized and studied to date are binuclear complexes with oxo, hydroxo, and carboxylato groups as bridging ligands. These systems usually exhibit strong intramolecular antiferromagnetic interactions. A large number of Fe(III) complexes of higher nuclearity with an oxo and hydroxo ligand environment have also been reported, many of which have been synthesized by rather serendipitous means. Of interest are the relatively small number of imidazolate-bridged multinuclear Fe complexes that have been reported in the literature. Except for a few polymeric chains of Fe(II),^{13–16} only three Fe(III) complexes of this type are known: these include a binuclear compound with porphyrins as peripheral ligands on the Fe atoms¹⁷ and two similar binuclear compounds with imidazolate, phenoxy, and methoxy or hydroxy groups as bridges.^{18,19} The great structural diversity that imidazole and imidazolate-based compounds offer as ligands with other metals justifies their wide utilization in many areas of inorganic chemistry, including the syntheses of one-, two-, or three-dimensional coordination polymers^{20,21} and the syntheses of models of the active sites of a variety of metalloenzymes, such as (Cu, Zn)SOD^{22,23} and cytochrome *c* oxidase.²⁴

A large number of complexes with functionalized imidazole or imidazolate as bridges functioning in different coordination modes have been reported. These include mononuclear Mn(III) and Mn(IV) complexes,²⁵ binuclear Rh²⁶ and Ir compounds,²⁷ and a series of binuclear 4,5-dicarboximidazolate-bridged Mn compounds isolated in

three different oxidation states, Mn^{III}Mn^{III}, Mn^{III}Mn^{IV}, and Mn^{IV}Mn^{IV}.^{28,29} Species of higher nuclearity, such as a cyclic tetramer, have been proposed to be synthesized from the reactions of oxovanadium(IV) with 4,5-dicarboximidazole, although none has been isolated.³⁰ Recently, two types of one-dimensional polymeric chains have been reported: one involves complexes of Mn(III) ions with 4,5-dicarboximidazole³¹ that are held together via intermolecular hydrogen bonds, and the other is composed of [Mn(phen)]²⁺ units (phen = 1,10-phenanthroline) and 4,5-dicarboximidazole, with the latter acting as a μ_2 -bridging ligand between two neighboring Mn(II) centers.³² Three-dimensional frameworks supported by H bonds have also been constructed by 4,5-dicarboximidazole³³ and 4-carboxy-1-hydroxymethylimidazole³⁴ in combination with various bivalent metal ions.

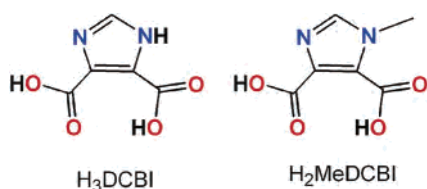
Magnetic susceptibility studies carried out in multinuclear complexes with paramagnetic metal centers bridged by imidazolate-based ligands have shown that the imidazolate moiety generally induces moderate to weak intramolecular magnetic interactions. For binuclear Cu(II) complexes bridged by the imidazolate ion, it has been found that the interactions are relatively strong (J ranges from -40 to -160 cm⁻¹) but their magnitude depends on the geometry of the Cu(II) coordination.³⁵ Weaker interactions have been observed in the case of the binuclear 4,5-dicarboximidazolate-bridged Mn^{IV}Mn^{IV} complex in which the Mn centers are antiferromagnetically coupled with $J = -2.3$ cm⁻¹.²⁸ Weak intramolecular antiferromagnetic exchange interactions are also operating among the Mn(II) centers in the polymeric chain of Mn(II) and 4,5-dicarboximidazole with $J \approx 0.1$ cm⁻¹.³² Interestingly, in the analogous Mn^{III}Mn^{IV} compound, weak ferromagnetic interactions were observed with $J = +1.4$ cm⁻¹, which led to the first EPR spectrum of an $S = 7/2$ ground state for such a dimer.²⁹

In this article, we have used the anions of two carboxylate-substituted imidazole-based compounds, 4,5-dicarboximidazole (H₃DCBI) and 4,5-dicarboxy-1-methyl-1H-imidazole (H₂MeDCBI) (Chart 1), as scaffolds to synthesize selectively and study the magnetic properties of a series of Fe(III) complexes of different nuclearities. These include the mononuclear complex [Fe(3,5'-Bu₂salpn)(HMeDCBI)] (**1**), the topologically different binuclear complexes [Fe(3,5'-Bu₂salpn)(MeDCBI)Fe(3,5'-Bu₂salpn)] (**2**) and {[Fe(3,5'-Bu₂

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Chart 1



salpn)]₂(HDCBI)} (3), and the trinuclear complex {[Fe(3,5-'Bu₂salpn)]₂(DCBI)Fe(3,5-'Bu₂salpn)} (4). Solid-state magnetic susceptibility measurements were used to investigate the intramolecular magnetic exchange interactions that arise in the multinuclear complexes 2–4 through different magnetic exchange pathways that are available in ligands of this type.

Experimental Section

Materials and Techniques. Unless otherwise stated, the reactions and manipulations were performed under an argon atmosphere, using standard Schlenk line techniques. Commercial-grade solvents were dried and deoxygenated by reflux under a N₂ atmosphere for at least 24 h over appropriate drying agents and were freshly distilled prior to use.

The compounds 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, 1,3-diaminopropane, 4,5-dicarboximidazole, FeCl₃·6H₂O, NH₄PF₆, (Et₄N)(O₂CMe)·4H₂O were purchased from Aldrich, and 4,5-dicarboxy-1-methyl-1H-imidazole was purchased from Combi-Blocks. All chemicals were used without any further purification. (ⁿBu₄N)(H₂DCBI) was synthesized from the reaction of H₃DCBI with 1 equiv of 1.0 M ⁿBu₄NOH solution in MeOH using MeOH as the solvent. The resulting mixture was filtered and the product was isolated by slow addition of Et₂O to the filtrate as a white microcrystalline powder. [Fe(3,5-'Bu₂salpn)(O₂CMe)] was synthesized according to the published procedure for the synthesis of [Fe(salen)(O₂CMe)].³⁶

Elemental analyses were performed in the Chemical Analysis Laboratory in the Chemistry Department at The University of Michigan. Infrared spectra were recorded on a Nicolet 5DX IR spectrophotometer as KBr pellets. Mass spectrometry data (electrospray ionization) were recorded using CH₂Cl₂/MeOH solutions at the Mass Spectrometry facility at the University of Michigan. Cyclic voltammetry measurements were carried out at room temperature under argon atmosphere, in CH₂Cl₂ solutions that contained 0.1 M (ⁿBu₄N)(PF₆) as the supporting electrolyte. All potentials were referenced to the Ag/AgCl electrode, and under our experimental conditions, E_{1/2} for the Fc/Fc⁺ couple occurred at +0.600 V. Variable-temperature solid-state direct-current (dc) magnetic susceptibility data were collected on a Quantum Design 2000/2010 MPMS SQUID Magnetometer equipped with a 5.5-T dc magnet. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities.

Synthesis of [Fe(3,5-'Bu₂salpn)]₂O. [Fe(3,5-'Bu₂salpn)]₂O was synthesized according to a modification of a published procedure for the synthesis of [Fe(salpn)]₂O.³⁷ To 70 mL of a MeOH solution of 3.530 g (15.0 mmol) of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde in a round-bottom flask open to the air was added 0.63 mL (7.5 mmol) of 1,3-diaminopropane. The bright yellow mixture of the Schiff base was stirred at room temperature for 30 min and then a solution of 2.036 g (7.5 mmol) of FeCl₃·6H₂O in 20 mL of MeOH

was added. To the resulting dark blue solution was added 1.227 g (7.5 mmol) of NH₄PF₆ dissolved in 20 mL of a 1:1 mixture of MeOH and H₂O. The reaction mixture was stirred at room temperature for 30 min, and then 60 mL of distilled H₂O was added slowly under stirring, resulting in the precipitation of a purple-brown microcrystalline solid. The solid was collected by filtration, washed with distilled H₂O (2 × 25 mL), and dried under vacuum. The compound was recrystallized from MeCN and isolated as dark crystals.³⁸ Yield: 3.762 g (88%). Anal. Calcd for [Fe(3,5-'Bu₂salpn)]₂O·3H₂O (C₆₆H₁₀₂Fe₂N₄O₈) (found) (%): C 66.55 (66.31), H 8.57 (8.26), N 4.71 (4.67). IR (KBr disk, cm⁻¹): see Supporting Information.

Synthesis of [Fe(3,5-'Bu₂salpn)(HMeDCBI)] (1). To a mixture of 0.341 g (2.0 mmol) of H₂MeDCBI in 40 mL of MeCN in a round-bottom flask open to the air was added 1.241 g (2.0 mmol) of [Fe(3,5-'Bu₂salpn)(O₂CMe)]. The reaction mixture was stirred and heated at 50 °C for 18 h. Then it was allowed to reach room temperature, yielding a purple solid that was collected by filtration and recrystallized from wet MeCN and Et₂O. Yield: 0.906 g (62%). Anal. Calcd for 1·H₂O (C₃₉H₅₅FeN₄O₇) (found) (%): C 62.65 (62.41), H 7.36 (7.22), N 7.50 (7.45). +ESI-MS (*m/z*): 595 ([Fe(3,5-'Bu₂salpn)(H₂O)₂]⁺). IR (KBr disk, cm⁻¹): see Supporting Information.

Synthesis of [Fe(3,5-'Bu₂salpn)(MeDCBI)Fe(3,5-'Bu₂salpn)] (2). A 0.42-mL volume of 1.0 M ⁿBu₄NOH solution in MeOH was added dropwise to a mixture of 0.311 g (0.4 mmol) of [Fe(3,5-'Bu₂salpn)(HMeDCBI)] in 25 mL of dry MeCN under an Ar atmosphere. A 0.242-g (0.2-mmol) portion of [Fe(3,5-'Bu₂salpn)]₂O in 40 mL of dry MeCN was added via cannula to the resulting red mixture. The reaction mixture was stirred and heated at 45 °C for 20 h, yielding a microcrystalline precipitate. After filtration, a purple solid was isolated that was subsequently washed with cold MeCN (15 mL) and dried in vacuo. Yield: 0.296 g (54%). Anal. Calcd for 2 (C₇₂H₁₀₀Fe₂N₆O₈) (found) (%): C 67.08 (67.12), H 7.76 (7.56), N 6.52 (6.44). +ESI-MS (*m/z*): 595 ([Fe(3,5-'Bu₂salpn)(H₂O)₂]⁺). IR (KBr disk, cm⁻¹): see Supporting Information.

Synthesis of {[Fe(3,5-'Bu₂salpn)]₂(HDCBI)} (3). A 1.535-g (1.35-mmol) portion of [Fe(3,5-'Bu₂salpn)]₂O was added to a warm solution of 0.536 g (1.35 mmol) of (ⁿBu₄N)(H₂DCBI) and 0.354 g (1.35 mmol) of (Et₄N)(O₂CMe)·4H₂O in 40 mL of MeCN. The reaction mixture was stirred at room temperature for ~18 h, resulting in a microcrystalline purple precipitate that was collected by filtration, washed with cold MeCN (2 × 15 mL), and dried in vacuo. Yield: 1.343 g (78%). Anal. Calcd for 3·H₂O (C₇₁H₉₉Fe₂N₆O₉) (found) (%): C 65.99 (66.00), H 7.67 (7.85), N 6.51 (6.69). ESI-MS (*m/z*): 1274 ([Fe(3,5-'Bu₂salpn)]₂(DCBI))⁻. IR (KBr disk, cm⁻¹): see Supporting Information.

Synthesis of {[Fe(3,5-'Bu₂salpn)]₂(DCBI)Fe(3,5-'Bu₂salpn)} (4). A 0.41-mL (3.9-mmol) aliquot of 1.0 M solution of ⁿBu₄NOH in MeOH was added dropwise to a mixture of 0.500 g (3.9 mmol) of {[Fe(3,5-'Bu₂salpn)]₂(HDCBI)} in 25 mL of dry MeCN under an Ar atmosphere. To the resulting solution was added via cannula a 0.223-g (2.0-mmol) portion of [Fe(3,5-'Bu₂salpn)]₂O in 20 mL of dry MeCN. The reaction mixture was heated at ~40 °C and stirred for 8 h, yielding a microcrystalline precipitate. After filtration, the purple solid that was obtained was washed with cold MeCN (15 mL) and collected. Yield: 0.331 g (46%). Anal. Calcd for 4·2MeCN (C₁₀₈H₁₅₁Fe₃N₁₀O₁₀) (found) (%): C 67.67 (67.68), H 7.89 (7.87), N 7.31 (6.98). ESI-MS (*m/z*): 1274 ([Fe(3,5-'Bu₂

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Table 1. Crystal Data and Structure Refinement Parameters for [Fe(3,5-*t*-Bu₂salpn)(HMeDCBI)]·1.25MeCN (**1**·1.25MeCN), [Fe(3,5-*t*-Bu₂salpn)(MeDCBI)Fe(3,5-*t*-Bu₂salpn)]·2.5MeCN·1.5CH₂Cl₂ (**2**·2.5MeCN·1.5CH₂Cl₂), {[Fe(3,5-*t*-Bu₂salpn)]₂(HDCBI)} (**3**), and {[Fe(3,5-*t*-Bu₂salpn)]₂(DCBI)Fe(3,5-*t*-Bu₂salpn)]·2.5MeCN (**4**·2.5MeCN)

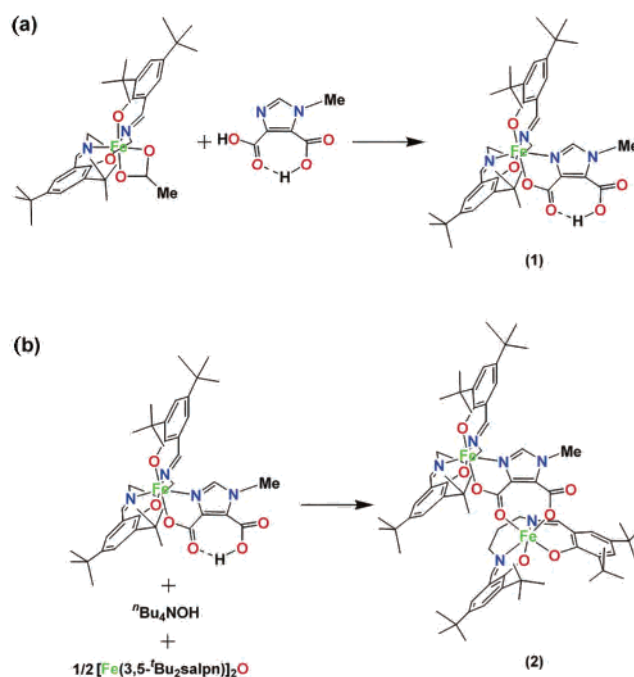
	1 ·1.25MeCN	2 ·2.5MeCN·1.5CH ₂ Cl ₂	3	4 ·2.5MeCN
formula	C _{41.50} H _{56.75} FeN _{5.25} O ₆	C _{78.50} H _{110.50} Cl ₃ Fe ₂ N _{8.50} O ₈	C ₇₁ H ₉₇ Fe ₂ N ₆ O ₈	C ₁₀₉ H _{152.50} Fe ₃ N _{10.50} O ₁₀
fw	781.02	1519.30	1274.25	1937.46
cryst system	triclinic	triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> ₂ / <i>c</i>
<i>a</i> (Å)	15.109(1)	11.162(3)	12.641(2)	26.567(5)
<i>b</i> (Å)	17.231(1)	19.736(4)	17.362(3)	15.983(3)
<i>c</i> (Å)	18.540(1)	21.367(5)	33.972(6)	26.753(5)
α (deg)	109.456(4)	68.170(4)	80.730(11)	90
β (deg)	111.060(4)	76.554(4)	88.282(11)	104.552(3)
γ (deg)	90.560(4)	74.682(4)	85.548(11)	90
<i>V</i> (Å ³)	4200.6(5)	4166.7(16)	7335(2)	10996(3)
<i>Z</i>	4	2	4	4
<i>D</i> _{calc} (g/cm ³)	1.235	1.211	1.154	1.170
cryst dimens (mm)	0.40 × 0.36 × 0.12	0.44 × 0.24 × 0.12	0.44 × 0.28 × 0.20	0.58 × 0.30 × 0.16
abs coeff (mm ⁻¹)	0.410	0.500	0.449	0.449
θ range (deg)	2.86 to 23.66	1.77 to 28.40	2.81 to 26.42	2.80 to 28.45
reflins colld	37984	83901	66017	130850
data/restr/params	26563/87/1028	20708/0/956	29894/0/1676	27591/0/1246
R1, wR2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0751, 0.1898	0.0591, 0.1742	0.0573, 0.1349	0.0439, 0.1126
R1, wR2 (all data)	0.1202, 0.2148	0.0787, 0.1851	0.0975, 0.1543	0.0715, 0.1267
goodness of fit	0.981	1.080	1.018	1.023

salpn)]₂(DCBI)]⁻, 595 ([Fe(3,5-*t*-Bu₂salpn)(H₂O)₂]⁺). IR (KBr disk, cm⁻¹): see Supporting Information.

X-ray Crystallography. Single crystals of suitable quality and size of **1**·1.25MeCN, **2**·2.5MeCN·1.5CH₂Cl₂, **3**, and **4**·2.5MeCN were mounted on the ends of quartz fibers and used for intensity data collection on a Bruker SMART 1K CCD-based X-ray diffractometer equipped with an LT-2 low-temperature device and normal-focus Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000-W power (50 kV, 40 mA). The frames were integrated with the Bruker SAINT software package with a narrow-frame algorithm.³⁹ For **1**·2.5MeCN, the data were processed and corrected for absorption with TWINABS,⁴⁰ whereas the data for **2**·2.5MeCN·1.5CH₂Cl₂, **3**, and **4**·2.5MeCN were processed and corrected for absorption with SADABS.⁴¹ The structures were solved and refined with the Bruker SHELXTL software package.⁴² All non-hydrogen atoms were refined anisotropically with the hydrogen placed in idealized positions. **1**·2.5MeCN was found to be a non-merohedral twin with two components related by a 180° rotation about the direct (0 1 0) axis and twin fraction of 0.3628(9). Cell parameters and basic information pertaining to data collection and structure refinement are summarized in Table 1.

Results

Syntheses and Crystal Structures. Schematic representations of the reactions described in this paper are given in Schemes 1 and 2. The reaction of H₂MeDCBI with 1 equiv of [Fe(3,5-*t*-Bu₂salpn)(O₂CMe)] in MeCN results in the synthesis of the mononuclear complex **1** in ~60% yield (Scheme 1a). Complex **1** was crystallized by slow evaporation of a MeCN solution in the triclinic space group *P* $\bar{1}$ with *Z* = 4 (there are two crystallographically distinct molecules

Scheme 1

in each unit cell). A view of its crystal structure is shown in Figure 1, and selected bond distances and angles are listed in Table 2. The central metal atom exists in a distorted octahedral coordination environment. HMeDCBI binds in a bidentate fashion through an oxygen atom of a carboxylate group and a nitrogen atom of a formally neutral imidazole ring. The carboxylate group coordinates to the metal center at a distance of 2.090[3] Å (the average value is given for the two crystallographically distinct molecules in the unit cell), and it is intramolecularly H-bonded to the other carboxylic acid of HMeDCBI. At the same time, the imidazole ring binds at the much longer distance of 2.189- [4] Å. The tetradentate ligand 3,5-*t*-Bu₂salpn donates two phenolate oxygen atoms to the iron center (at distances of 1.880[3] and 1.903[3] Å) and two imine nitrogen atoms (at

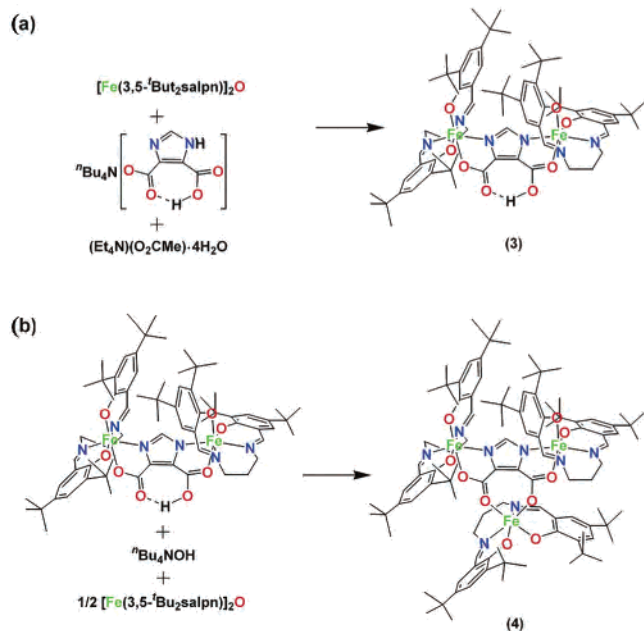
(39) SAINT Plus, version 7.01; Bruker Analytical X-ray Instruments: Madison, WI, 2003.

(40) Sheldrick, G. M. TWINABS, version 1.05; Bruker-Nonius Program for Scaling and Correction for Twinned Crystals; University of Göttingen: Göttingen, Germany, 2003.

(41) Sheldrick, G. M. SADABS, version 2.10; Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Göttingen, Germany, 2003.

(42) Sheldrick, G. M. SHELXTL, version 6.12; Bruker Analytical X-ray Instruments: Madison, WI, 2001.

Scheme 2



distances of 2.112[4] and 2.099[4] Å) adopting the β -cis configuration.

When complex **1** reacts with a strong base, such as OH^- , the second carboxylic group of HMeDCBI is deprotonated, resulting in the formation of $[\text{Fe}(3,5\text{-}t\text{Bu}_2\text{salpn})(\text{MeDCBI})]^-$, which subsequently reacts with $[\text{Fe}(3,5\text{-}t\text{Bu}_2\text{salpn})]_2\text{O}$ to give $[\text{Fe}(3,5\text{-}t\text{Bu}_2\text{salpn})(\text{MeDCBI})\text{Fe}(3,5\text{-}t\text{Bu}_2\text{salpn})]$ (**2**) in good yield (Scheme 1b). Crystals of complex **2** were obtained in the triclinic space group $P\bar{1}$ by slow evaporation of a MeCN/ CH_2Cl_2 solution. Selected geometric parameters of this complex are listed in Table 3, and a thermal ellipsoid plot is shown in Figure 2. Both of the metal atoms, Fe(1) and Fe(2), exhibit slightly distorted octahedral geometry. The coordination environment of Fe(2) is similar to that of Fe(1) in the mononuclear complex **1**, and Fe(2) exhibits similar geometrical characteristics: it is surrounded by O(6) of one of the carboxylate groups of MeDCBI at a distance of 2.130(2) Å, N(6) of the formally neutral imidazole ring at a distance of 2.140(2) Å, and two nitrogen and two oxygen atoms of a tetradentate 3,5- $t\text{Bu}_2\text{salpn}$ (with average Fe–N and Fe–O distances of 2.115[3] and 1.906[3] Å, respectively). The second Fe atom of complex **2**, Fe(1), is attached to MeDCBI through O(5) and O(7) of the two carboxylate groups with Fe(1)–O(5) and Fe(1)–O(7) bond distances of 2.094(2) and 1.998(2) Å, respectively. The coordination

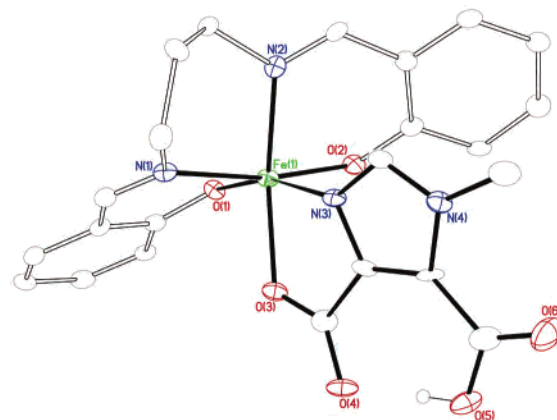


Figure 1. View of $[\text{Fe}(3,5\text{-}t\text{Bu}_2\text{salpn})(\text{HMeDCBI})]$ (**1**) with the atoms represented by thermal ellipsoids at the 35% probability level. H atoms (except for the one attached to the carboxylate group) and *tert*-butyl groups are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2**

Bond Distances			
Fe(1)–O(2)	1.932(2)	Fe(2)–O(3)	1.902(2)
Fe(1)–O(1)	1.939(2)	Fe(2)–O(4)	1.910(2)
Fe(1)–O(7)	1.998(2)	Fe(2)–N(3)	2.104(2)
Fe(1)–O(5)	2.094(2)	Fe(2)–N(4)	2.126(2)
Fe(1)–N(1)	2.115(2)	Fe(2)–O(6)	2.130(2)
Fe(1)–N(2)	2.141(2)	Fe(2)–N(6)	2.140(2)
Bond Angles			
O(7)–Fe(1)–N(2)	169.95(8)	O(3)–Fe(2)–N(4)	172.34(8)
O(2)–Fe(1)–N(1)	167.89(8)	O(4)–Fe(2)–O(6)	164.47(7)
O(1)–Fe(1)–O(5)	174.31(7)	N(3)–Fe(2)–N(6)	161.53(8)
O(7)–Fe(1)–O(5)	86.65(8)	N(4)–Fe(2)–N(6)	97.33(8)
O(2)–Fe(1)–O(5)	93.54(7)	O(3)–Fe(2)–N(6)	90.19(8)
O(2)–Fe(1)–O(7)	98.79(8)	O(6)–Fe(2)–N(6)	75.28(7)
O(5)–Fe(1)–N(1)	89.09(8)	O(4)–Fe(2)–N(6)	92.14(8)
O(5)–Fe(1)–N(2)	83.70(8)	N(4)–Fe(2)–O(6)	86.82(7)

environment of Fe(1) is completed with two nitrogen and two oxygen atoms of a β -cis-coordinated 3,5- $t\text{Bu}_2\text{salpn}$ ligand with typical Fe–N and Fe–O distances. Fe(1) and Fe(2) in complex **2** are ~ 5.8 Å apart. They do not lie on the same plane (defined by the imidazole ring and the carboxylate groups of MeDCBI). Although Fe(2) is almost coplanar with the imidazole ring, Fe(1) is not, as both of the carboxylate groups of MeDCBI are slightly rotated about the $\text{C}_{\text{imidazole}}\text{--}\text{C}_{\text{carboxylate}}$ bond so that the coordinated oxygen atoms O(5) and O(7) keep Fe(1) more than 1 Å out of the plane of the bridging MeDCBI.

Upon reaction of H_3DCBI with 1 equiv of $t\text{Bu}_4\text{NOH}$ ($t\text{Bu}_4\text{N})(\text{H}_2\text{DCBI})$ is formed. Subsequent reaction of this salt with 1 equiv of $[\text{Fe}(3,5\text{-}t\text{Bu}_2\text{salpn})]_2\text{O}$ in the presence of

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**^a

Bond Distances			
Fe(1)–O(1)	1.877(2), 1.883(2)	Fe(1)–N(2)	2.095(3), 2.102(3)
Fe(1)–O(2)	1.907(2), 1.899(2)	Fe(1)–N(1)	2.112(2), 2.112(3)
Fe(1)–O(3)	2.087(2), 2.093(2)	Fe(1)–N(3)	2.201(3), 2.176(2)
Bond Angles			
O(3)–Fe(1)–N(2)	160.44(10), 162.41(8)	O(2)–Fe(1)–N(3)	89.44(9), 89.24(9)
O(1)–Fe(1)–O(2)	92.88(9), 93.26(9)	O(1)–Fe(1)–O(3)	88.61(9), 88.48(8)
N(1)–Fe(1)–N(3)	94.35(9), 94.69(10)	O(3)–Fe(1)–N(3)	75.34(9), 75.50(8)
O(1)–Fe(1)–N(3)	163.95(10), 163.97(10)	N(2)–Fe(1)–N(3)	85.43(10), 87.36(9)

^a The second value in each column refers to the corresponding bond distances and angles for the second crystallographically distinct molecule of the unit cell.

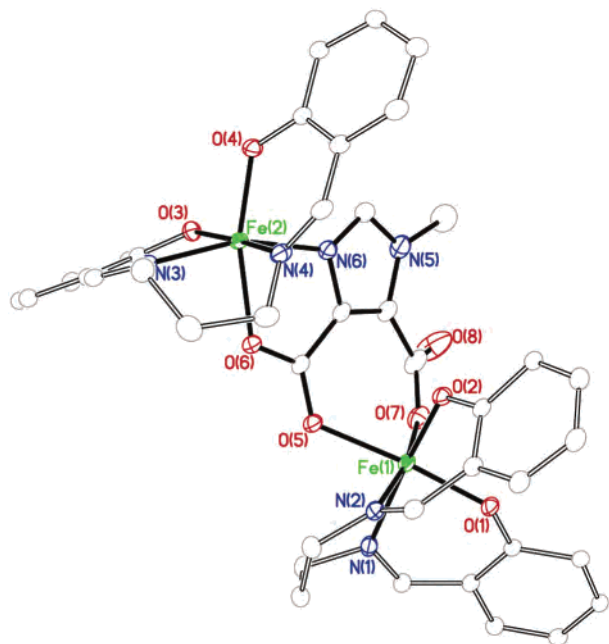


Figure 2. View of $[\text{Fe}(3,5\text{'-Bu}_2\text{salpn})(\text{MeDCBI})\text{Fe}(3,5\text{'-Bu}_2\text{salpn})]$ (**2**) with the atoms represented by thermal ellipsoids at the 35% probability level. H atoms and *tert*-butyl groups are omitted for clarity.

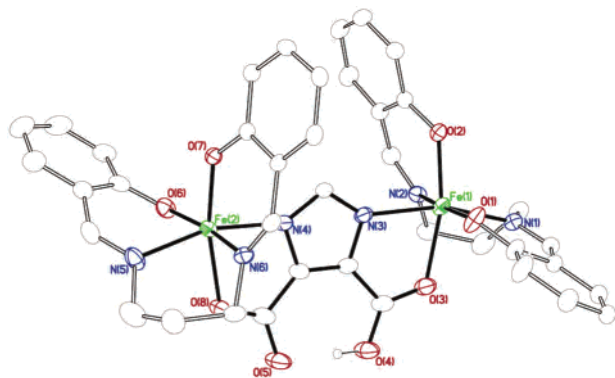


Figure 3. View of $\{[\text{Fe}(3,5\text{'-Bu}_2\text{salpn})]_2(\text{HDCBI})\}$ (**3**) with the atoms represented by thermal ellipsoids at the 35% probability level. H atoms (except from the one attached to the carboxylate group) and *tert*-butyl groups are omitted for clarity.

$(\text{Et}_4\text{N})(\text{O}_2\text{CMe})$ in MeCN results in synthesis of the binuclear compound $\{[\text{Fe}(3,5\text{'-Bu}_2\text{salpn})]_2(\text{HDCBI})\}$ (**3**) in $\sim 78\%$ yield (Scheme 2a). Complex **3** was crystallized by slow evaporation of a MeCN solution in the triclinic space group $P\bar{1}$ with $Z = 4$ (there are two crystallographically distinct molecules in each unit cell). A view of its crystal structure is shown in Figure 3. The two metal centers are related to each other by a noncrystallographic pseudo- C_2 axis that bisects the imidazole ring and passes through C(18) and the midpoint of the C(19)–C(20) bond. The two iron atoms have identical coordination sphere ligations: each exists in an octahedral coordination environment consisting of an oxygen atom of a carboxylate group of HDCBI, a nitrogen atom of the imidazole ring of HDCBI, and two oxygen and two nitrogen atoms of a β -cis-coordinated 3,5'-Bu₂salpn ligand. As reported in Table 4, the Fe–O_{carboxylate} distances are 2.160[3] and 2.188[3] Å (the average values are given for the two crystallographically distinct molecules in the unit cell). The

uncoordinated oxygen atoms of the two CO₂ groups of HDCBI are intramolecularly H-bonded to each other. The Fe–N_{imidazolate} bond distances for the two metal atoms are 2.129[4] and 2.119[4] Å. The Fe–O and Fe–N bond distances and angles related to the 3,5'-Bu₂salpn ligands are unexceptional. Unlike the unsymmetrical binuclear complex **2**, in the symmetrical binuclear complex **3**, the imidazolate ring and the two iron atoms are coplanar with an Fe \cdots Fe separation of ~ 6.5 Å.

The trinuclear complex $\{[\text{Fe}(3,5\text{'-Bu}_2\text{salpn})]_2(\text{DCBI})\text{Fe}(3,5\text{'-Bu}_2\text{salpn})\}$ (**4**) is synthesized from the reaction of $[\text{Fe}(3,5\text{'-Bu}_2\text{salpn})]_2\text{O}$ with the binuclear complex **3** that had been previously deprotonated by a strong base (Scheme 2b). It was crystallized together with interstitial MeCN molecules in the monoclinic space group $P2_1/c$. A drawing of its crystal structure is presented in Figure 4. The coordination of the $[\text{Fe}(3,5\text{'-Bu}_2\text{salpn})]^+$ moiety to the free binding site of the binuclear complex **3** associated with the two carboxylate groups destroys the pseudo- C_2 axis that bisects the imidazole bridge of complex **3**. The coordination environments of Fe(2) and Fe(3) are identical to those of the corresponding iron atoms of the parent, symmetrical binuclear complex **3**, whereas that of Fe(1) is identical to that of Fe(1) of the unsymmetrical binuclear complex **2**. Examination of the bond distances and angles of complex **4** (Table 5) reveals that the three iron centers exhibit structural characteristics comparable to those in complex **3**. However, they are slightly shorter than those observed in complex **2**. This difference can be ascribed to the charged imidazolate ring in **4** as compared to the neutral imidazole ring in **2**. In the trinuclear complex **4**, the two iron atoms coordinated to the nitrogen atoms of the imidazole ring, Fe(2) and Fe(3), are separated by ~ 6.4 Å, and each of them is at distance of ~ 6.1 Å from the third iron atom at the carboxylate position, Fe(1), forming a core structure that resembles that of an isosceles triangle. In contrast to the unsymmetrical binuclear complex **2**, in the trinuclear complex **4**, the Fe atom coordinated to the carboxylate position of DCBI lies in the same plane as the other two iron atoms and the imidazole ring. Apparently, this is due to the fact that, in **4**, the negatively charged imidazolate ring of DCBI together with the two carboxylate groups form an extended conjugated π system, whereas in **2** such conjugation is not likely to occur.

Magnetic Susceptibility. The magnetic properties of compounds **1–4** were investigated by solid-state magnetic susceptibility measurements in the 4–300 K temperature range and in a dc field of 2000 G. The temperature dependence of the molar magnetic susceptibility of compound **1** in the form of $\chi_{\text{M}}T$ versus T and $1/\chi_{\text{M}}$ versus T plots is shown in Figures S1-1 and S1-2 (Supporting Information). The $\chi_{\text{M}}T$ value at room temperature is ~ 4.3 cm³ mol⁻¹ K and it stays invariant over the temperature range 20–300 K. This value corresponds to the spin-only value of a mononuclear high-spin d⁵ Fe(III) complex with $t_{2g}^3e_g^2$ electronic configuration. A deviation from Curie–Weiss behavior is observed at temperatures below 15–20 K.

The temperature dependences of the molar magnetic susceptibilities of compounds **2** and **3** in the form of $\chi_{\text{M}}T$

Table 4. Selected Bond Distances (Å) and Angles (deg) for **3^a**

		Bond Distances	
Fe(1)–O(1)	1.884(2), 1.894(2)	Fe(2)–O(6)	1.896(2), 1.890(2)
Fe(1)–O(2)	1.906(2), 1.901(2)	Fe(2)–O(7)	1.906(2), 1.883(2)
Fe(1)–N(1)	2.110(3), 2.116(3)	Fe(2)–N(5)	2.108(3), 2.102(3)
Fe(1)–N(2)	2.123(3), 2.121(2)	Fe(2)–N(6)	2.117(3), 2.123(3)
Fe(1)–N(3)	2.137(3), 2.121(3)	Fe(2)–N(4)	2.126(3), 2.111(2)
Fe(1)–O(3)	2.155(2), 2.164(2)	Fe(2)–O(8)	2.153(2), 2.223(2)
		Bond Angles	
O(2)–Fe(1)–O(3)	165.81(9), 165.87(9)	O(7)–Fe(2)–O(8)	168.37(9), 169.86(8)
O(1)–Fe(1)–N(2)	170.99(10), 171.50(10)	O(6)–Fe(2)–N(6)	168.89(10), 170.76(10)
N(1)–Fe(1)–N(3)	162.74(10), 162.85(10)	N(5)–Fe(2)–N(4)	163.51(11), 158.12(10)
O(1)–Fe(1)–N(3)	93.91(10), 92.41(9)	O(6)–Fe(2)–N(5)	85.28(10), 87.93(10)
O(2)–Fe(1)–N(3)	91.71(9), 92.37(9)	O(7)–Fe(2)–N(4)	92.72(9), 94.62(9)
N(2)–Fe(1)–N(3)	94.78(10), 95.46(10)	N(6)–Fe(2)–N(4)	93.46(10), 91.07(10)
N(3)–Fe(1)–O(3)	77.75(9), 77.49(9)	N(4)–Fe(2)–O(8)	77.65(9), 76.62(9)
O(3)–Fe(1)–N(2)	85.40(10), 85.24(10)	O(8)–Fe(2)–N(6)	87.64(9), 87.74(9)

^a The second value in each column refers to the corresponding bond distances and angles for the second crystallographically distinct molecule of the unit cell.

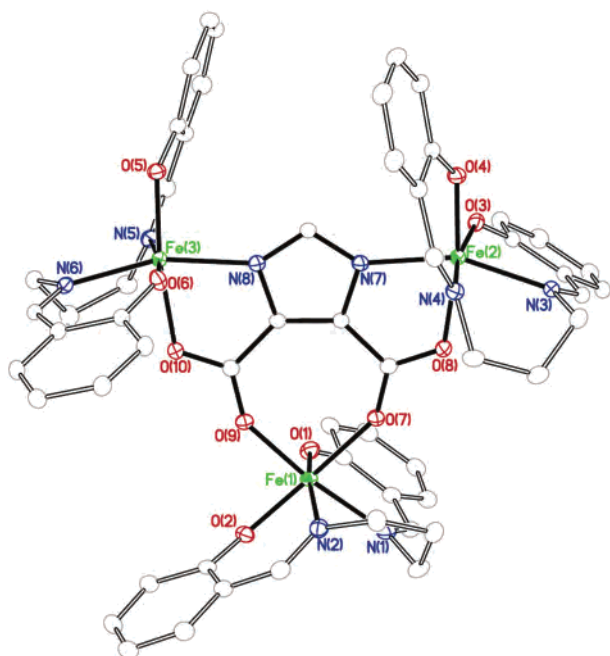


Figure 4. View of $\{[\text{Fe}(3,5\text{-}t\text{Bu}_2\text{salpn})_2(\text{DCBI})\text{Fe}(3,5\text{-}t\text{Bu}_2\text{salpn})\}$ (**4**) with the atoms represented by thermal ellipsoids at the 35% probability level. H atoms and *tert*-butyl groups are omitted for clarity.

versus T plots are shown in Figure 5. For the former, the room-temperature $\chi_{\text{M}}T$ value is $\sim 8.2 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, and for the latter, it is $\sim 8.0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. Both of these values are less than the calculated spin-only value of $8.8 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for two noninteracting Fe(III) centers with $g = 2.0$. The $\chi_{\text{M}}T$ values decrease steadily with decreasing temperature, reaching values of ~ 1.1 and $\sim 0.8 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 4 K for compounds **2** and **3**, respectively; however, these values do not extrapolate to zero as temperature approaches 0 K. The spin Hamiltonian describing the isotropic interaction between two magnetic centers with local spins $S_{\text{A}1}$ and $S_{\text{A}2}$ and an interaction parameter J in zero field is

$$\mathbf{H}_{\text{ex}} = -J(S_{\text{A}1} \cdot S_{\text{A}2})$$

the eigenvalues of which are given by

$$E(S) = -\frac{J}{2}S(S+1)$$

Table 5. Selected Bond Distances (Å) and Angles (deg) for **4**

Bond Distances			
Fe(1)–O(1)	1.897(2)	Fe(2)–O(8)	2.117(1)
Fe(1)–O(2)	1.909(1)	Fe(2)–N(3)	2.122(1)
Fe(1)–O(9)	2.016(1)	Fe(2)–N(4)	2.140(1)
Fe(1)–O(7)	2.077(1)	Fe(3)–O(6)	1.891(1)
Fe(1)–N(2)	2.127(1)	Fe(3)–O(5)	1.895(1)
Fe(1)–N(1)	2.146(1)	Fe(3)–N(8)	2.107(1)
Fe(2)–O(3)	1.899(1)	Fe(3)–O(10)	2.107(1)
Fe(2)–O(4)	1.901(1)	Fe(3)–N(5)	2.121(1)
Fe(2)–N(7)	2.114(1)	Fe(3)–N(6)	2.101(1)
Bond Angles			
O(1)–Fe(1)–N(2)	167.60(5)	N(7)–Fe(2)–N(4)	92.52(5)
O(2)–Fe(1)–O(7)	173.56(4)	O(3)–Fe(2)–N(7)	98.46(5)
O(9)–Fe(1)–N(1)	170.19(5)	O(4)–Fe(2)–N(7)	94.74(5)
O(1)–Fe(1)–O(9)	98.29(5)	N(4)–Fe(2)–O(8)	89.50(4)
O(1)–Fe(1)–O(7)	93.76(5)	O(5)–Fe(3)–O(10)	168.51(4)
O(9)–Fe(1)–O(7)	89.19(4)	O(6)–Fe(3)–O(5)	94.65(4)
O(9)–Fe(1)–N(2)	93.82(5)	N(8)–Fe(3)–N(6)	161.08(5)
O(7)–Fe(1)–N(2)	89.05(5)	N(8)–Fe(3)–O(10)	76.96(4)
O(4)–Fe(2)–O(8)	169.39(4)	N(8)–Fe(3)–N(5)	93.10(5)
O(3)–Fe(2)–N(4)	168.41(5)	O(6)–Fe(3)–N(8)	93.38(5)
N(7)–Fe(2)–N(3)	157.12(5)	O(5)–Fe(3)–N(8)	94.64(5)
N(7)–Fe(2)–O(8)	76.54(4)	O(10)–Fe(3)–N(5)	86.40(4)

where $S = S_{\text{A}1} + S_{\text{A}2}$. Using this model and employing the interaction parameters J and J' to indicate the two different types of interaction pathways in compounds **2** and **3**, the susceptibility data were fit to give $J = -4.0(1) \text{ cm}^{-1}$ and $g = 2.005(3)$ ($R^2 = 0.9997$) and $J' = -4.8(2) \text{ cm}^{-1}$ and $g = 2.001(5)$ ($R^2 = 0.9987$) for **2** and **3**, respectively. These results are consistent with the presence of weak intramolecular antiferromagnetic exchange interactions within the binuclear compounds **2** and **3**.

In Figure 6 is shown the temperature dependence of the molar magnetic susceptibility for the trinuclear compound **4** in the form of a $\chi_{\text{M}}T$ versus T plot. The room-temperature $\chi_{\text{M}}T$ value of $\sim 11.8 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ is lower than the expected value of $13.1 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for three uncoupled Fe(III) centers with $S = 5/2$ and $g = 2.0$. There is a gradual decrease of the $\chi_{\text{M}}T$ products as the temperature decreases, reaching the value of $\sim 2.0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 4 K. The basic structure of compound **4** can be described as an isosceles triangle containing two different types of interaction pathways between the local spins $S_{\text{A}1}$, $S_{\text{A}2}$, and S_{B} , i.e., through the imidazolate ring (A–A) and through the carboxylate groups (A–B), with J' and J interaction parameters, respectively (Chart 2). Then the spin Hamiltonian used to describe the low-lying electronic

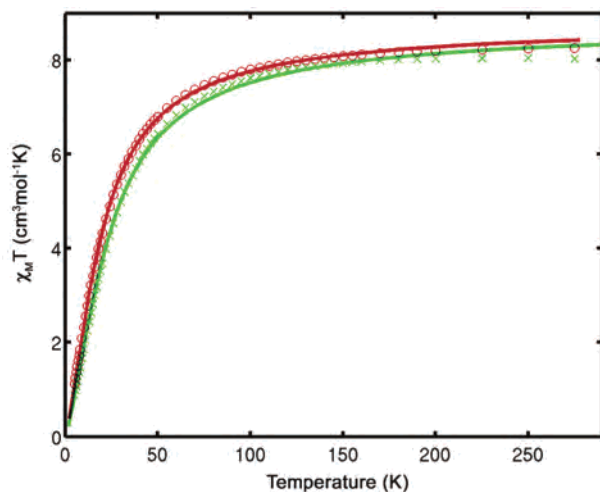


Figure 5. Plots of $\chi_M T$ as a function of temperature for **2** (red, \circ) and **3** (green, \times). The solid lines correspond to the theoretical fits (see text for details).

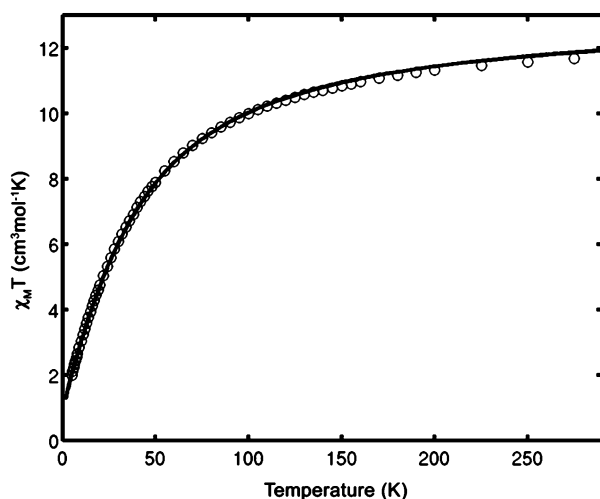
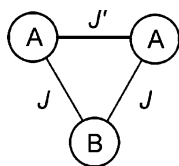


Figure 6. Plot of $\chi_M T$ as a function of temperature for **4**. The solid line corresponds to the theoretical fit (see text for details).

Chart 2



states in zero field is

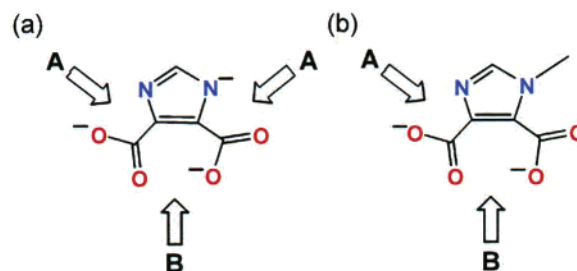
$$\mathbf{H}_{\text{ex}} = -J(\mathbf{S}_{A1} \cdot \mathbf{S}_B + \mathbf{S}_{A2} \cdot \mathbf{S}_B) - J'(\mathbf{S}_{A1} \cdot \mathbf{S}_{A2})$$

The energies of these spin states as functions of the exchange integrals J and J' are given by

$$E(S, S') = -\frac{J}{2}S(S+1) - \frac{J' - J}{2}S'(S'+1)$$

where $S' = S_{A1} + S_{A2}$ and $S = S' + S_B$. Using this model and assuming isotropic interactions between the metal centers, the magnetic susceptibility data for **4** were fit yielding $J = -5.1(1) \text{ cm}^{-1}$, $J' = -3.6(1) \text{ cm}^{-1}$, and $g = 2.001(2)$ ($R^2 = 0.9994$). This behavior is consistent with the presence of weak intramolecular antiferromagnetic exchange

Chart 3



interactions within the trinuclear complex with a nonzero spin ground state.

Electrochemistry. The electrochemical behavior of the complexes **1–4** was examined by cyclic voltammetry measurements in CH_2Cl_2 solutions. All compounds exhibit irreversible reduction processes. The mononuclear complex **1** displays an irreversible redox process with a reduction wave at -0.68 V , which corresponds to the reduction $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$. Subsequently, there are two weak return oxidation waves (-0.56 and $+0.05 \text{ V}$) (see Figure S1-3) that might correspond to a small degree of complex reorganization. The behavior of the unsymmetrical binuclear compound **2** is more complicated: its cyclic voltammogram in the region from 0 to -1.60 V exhibits a series of irreversible redox events with three reduction processes (-0.68 , -0.89 , and -1.14 V), followed by two return oxidation waves. The first reduction takes place at the same potential as the reduction of the mononuclear compound **1**. In the cases of the DCBI-bridged complexes, the symmetrical binuclear compound **3** shows a reduction wave at -0.69 V , another very weak reduction wave at a more negative potential, and a very weak return oxidation wave, whereas the trinuclear compound **4** shows more complex behavior with three reduction processes (-0.69 , -0.96 , and -1.26 V) and two very weak oxidation waves. In the latter two compounds, **3** and **4**, the first reduction processes take place at potentials close to the potential that corresponds to the reduction of the mononuclear compound **1**. Cyclic voltammograms of **2–4** can be found in the Supporting Information (Figures S2-1, S3-1, and S4-1, respectively).

Discussion

The use of the carboxylate-substituted imidazole-based compounds DCBI and MeDCBI as scaffold ligands, together with $3,5\text{-}t\text{Bu}_2\text{salpn}$ as peripheral ligands, for Fe(III) ions offers an attractive approach for the synthesis of multinuclear Fe(III) complexes in which both the nuclearity and topology can be controlled. These variously prepared compounds allowed for the study of intramolecular magnetic exchange interaction in multinuclear Fe(III) complexes at the weak exchange limit. DCBI presents three well-defined metal binding sites and can potentially give rise to mono-, bi-, and trinuclear metal complexes (Chart 3a). Two of these sites are associated with the two imidazole N atoms and a carboxylate group (type A), and the third is associated with the two carboxylate groups only (type B). In the case of MeDCBI, in which one of the imidazole N atoms is

Table 6. Calculated Values of the Parameters g , J , and J' for 2–4

	2	3	4
g	2.005(3)	2.001(5)	2.001(2)
J (cm ⁻¹)	-4.0(1)	N/A	-5.1(1)
J' (cm ⁻¹)	N/A	-4.8(2)	-3.6(1)
R^2	0.9997	0.9987	0.9994

alkylated, there are two well-defined metal binding sites, an A-type site and a B-type site, that allow for the synthesis of mono- and binuclear metal complexes (Chart 3b). For both ligands, the basicities of the various binding sites differ. Thus, by suitable control of the reaction conditions, it is possible to direct the binding of metal ions to a particular site and, consequently, to synthesize complexes of desired nuclearity in a selective way. Indeed, the mononuclear compound **1** was obtained by coordination of the [Fe(3,5-'Bu₂salpn)]⁺ moiety to the more basic type-A binding site of MeDCBI, whereas the unsymmetrical binuclear compound **2** was obtained from compound **1** after deprotonation of the carboxylic acid related to the type-B binding site of MeDCBI. In the case of compound **3**, the two [Fe(3,5-'Bu₂salpn)]⁺ moieties are coordinated to the two more basic type-A binding sites of HDCBI forming a symmetrical binuclear complex that is topologically different than **2**. The trinuclear compound **4** was obtained from compound **3** after deprotonation of the type-B site of DCBI.

The presence of two different types of binding sites in the MeDCBI and DCBI ligands creates two different pathways for magnetic and electronic communication among the Fe(III) centers: through the imidazole ring, A–A pathway, and through the carboxylate groups, A–B pathway. Variable-temperature magnetic susceptibility measurements were used to investigate the intramolecular magnetic exchange interactions among the Fe(III) centers through the two magnetic exchange pathways A–A and A–B in the multinuclear compounds 2–4. The small and negative values of the interaction parameters that were calculated and are summarized in Table 6 indicate the presence of weak intramolecular antiferromagnetic interactions.

In the particular case of the binuclear compounds **2** and **3**, the symmetrical compound **3** was found to exhibit slightly stronger interactions than the unsymmetrical **2**. Considering that DCBI and MeDCBI as ligands are structurally very similar and that the only substantial difference between compounds **2** and **3** is their topology, it can be concluded that the magnetic interaction that arises between the metal centers through the A–A pathway is stronger than that arising through the A–B pathway ($J < J'$). However, this conclusion is valid only for these two compounds, and it cannot be generalized. In the symmetrical compound **3**, the two metal centers are coplanar with the imidazolate ring of the HDCBI ligand, whereas in the unsymmetrical compound **2**, the metal center coordinated to the type-B binding site of MeDCBI deviates from the plane defined by the other Fe

center and the bridging ligand MeDCBI by more than 1 Å. Because the Fe centers in both complexes are high-spin d⁵ ions and have electrons in both the t_{2g} and e_g molecular orbitals, the magnetic communication between the two metal atoms is mediated through both σ- and π-orbital pathways (overlap of the t_{2g} electrons with the π system of the DCBI or MeDCBI). However, because the π-orbital pathway in **2** is somewhat disrupted due to the nonplanarity of the system, the magnetic communication between the metal centers through the A–B pathway becomes less effective, resulting in a weaker magnetic exchange interaction.

In contrast, in the case of the trinuclear compound **4**, the magnetic interaction that arises between two Fe centers through the A–B pathway appears to be stronger than that through the A–A pathway ($J > J'$). This result is not completely unexpected. Considering that the isotropic interaction between metal centers (which has been assumed for the compounds 2–4) is electrostatic in nature and that shorter intermetallic distances give rise to stronger magnetic exchange interactions, because the Fe···Fe separation through the A–B pathway is shorter than through the A–A pathway (~6.1 vs ~6.4 Å), the magnetic interaction through the A–B pathway should be expected to be stronger. The calculated value of the interaction parameter J through the A–B pathway in **4** is found to be larger than the corresponding interaction parameter in **2**. This is because, in **4**, the Fe centers, the imidazolate ring, and the carboxylate groups are coplanar, whereas in **2**, they are not. Consequently, in **4**, the magnetic communication between the metal atoms through the A–B pathway is more effective because it is mediated through both the σ and π orbital pathways.

The calculated exchange interaction parameters for the three compounds 2–4 are weak (Table 6), but not inconsequential. In fact, they are relatively substantial when one considers the long intermetallic distances (~6 Å). Interestingly, the two magnetic exchange pathways A–A and A–B seem to be independent from one another. We obtain reasonable fits to the magnetic data of the trinuclear system **4** by utilizing the values of J and J' obtained from fits of the magnetic data for the binuclear compounds **2** and **3**. This apparent pathway independence is not surprising for exchange coupling of high-spin Fe(III) species. A more interesting case might occur in future studies if other transition metal ions, such as Mn(III), that exhibit Jahn–Teller distortions are bound to the DCBI ligand.

It is of interest to compare our results with those obtained for other multinuclear DCBI-bridged systems. For a porphyrin-capped imidazolate-bridged binuclear Fe(III) complex, an antiferromagnetic exchange interaction of -29.4 cm⁻¹ has been reported.¹⁷ For a related imidazolate-, phenoxy-, and methoxy-bridged binuclear Fe(III) compound, an exchange parameter of -8.0 cm⁻¹ has been reported. In this case, the imidazole bridge does not have a suitable coordination geometry to contribute to the exchange interaction, which is basically mediated through phenoxy and methoxy bridges.¹⁸ Weaker exchange interactions (-2.0 cm⁻¹) have been observed between the metal centers in imidazolate-bridged polymeric Fe(II) chains reported by Storr and

Thompson.¹⁴ In the cases of related multinuclear DCBI-bridged Mn complexes, different types of exchange interactions of similar strength have been observed: antiferromagnetic interactions in the binuclear Mn^{IV}Mn^{IV} complex²⁸ with $J \approx -2.3 \text{ cm}^{-1}$ and in the one-dimensional polymeric chain $[\text{Mn}(\text{phen})(\text{HDCBI})]_n$ ³² with $J \approx -0.1 \text{ cm}^{-1}$ and ferromagnetic interactions in the Mn^{III}Mn^{IV} complex²⁹ with $J \approx +1.4 \text{ cm}^{-1}$. In contrast, in related binuclear Cu(II) imidazolate-bridged complexes, in which the metal ions have filled t_{2g} orbital levels and one unpaired electron in the e_g orbital level and the magnetic communication is mediated only through the π -orbital pathway, much larger coupling constants have been calculated (ranging from -20 to -80 cm^{-1}).⁴³

Electrochemical measurements of the multinuclear complexes **2**, **3**, **4** in CH₂Cl₂ solutions suggest that there is a degree of electronic communication between the Fe(III) centers. However, the electrochemical behavior of these compounds cannot be fully understood. This is due to the fact that the electron-transfer processes are accompanied by chemical reactions. The symmetrical binuclear compound **3** (in which the Fe(III) ions are coordinated to the type-A sites) shows a relatively simple electrochemical behavior, whereas the unsymmetrical compound **2** and the trinuclear compound **4** (in which the Fe(III) ions are bound to the type-A and -B sites) exhibit more complex behavior. Mass spectrometry data of the compounds **2** and **4**, recorded in CH₂Cl₂/MeOH solutions, suggest that, in solution, the Fe(III) ions are not strongly bound to the type-B site, as only mononuclear and binuclear fragments are observed in their mass spectra (in contrast to compound **3** for which the molecular ion can be detected). In other words, there is actually no clear evidence that the species in solution correspond to those observed in the solid. Thus, it might be possible that, in solution, compounds **2** and **4** partially dissociate to mononuclear and binuclear species and the observed electrochemical behavior can be attributed to a complex equilibrium between species of different nuclearities.

Concluding Remarks

Two polydentate compounds of the family of dicarboximidazoles, H₂MeDCBI and H₃DCBI, have been used in reactions with $[\text{Fe}(3,5\text{-Bu}_2\text{salpn})]^+$ units for the syntheses of multinuclear Fe(III) complexes. MeDCBI and DCBI exhibit two types of metal binding sites: one of them is associated with the imidazole N atoms and a carboxylate group (type A), and the other is associated with the carboxylate groups only (type-B binding site). This makes MeDCBI and DCBI good candidates for the synthesis of complexes in which both the nuclearity and topology can be controlled. Four complexes have been synthesized selectively: $[\text{Fe}(3,5\text{-Bu}_2\text{salpn})(\text{HMeDCBI})]$ (**1**), $[\text{Fe}(3,5\text{-Bu}_2\text{-$

$\text{salpn})(\text{MeDCBI})\text{Fe}(3,5\text{-Bu}_2\text{salpn})]$ (**2**), $\{[\text{Fe}(3,5\text{-Bu}_2\text{salpn})]_2\text{-(HDCBI)}\}$ (**3**), and $\{[\text{Fe}(3,5\text{-Bu}_2\text{salpn})]_2(\text{DCBI})\text{Fe}(3,5\text{-Bu}_2\text{salpn})\}$ (**4**). Complexes **2** and **3**, although of the same nuclearity, are topologically different, given that, in the former, the two Fe(III) ions are coordinated to both of type-A and -B binding sites, whereas in the latter, the two type-A binding sites are occupied. In the trinuclear complex **4**, the metal centers are arranged at the vertices of an isosceles triangle.

Variable-temperature magnetic susceptibility measurements have provided information on the electronic structure and the extent of magnetic communication among the Fe(III) centers in these multinuclear complexes. The mononuclear compound **1** is an Fe(III) complex with $t_{2g}^3e_g^2$ electron configuration, whereas the data for compounds **2–4** suggest the presence of weak intramolecular antiferromagnetic exchange interactions with interaction parameters ranging from -3.6 to -5.1 cm^{-1} . Differences in the extent of the magnetic communication between the metal centers through the two different magnetic exchange pathways of the MeDCBI and DCBI ligands (through the imidazole ring, A–A pathway, and through the carboxylate groups, A–B pathway) have been observed. The main factors that affect the magnetic communication are the separation of the metal centers and the coplanarity of metal ion orbitals with the π system of the ligands. In the case of the binuclear complexes **2** and **3**, which are of the same nuclearity but are topologically different, it has been found that magnetic interaction through the A–A pathway is slightly stronger than the magnetic interaction through the A–B pathway. However, this result cannot be considered general, and it applies only in the particular cases of compounds **2** and **3**, as the poorer magnetic communication in compound **2** is probably the result of the nonplanarity of the Fe ion coordinated to the type-B site with the π system of MeDCBI. Indeed, in the case of the trinuclear compound **4**, in which all of the metal atoms are coplanar with the aromatic π system of DCBI, the magnetic communication is more effective through the A–B than the A–A pathway.

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Supporting Information Available: Listings of IR stretching frequencies of all compounds; $\chi_M T$ vs T and $1/\chi_M$ vs T graphs for **1**; cyclic voltammograms of **1–4**; thermal ellipsoid plots, complete tables with bond distances, bond angles, atomic coordinates, and X-ray crystallographic data in CIF format for **1**·1.25MeCN, **2**·2.5MeCN·1.5CH₂Cl₂, **3**, and **4**·2.5MeCN. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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