Inorganic Chemistry

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Molecular [$(Fe_3)-(Fe_3)$] and [$(Fe_4)-(Fe_4)$] Coordination Cluster Pairs as Single or Composite Arrays

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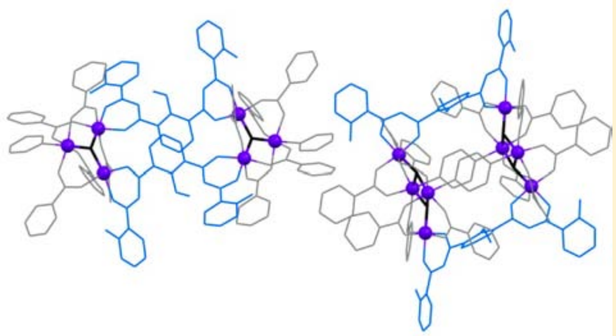
Supporting Information



ABSTRACT: The synthesis of molecular cluster pairs is a challenge for coordination chemists due to the potential applications of these species in molecular spintronics or quantum computing. The ligand H_4L, 1,3-bis-(3-oxo-3-(2-hydroxyphenyl)-propionyl)-2-methoxybenzene, has been successfully used to obtain a series of such complexes using the basic Fe(III) trinuclear carboxylates as starting materials. Synthetic control has allowed the isolation of the two molecular cluster pairs that form the composite $[Fe_4O_2(PhCO_2)_6(H_2L)(pz)]_2[Fe_3O(PhCO_2)_5(py)(H_2L)]_2$ (**1**). The dimers of trinuclear units, $[Fe_3O(PhCO_2)_5(H_2O)(H_2L)]_2$ (**2**) and $[Fe_3O(o\text{-}MePhCO_2)_5(H_2L)(py)]_2$ (**3**), and the dimers of tetranuclear units, $[Fe_4O_2(PhCO_2)_6(H_2L)(pz)]_2$ (**4**) and $[Fe_4O_2(o\text{-}MePhCO_2)_6(H_2L)(pz)]_2$ (**5**), are presented here. The magnetic properties of the reported aggregates show that they are pairs of semi-independent clusters weakly interacting magnetically as required for two-qubit quantum gates.

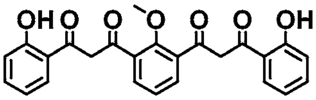
■ INTRODUCTION

The bottom-up approach to nanotechnology implies the preparation and manipulation of molecular objects for the construction of functional devices.[1,2] Such arrays not only will push the borders of miniaturization to its ultimate molecular-scale limit but will offer the possibility of exploiting quantum effects.[3] In this context, the impressive development that has occurred with regard to the synthesis of coordination spin clusters has opened very attractive possibilities. Among these are the potential of using molecules individually for the storage of magnetic information (single-molecule magnets, SMMs,[4−6]) and for the implementation of quantum computing[7] as one or two qubits[8] or the use of such molecules in spintronic devices.

Chemical synthesis is the first step in the process of development of functional molecules. In the case of cluster nanomagnets, the vast majority of useful molecules have been synthesized using coordination chemistry through the "serendipitous self-assembly" approach.[9] Nevertheless, deliberate synthetic strategies for specific purposes have been implemented with success, for example, to prepare[10] or modify existing SMMs[11−14] or for tuning the weak magnetic exchange between spin-cluster based qubits.[15] The latter are species that exhibit two low-lying quantum (magnetic) states, which can be considered the two states of a qubit. Chemical design should allow achievement of these properties and facilitate the resonance between both states with long coherence times. With chemistry, it may also be possible to locate such qubits in the appropriate disposition for the realization of quantum gates (QGs).[24,25]

For some years, we have been engaged in a program for the design and synthesis of multidentate ligands aimed at the preparation of coordination clusters with predetermined structures and properties. A family of ligands has been created featuring several β-diketone and phenol groups in a linear fashion with the purpose of gathering several paramagnetic transition metal centers within molecules in the form of chains or "molecular wires".[16] Thus, several clusters have ensued, with expected topologies such as [M···M],[17] [M−M···M],[18] [M···M···M],[19] [M−M−M−M],[20] $[M{-}M{-}M{-}M]_2$,[21] [M−M···M−M][22] or [M′−M···M−M′][22] (M = Mn, Ni, Cu, Co; M′ = Cu). Also, we have probed the possibility of using one such ligand (H_4L, 1,3-bis-(3-oxo-3-(2-hydroxyphenyl)-propionyl)-2-methoxybenzene, Scheme 1) to link two independent metal aggregates within stable molecules. We succeeded with the preparation of a series of molecular species containing pairs of semi-independent coordination clusters, $[(Mn_4)-(Mn_4)]$.[23] This is a possible entry into the synthesis of a rare type of molecules containing separated spin clusters, slightly interacting

Scheme 1. The Ligand H_4L



Received: May 14, 2012
Published: July 17, 2012

magnetically with each other, as required for two-qubit quantum gates.[24,25]

Incorporation of Fe as the spin carrier within molecular pairs of clusters is an attractive possibility with regard to the search of spin-based two-qubit quantum gates. Indeed, long enough coherence times, necessary for qubit manipulations, have been observed on Fe(III)-based SMMs.[26] In addition, a theoretical proposal suggests the use of connected isosceles Fe(III) triangles for realizing quantum operations.[27] We report here the use of H_4L as an entry into real molecular entities in the form of two weakly interacting clusters of Fe(III). Thus, a remarkable composite array including two types of molecular cluster pairs within the crystal lattice, $[(Fe_3)-(Fe_3)]$ and $[(Fe_4)-(Fe_4)]$, has been obtained. Moreover, we report here synthetic methods allowing us to prepare independently both members of the composite as pure products, in order to investigate without interference their physical properties.

EXPERIMENTAL SECTION

All chemicals were purchased from commercial sources and used as received. Complexes $[Fe_3O(O_2CPhR)_6(X)_3]NO_3$ (R = H, Me; X = H_2O, py) were prepared as previously reported.[36] The ligand 1,3-bis-(3-oxo-3-(2-hydroxyphenyl)-propionyl)-2-methoxybenzene (H_4L) was prepared as previously reported.[23]

$[Fe_4O_2(PhCO_2)_6(H_2L)(pz)]_2[Fe_3O(PhCO_2)_5(py)(H_2L)]_2$ (1). The complex $[Fe_3O(PhCO_2)_6(py)_3]NO_3$ (0.17 g, 0.14 mmol) was mixed with 0.06 g (0.14 mmol) of H_4L and 0.025 g (0.3 mmol) of pyrazine (pz) in 10 mL of $CHCl_3$. The reaction mixture was heated to the boiling point of the solvent and then kept in reflux for 3 h. After this time, the red solution obtained was allowed to cool to room temperature. A small amount of solid was filtered off, and the resulting solution was layered with an equal volume of hexanes. Crystals suitable for single-crystal X-ray diffraction were obtained in 5−7 days in 54% yield. Better quality crystals could be obtained by recrystallization in $CHCl_3$/hexanes. Elemental analyses for $1{\cdot}4H_2O{\cdot}4CHCl_3$ experimental (calculated): 54.24 (54.48) %C, 2.87 (3.48) %H, 2.24 (1.37) %N.

$[Fe_3O(PhCO_2)_5(H_2O)(H_2L)]_2$ (2). Compound $[Fe_3O(PhCO_2)_6(py)_3]NO_3$ (0.347 g, 0.28 mmol) was mixed with 0.123 g (0.28 mmol) of H_4L in 10 mL of $CHCl_3$. The mixture was heated to the boiling point of the solvent and kept in reflux for 3 h. During this time, the solids dissolved, and a red solution was obtained. The red solution was allowed to cool to room temperature, and a small amount of solid was filtered off. The solution obtained was layered with an equal volume of hexanes, and crystals were obtained in 82% yield after 5−7 days. These were recrystallized in $CHCl_3$/hexanes in order to obtain single crystals of good quality for X-ray diffraction studies. Elemental analyses for **2** experimental (calculated): 56.50 (56.01) %C, 3.50 (3.58) %H.

$[Fe_3O(o\text{-}MePhCO_2)_5(H_2L)(py)]_2$ (3). Compound $[Fe_3O(o\text{-}MePhCO_2)_6(py)_3]NO_3$ (0.31 g, 0.24 mmol) was mixed with 0.078 g (0.18 mmol) of H_4L in 10 mL of $CHCl_3$. The reaction mixture was heated to the boiling point of the solvent and then kept in reflux for 3 h. After this time, the red solution obtained was allowed to cool to room temperature. A small amount of solid was filtered off, and the resulting solution was layered with an equal volume of hexanes. Crystals were obtained in 5−7 days in 50% yield. Elemental analyses for $3{\cdot}2CHCl_3$ experimental (calculated): 57.18 (57.30) %C, 4.07 (4.00) %H, 2.14 (0.94) %N.

$[Fe_4O_2(PhCO_2)_6(H_2L)(pz)]_2$ (4). Compound $[Fe_3O(PhCO_2)_6(py)_3]NO_3$ (0.30 g, 0.24 mmol) was mixed with 0.078 g (0.18 mmol) of H_4L and 0.078 g (0.96 mmol) of pyrazine (pz) in 10 mL of $CHCl_3$. The reaction mixture was heated to the boiling point of the solvent and then kept in reflux for 3 h. After this time, the red solution obtained was allowed to cool to room temperature. A small amount of solid was filtered off, and the resulting solution was layered with an equal volume of hexanes. Crystals were obtained in 5−7 days in 60% yield. Elemental analyses for $4{\cdot}2H_2O{\cdot}CHCl_3$ experimental (calculated): 54.68 (54.68) %C, 3.70 (3.56) %H, 3.55 (1.78) %N.

$[Fe_4O_2(o\text{-}MePhCO_2)_6(H_2L)(pz)]_2$ (5). Compound $[Fe_3O(o\text{-}MePhCO_2)_6(py)_3]NO_3$ (0.31 g, 0.24 mmol) was mixed with 0.078 g (0.18 mmol) of H_4L and 0.078 g (0.96 mmol) of pyrazine (pz) in 10 mL of $CHCl_3$. The reaction mixture was heated to the boiling point of the solvent and then kept in reflux for 3 h. After this time, the red solution obtained was allowed to cool to room temperature. A small amount of solid was filtered off, and the resulting solution was layered with an equal volume of hexanes. Crystals were obtained in 5−7 days in 62% yield. Elemental analyses for $5{\cdot}2CHCl_3$ experimental (calculated): 55.68 (55.28) %C, 3.98 (3.36) %H, 2.82 (1.65) %N.

Elemental analyses were performed at the Serveis Científico-Tècnics of the Universitat de Barcelona on several samples of each reported complex. Catalysts were used to improve burning of the complexes, but complete combustion was not achieved due to the polyaromatic nature of the complexes. Single-crystal diffraction data for **1** were collected on station 16.2 SMX of the Daresbury synchrotron facility (T = 150 K, λ = 0.7848 Å). Data were collected for **2** on station 9.8 at Daresbury Synchrotron Radiation Source (UK) (T = 150 K, λ = 0.69110 Å). Data for complexes **3** and **5** were collected at the Unidade de Raios X, RIAIDT, University of Santiago de Compostela, Spain, using Mo Kα radiation. The structures were solved by direct methods and refined on F^2 with SHELXTL suite.[37] Hydrogen atoms were included on calculated positions, riding on their carrier atoms.

RESULTS AND DISCUSSION

The reaction in $CHCl_3$ of the known cluster $[Fe_3O(PhCO_2)_6(py)_3]NO_3$[36] ($HPhCO_2$ = benzoic acid) with H_4L and pyrazine (pz) in the 1:1:2 molar ratio produced red crystals upon layering with hexanes. Single-crystal X-ray diffraction studies revealed a fascinating composite coordination system described by the formula $[Fe_6O_2(BzO)_{10}(H_2L)_2(py)_2]$-$[Fe_8O_4(BzO)_{12}(H_2L)_2(pz)_2]$ (**1**). The structure of compound **1** (see Table S1, Supporting Information, for metric parameters) displays two distinct neutral complexes, both described as a pair of oxo/carboxylato Fe(III) clusters, linked and maintained as quasi-independent entities by two H_2L^{2-} ligands via their β-diketonate coordination pockets (Figure 1; Figures S1 and S2, Supporting Information).

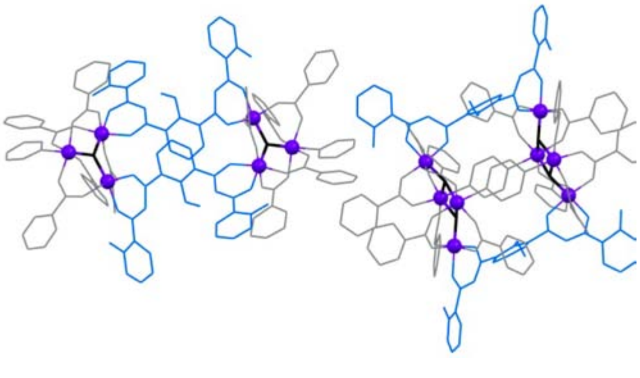


Figure 1. Graphic representation of complexes $[Fe_6O_2(BzO)_{10}(H_2L)_2(py)_2]$ and $[Fe_8O_4(BzO)_{12}(H_2L)_2(pz)_2]$ as present in the composite compound **1**. Purple balls are Fe(III) atoms and the rest are C, N, or O atoms. Hydrogen atoms are not shown. Emphasized in blue are H_2L^{2-} ligands, connecting pairs of clusters.

One of the cluster pairs of **1** is formed by two oxo-centered triangles of octahedral Fe(III) ions with two edges spanned by a total of four *syn,syn* benzoate ligands (two per side) and the third edge capped by only one benzoate group. The metals of this edge also act as the anchoring points for the H_2L^{2-} ligands to link both triangles (holding them ca. 11 Å apart). The third Fe center of each triangle is also bound to one pyridine ligand. The structure of this $[(Fe_3)-(Fe_3)]$ entity is described later in greater detail when discussing the cluster as obtained individually (see below and Figure 2). The other cluster pair exhibits two tetranuclear aggregates of Fe(III) held within the same molecule nearly 7 Å from each other by two H_2L^{2-} species. The (Fe_4) aggregates show the known $[Fe_4O_2]^{8+}$ "butterfly" arrangement,[28] with two μ_3-O^{2-} ligands and a total of six benzoate ligands linking the body ions to the wingtip metals in the *syn,syn* bridging mode. The connection between both (Fe_4) clusters occurs at the wingtip metals through the H_2L^{2-} ligands via their β-diketonate units. An additional link between both "butterfly" units occurs via two pyrazine (pz) ligands, which bridge the central Fe ions of one (Fe_4) cluster to their counterparts from the other. More details on this structure are provided with the description of the molecule crystallized alone (see below and Figure 3). The packing forces cementing the composite array in **1** are of van der Waals type or $\pi\cdots\pi$ interactions, as a result of the hydrophobic shell surrounding both types of molecules. The shortest intermolecular Fe···Fe distance encountered is of 8.933 Å.

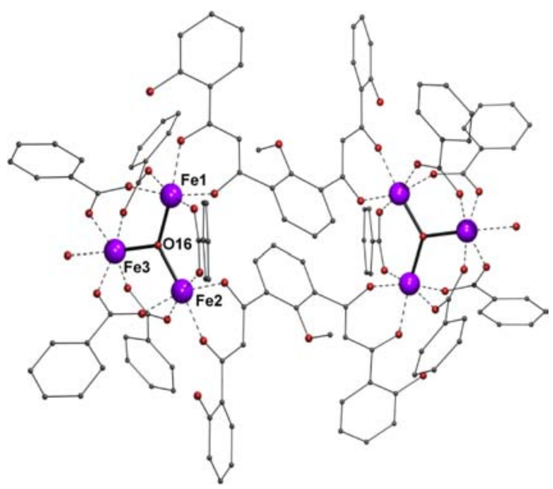


Figure 2. POV-ray representation of the structure of $[Fe_6O_2(BzO)_{10}(H_2L)_2(H_2O)_2]$ (**2**) synthesized as pure product. H atoms not shown.

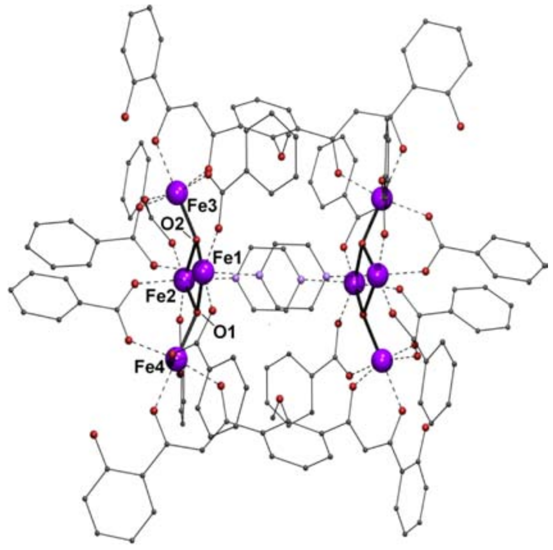


Figure 3. POV-ray representation of the structure of $[Fe_8O_4(o\text{-}MePhCO_2)_{12}(H_2L)_2(pz)_2]$ (**5**) synthesized as pure product. H atoms and toluate CH_3's not shown.

The $[(Fe_3)-(Fe_3)]$ and $[(Fe_4)-(Fe_4)]$ species cocrystallized in **1** constitute a unique combination of two coordination complexes of the very small group found under the category of "molecular cluster pairs". The only two reported pairs of well-defined Fe(III) butterfly clusters are based on polycarboxylate ligands[29] or combine simple carboxylates with alkaline cations helping to bridge both clusters.[30] Ferric $[Fe_3O]^{7+}$ triangles constitute a convenient building block in the construction of "clusters of aggregates".[31] Of these, the very few existing $[(Fe_3)-(Fe_3)]$ molecules make use of only carboxylates[32] or include other ligands.[33] The discovery of this supramolecular assembly immediately posed the challenge of synthesizing both components independently. As an attempt of isolating only the pair of Fe triangles, the above reaction was performed in the absence of pyrazine. Thus, mixing the complex $[Fe_3O(PhCO2)_6(py)_3]NO_3$ with 1 equiv of H_4L in $CHCl_3/Et_2O$ led to crystals that were analyzed by X-ray diffraction (Table 1). The product was identified as $[Fe_3O(PhCO_2)_5(H_2L)(py)]_2$ (**2**), the expected $[(Fe_3)-(Fe_3)]$ single component. Complex **2** (Figure 2 and Figure S3, Supporting Information) is a centrosymmetric molecule formed by two (Fe_3) oxo-centered parallel triangles linked by two H_2L^{2-} ligands, almost identical to its equivalent in **1** with the difference that the sole terminal ligand is now a molecule of water (O1) instead of pyridine. As in the pair of triangles of **1**, two edges per triangle of **2** are bridged by two *syn,syn*-caboxylates and the third edge by only one such ligand. A list of interatomic distances and angles is given in Table S2, Supporting Information. All Fe(III) centers display octahedral geometry and exhibit shortest intermetallic distances (within triangular units) of 3.405 Å (Fe1,Fe2), 3.280 Å (Fe2,Fe3), and 3.269 Å (Fe3,Fe1). The bis-β-diketonate ligands maintain both triangles separated within the molecule, with their Fe(III) ions lying at 10.693 Å or further apart. Interestingly, the shortest intertriangle Fe···Fe distances (5.346 Å) correspond to triangles from different molecules, rather than those within the same molecule. In fact, the molecules of **2** interact with each other by means of hydrogen bonds, established between the terminal water ligands and oxygen atoms from benzoate ligands of the neighboring molecules. The result is the formation of a 1D supramolecular organization in the form of a zigzag chain (Figure S4, Supporting Information). If the reaction is performed with $[Fe_3O(o\text{-}MePhCO_2)_6(py)_3]NO_3$ (o-$MePhCO_2H$ = *ortho*-toluic acid), crystals of another pair of triangles, $[Fe_6O_2(o\text{-}MePhCO_2)_5(H_2L)_2(py)_2]$ (**3**), are obtained (see Table S3, Supporting Information, for full structural details). There are important differences (Figure S5, Supporting Information) from the structure of **2**, besides the nature of the carboxylate. First is the presence of two terminal pyridine ligands instead of H_2O. Thus, the molecules of **3** are isolated in the crystal structure and not forming hydrogen-bonded supramolecular chains. The other main difference is the conformation of H_2L^{2-}, causing now the central anisole moieties to lie face to face pointing approximately in the same direction, and both Fe_3 triangles of the cluster to form an angle of 53.32° instead of being parallel. The shortest intertriangle Fe···Fe distance within **3** is 9.683 Å, whereas between molecules, this distance is again shorter (8.098 Å). Steric reasons involving the methyl groups of the toluate groups are at the root of this new molecular conformation.

An equally important challenge was the separate synthesis of the $[(Fe_4)-(Fe_4)]$ component of **1**. This aggregate could also be isolated by appropriately adjusting the reaction variables. In this

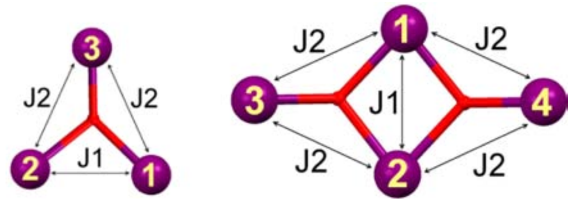
Table 1. Crystal Data for Compounds **1**−**3** and **5**

	1	**2**	**3**	**5**
formula	$C_{280}H_{216}Cl_{24}Fe_{14}N_6O_{82}$	$C_{120}H_{98}Fe_6O_{42}$	$C_{143}H_{119}Cl_9Fe_6N_2O_{36}$	$C_{158}H_{132}C_{l12}Fe_8N_4O_{42}$
FW, g/mol	6609.29	2547.08	3095.55	3630.88
crystal system	triclinic	monoclinic	triclinic	monoclinic
space group	$P\overline{1}$	$P2_1/c$	$P\overline{1}$	$P2_1/n$
a, Å	20.151(2)	18.941(4)	16.209(2)	15.3941(6)
b, Å	20.915(2)	11.936(3)	21.766(2)	27.2076(10)
c, Å	22.034(3)	27.249(6)	22.642(2)	19.6672(6)
α, deg	117.5220(10)	90	109.537(4)	90
β, deg	93.717(2)	103.558(2)	102.182(4)	109.284(2)
γ, deg	91.867(2)	90	100.760(4)	90
V, Å^3	8197.4(16)	5989(2)	7066.0(13)	7775.2(5)
Z	1	2	2	2
ρ_{calc}, g/cm^3	1.339	1.412	1.455	1.551
μ, mm^{-1}	1.134	0.730	0.848	1.013
T, K	100	150	100	100
transmission range	0.87−0.95	0.94−0.99	0.87−0.97	0.81/0.94
unique reflections	15589	6101	11134	15999
params/restraints	1846/380	775/67	1737/1334	1185/286
wR2 (all data)	0.2591	0.1454	0.3747	0.1863
R1 (all data)	0.1194	0.0959	0.1865	0.1340
S (all data)	1.011	0.962	1.013	1.020
wR2 [$I > 2\sigma(I)$]	0.2221	0.1304	0.3416	0.1450
R1 [$I > 2\sigma(I)$]	0.0815	0.0576	0.1333	0.0646
S [$I > 2\sigma(I)$]	1.014	0.961	1.046	1.013

case, using a larger ratio of pz opened the way to isolate $[Fe_4O_2(PhCO_2)_6(H_2L)(pz)]_2$ (**4**) from its reaction with $[Fe_3O(PhCO2)_6(py)_3]NO_3$ and H_4L (in the 4:1:0.75 molar ratio of pz/[Fe$_3$]/H_4L). Crystals for this assembly were obtained when using the precursor $[Fe_3O(o\text{-}MePhCO_2)_6(py)_3]NO_3$), which allowed us to establish the structural details of the corresponding pair of "butterfly" ensembles $[Fe_8O_4(o\text{-}MePhCO_2)_{12}(H_2L)_2(pz)_2]$ (**5**). This complex (Figure 3 and Table S4, Supporting Information, for full structural details) does exhibit the same structure as the [(Fe$_4$)−(Fe$_4$)] component of **1**; it features two "butterfly" [Fe(III)$_4$] fragments linked through their "tips" by the β-diketonate moieties of two H_2L^{2-} ligands and through the "body" metals via two μ-pz bridges. The latter lie in front of each other, thereby establishing a $\pi-\pi$ interaction (intercentroid distance, 3.278 Å). The "body−tip" intermetallic separations range from 3.281 to 3.411 Å, whereas the "body−body" and "tip−tip" distances amount to 2.549 and 5.869 Å, respectively. The closest intermetallic separation between [Fe$_4$] clusters within the molecule of **5** is 7.237 Å. The closest such distance between molecules is 10.101 Å.

The magnetic properties of the coordination assemblies **1**−**5** were investigated through bulk magnetization measurements. Data were collected at an applied field of 0.5 T and in the 300 to 2 K temperature range. The results in the form of $\chi_M T$ vs T plots (Figure 3) reveal $\chi_M T$ values at 300 K well below these expected for fourteen (**1**), six (**2**, **3**), or eight (**4**, **5**) independent Fe(III) ions with $S = 5/2$ and $g = 2.0$ (expected/found: 61.25/26.01, 26.25/9.56, 26.25/13.90, 35/9.41, 35/9.90 cm^3 K mol^{-1}, for **1**, **2**, **3**, **4**, and **5**, respectively). This is common for polynuclear Fe(III) complexes with oxido and carboxylato ligands,[30] which mediate strong antiferromagnetic coupling. Thus, as temperature decreases, so does the χT product due to the Boltzman depopulation of excited states with higher spin values. The size of the spin matrices for the Fe$_8$ (1 679 616 terms) and Fe$_6$ (46 656 terms) complexes demand prohibitive computation capacities. Nevertheless, the Kambe method[34] allows writing an analytical Van Vleck equation, if the ensembles are treated as [Fe$_3$] and [Fe$_4$] units, which are then weakly coupled. This model is realistic and provides a Hamiltonian for the [Fe$_3$] and [Fe$_4$] subclusters (eqs 1 and 2; $S_i = 5/2$ and labels from Scheme 2) that can be analytically solved to obtain a Van Vleck equation using the Kambe approach. These equations are used to fit the experimental data. The interaction between clusters is considered including the zJ' parameter from the mean field theory.[35] These equations feature the triangles as isosceles and consider two different exchange pathways within the "butterfly" clusters.

Scheme 2. Coupling Scheme and Labeling Used to Model the Magnetic Exchange within the Cores of **2**−**5**



$$H = -2J_1S_1S_2 - 2J_2(S_1S_3 + S_2S_3) \tag{1}$$

$$H = -2J_1S_1S_2 - 2J_2(S_1S_3 + S_1S_4 + S_2S_3 + S_2S_4) \tag{2}$$

Data from the [(Fe$_3$)−(Fe$_3$)] (**2**, **3**) and [(Fe$_4$)−(Fe$_4$)] (**4**, **5**) complexes were fit using these equations, and the results are summarized in Table 2. For comparison, data for the triangular complex $[Fe_3O(PhCO_2)_6(H_2O)_3]NO_3$ were also collected and fit with the same model (excluding the zJ' term), and the results are also featured in Table 2 and Figure 4. The results reflect the expected moderate to strong antiferromagnetic interactions usually observed within oxo/carbolylato Fe(III) aggregates,

Table 2. Magnetic Fitting Parameters for Complexes 2−5 (See Text)

complex	g	J_1 (cm^{-1})	J_2 (cm^{-1})	zJ' (cm^{1})
[(Fe_3)−(Fe_3)] **2**	2.05	−23.02	−40.25	−1.48
[(Fe_3)−(Fe_3)] **3**	2.05	−7.45	−27.64	−0.32
[(Fe_4)−(Fe_4)] **4**	2.08	−45.59	−34.39	−3.36
[(Fe_4)−(Fe_4)] **5**	2.08	−35.32	−29.98	−3.5
[Fe_3][a]	2.05	−33.00	−26.00	

[a] Fitting parameters for [$Fe_3O(PhCO_2)_6(H_2O)_3$]NO_3 for comparison.

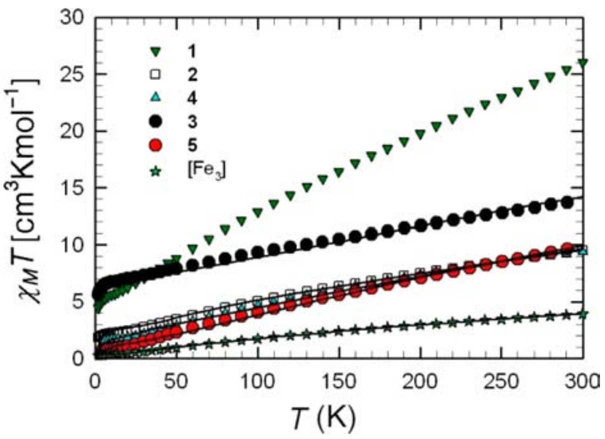


Figure 4. Plots of $\chi_M T$ vs T for complexes **1**−**5**. Data for the complex [$Fe_3O(PhCO_2)_6(H_2O)_3$]NO_3 are also included for comparison. The solid lines are fits of the data (see text).

leading to spin ground states of $S = 3/2$ for each [Fe_3] unit of complex **2**, $S = 5/2$ for each [Fe_3] unit of complex **3**, $S = 1$ for each [Fe_4] unit of complex **3**, and $S = 1$ for each [Fe_4] unit of complex **4**. It is important to note that all the fits predict a weak antiferromagnetic interaction between [Fe_x] subunits, leading to diamagnetic ground states with low-lying non-zero spin excited states for the complexes. This intercluster interaction appears stronger if mediated through pyrazine moieties. For the case of the [(Fe_3)−(Fe_3)] clusters, the most relevant intertriangle interactions may occur between different molecules rather than within the hexanuclear assemblies. This is most likely the case for complex **2**, which exhibits intermolecular [Fe_3] distances of only 5.346 Å between triangles that exhibit two strong complementary H-bonds involving H_2O molecules bound to the metals (Figure S4, Supporting Information). Complex **3** does not exhibit these interactions and shows in turn the weakest zJ' value. The presence of excited states with higher S values near the ground state is also reflected in the magnetization vs field plot at 2 K (Figure S6, Supporting Information), where Boltzman population of the excited states is evident.

■ SUMMARY

In summary, we have shown that the use of bis-β-diketone gives access to a variety of coordination architectures described as covalent pairs of Fe(III) aggregates, as a promising approach to possible molecular spin-based two-qubit quantum gates. Crucial for exploring this approach is the chemical control for selecting the architecture of the final assembly and fine-tuning their properties. The synthetic work presented here is a promising step in this direction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Bond distances of the Fe coordination spheres and angles of the Fe−O−Fe bridges for structures **1**, **2**, **3**, and **5**, hydrogen bonds in compounds **1**−**3**, structural representations of compounds **1**−**3**, magnetization versus field plots for complexes **1**−**5**, IR spectra, and structural information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data files for the complexes are available free of charge from the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 856827, 856828, 856929, and 856830 (CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax +(44)1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

G.A. thanks the Generalitat de Catalunya for the prize ICREA Academia 2008 and the ERC for a Starting Grant (ERC-2010-StG; 258060 FuncMolQIP). The authors thank the Spanish MCI through CTQ2009-06959 (G.A., E.C.S., and A.P.), MAT2011-24284 (O.R.) and a "Ramón y Cajal" Contract (E.C.S.), and the ERC for a doctoral fellowship through ERC-2010-StG-258060 (J.S.U.).

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