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Modulated Magnetic Coupling in Alkoxoiron(III) Rings by Host−Guest Interactions with Alkali Metal Cations

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Introduction

Noncovalent interactions are understood to be the driving force to generate complex molecular structures. Supramolecular chemistry[2] aims to employ molecular approaches to prepare molecular systems with a preordained property. Although prior to now supramolecular chemistry and magnetism have not been closely related, it is becoming clear that molecular magnetism may be considered as the facet of supramolecular chemistry dealing with open-shell molecules.[3]

Among the supramolecular aspects which have received more attention so far in molecular magnetism are hydrogen bonds[4] and host−guest interactions.[5] The latter in particular have proven to be of paramount importance for the template synthesis of large magnetic clusters.[6−8] However, so far it has not been possible to unambiguously prove how the guests influence the magnetic coupling in the clusters.

Recently, we performed detailed structural and magnetic studies on a novel class of cyclic hexairon(III) clusters synthesized in our laboratories,[7,8] $[NaFe_6(OCH_3)_{12}(dbm)_6]^+$ (**1**) and $[NaFe_6(OCH_3)_{12}(pmdbm)_6]^+$ (**2**).[9] An interesting feature of these compounds is the presence of a sodium ion trapped in the hollow core of the cluster, which acts as an inorganic crown ether with the [12]crown-6 structure.[7] In order to establish the influence of the encapsulated alkali metal ion on the properties of the core, we attempted the synthesis of potassium- and lithium-containing cyclic clusters. The former attempt was unsuccessful, as expected on the basis of the large ionic radius of potassium. However, the complexes $[LiFe_6(OCH_3)_{12}(dbm)_6]X\cdot xCHCl_3\cdot yCH_3OH$ ([**3**]$X\cdot xCHCl_3\cdot yCH_3OH$, [**3**]X for short), with X = PF_6^- and ClO_4^-, were readily obtained as crystalline materials. We intend to show here how changing the guests on hexanuclear iron(III) rings can vary the extent of the magnetic coupling between the metal ions, thus providing an important tool for the modulation of the properties of molecular magnets.

Experimental Section

Synthesis. All manipulations were performed under aerobic conditions with use of materials as received. Methanol (Aldrich) was distilled over $Mg(OCH_3)_2$ shortly before use. **Warning!** *Appropriate care should be taken in the use of perchlorate salts. The described compounds have not displayed any explosive tendencies, but caution is advised.* To iron(III) chloride (10 mmol) dissolved in 30 mL of anhydrous methanol was slowly added with vigorous stirring a solution of Hdbm (10 mmol) and lithium methylate (40 mmol) in 120 mL of anhydrous methanol (45 min). The mixture was stirred for an additional hour; the yellow precipitate was then filtered off, washed with methanol, and dried under vacuum. Next, 0.7 g of the above solid and 1 mmol of anhydrous lithium perchlorate were suspended in 30 mL of a $CHCl_3/CH_3OH$ mixture (1:1 v/v). Chloroform was then added dropwise until complete dissolution. Slow, spontaneous concentration of the resulting deep-red solution led to orange-red crystals of [**3**]ClO_4 in quantitative yield. Anal. Found on vacuum-dried samples: C, 58.43; H, 4.83; Cl(tot), 1.66; Cl^-, undetectable by potentiometric titration with $AgNO_3$ in an acetone/water mixture. Calcd for [**3**]ClO_4: C, 58.44; H, 4.80; Cl, 1.65. Deep-red cubic crystals of [**3**]PF_6 were obtained by replacing $LiClO_4$ with $LiPF_6$ (0.1 M solution in methanol) in the above procedure. Anal. Found on vacuum-dried samples: C, 55.13; H, 4.73; Cl(tot), 0.2; Cl^-, undetectable. Calcd for [**3**]PF_6: C, 55.72; H, 4.68. A 0.1 M solution of $LiPF_6$ was prepared by reaction of KPF_6 (10 mmol) and LiCl (10 mmol) in 60 mL of methanol. KCl was filtered off, and methanol was added to the solution to reach a 100-mL volume.

X-ray Data Collection and Structure Refinement. Diffraction data for [**3**]PF_6 were collected on an Enraf-Nonius CAD4 four-circle diffractometer with graphite-monochromated Mo Kα radiation. Selected experimental parameters and crystal data are reported in Table 1. A total of 5909 reflections were measured in the range $5° < 2\theta < 50°$; corrections for Lorentz polarization and absorption (ψ scans) were applied. The structure was solved by direct methods (SIR92[10]) and refined by SHELXL-93[11] package. For 245 parameters and 3508 unique reflections, the largest peak and hole in the final Fourier map were 0.7 and −0.3 e Å^{-3}, respectively. The poorly-resolved PF_6 anion resides on the $\bar{3}$ axis and is disordered over two positions related by an inversion center. Additional low-intensity peaks outside the cluster were attributed to disordered chloroform and methanol molecules (9 CH_3OH + 0.5 $CHCl_3$ per unit cell). However, experimental density suggests that additional highly-disordered solvent molecules may be present in the lattice. Anisotropic thermal parameters were refined for Cl and P atoms and for all non-hydrogen atoms of **3**. Hydrogen atoms were treated as fixed contributors in calculated positions with isotropic thermal parameters $B(H) = 1.2B_{eq}(C)$. Selected interatomic distances and angles are listed in Table 2. A full listing of crystal data, experimental parameters, final atom positional and thermal parameters, and bond lengths and angles is given in the Supporting Information.

Magnetic Susceptibility Measurements and NMR Studies. Magnetic susceptibilities of vacuum-dried powdered samples of [**3**]X were measured by using a Métronique Ingénierie MS03 SQUID magnetometer in the temperature range 2.6−300 K with an applied field of 1 T. The molecular weight of the unsolvated [**3**]X was used for data reduction, consistent with elemental analysis results. Corrections for the contribution of the sample holder and for molecular diamagnetism, estimated from Pascal's constants, were applied. ^1H, ^{23}Na, and ^7Li NMR spectra were recorded with the apparatus described in ref 8. In a typical experiment, a 40-mg sample of crystalline [**3**]ClO_4 was dissolved in 0.5 mL of $CDCl_3$ to yield a ~0.03 M solution. $NaBPh_4$ was used as a 0.3 M solution in $CHCl_3/CH_3OH$ (2:1 v/v); $LiBPh_4$ was

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(9) Abbreviations used: Hdbm = 1,3-diphenyl-1,3-propanedione (dibenzoylmethane); Hpmdbm = 1,3-bis(*p*-methoxyphenyl)-1,3-propanedione.

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Table 1. Crystal Data and Experimental Parameters for [**3**]$PF_6 \cdot xCHCl_3 \cdot yCH_3OH$

chem formula[a]	$Fe_6LiC_{111.5}H_{138.5}O_{33}Cl_{1.5}PF_6$	formula weight[a]	2546.91
a	14.523(2) Å	space group	$R\bar{3}$ (No. 148)
α	84.35(1)°	T	298(2) K
V	3021.3(7) Å^3	λ	0.71069 Å
Z	1	μ[a]	8.31 cm^{-1}
ρ_{obsd}	1.45(1) g cm^{-3}	R1[b]	0.073
ρ_{calcd}[a]	1.400 g cm^{-3}	wR2[c]	0.253

[a] For $x = 0.5$, $y = 9$. [b] On 2085 independent reflections with $I > 2\sigma(I)$; $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] On all data; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o)^4]^{1/2}$, with $w = 1/[\sigma^2(F_o^2) + (0.1339P)^2]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **2** and **3**[a]

	2 (M = Na)	**3** (M = Li)
Fe···Fe^a	3.2152(5)	3.140(1)
Fe···Fe^b	5.5627(9)	5.429(2)
Fe···Fe^c	6.425(1)	6.272(3)
Fe−O1	2.023(3)	2.016(3)
Fe−O1^a	2.041(3)	2.046(3)
Fe−O2	2.000(4)	1.992(3)
Fe−O2^a	2.014(3)	2.000(4)
Fe−O3	2.001(3)	1.985(4)
Fe−O4	1.982(3)	1.974(4)
M−O1	2.352(1)	2.199(3)
Fe···Fe^a···Fe^b	119.781(4)	119.66(2)
O2−Fe−O1	74.8(1)	77.9(1)
O2^a−Fe−O1^a	74.1(1)	77.0(1)
O4−Fe−O3	85.8(1)	86.8(2)
O1−M−O1^a	78.2(1)	80.1(1)
O1−M−O1^b	101.8(1)	99.9(1)
Fe−O1−Fe^e	104.6(2)	101.3(1)
Fe−O2−Fe^e	106.5(2)	103.8(2)

[a] Superscripts are used for symmetry-equivalent atoms [$X^a = S_6^1(X)$, $X^b = S_6^2(X)$, $X^c = S_6^3(X)$, etc.].

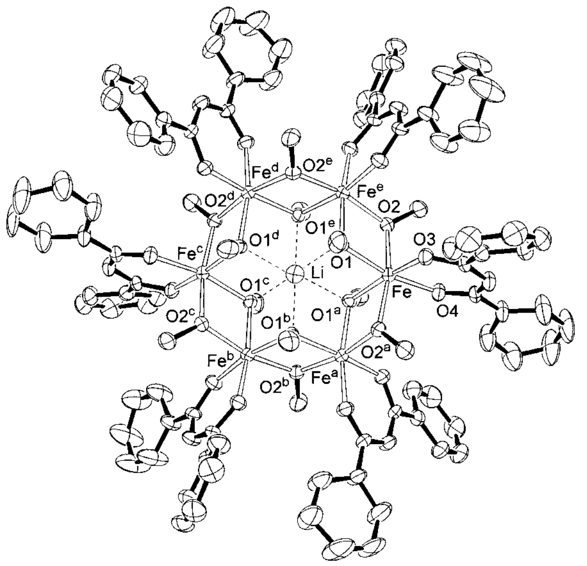

Figure 1. Molecular structure of **3** at 298 K, showing the atom labeling scheme (see footnote *a* in Table 2). Thermal ellipsoids at 25% probability. Hydrogen atoms have been omitted for clarity.

prepared by reaction of $NaBPh_4$ and LiCl in methanol and was used as a 0.3 M solution in $CHCl_3/CH_3OH$ (10:1 v/v). The ^7Li chemical shifts were referenced to external LiCl (saturated solution in $CDCl_3$). Acquisition parameters for ^7Li at 155.50 MHz: spectral width, 800 ppm; FID resolution, 1.9 Hz; relaxation delay, 0.1 s; no. of scans, 8K; a 4-points left shift and an enhancement function (LB = 500 Hz) were applied before Fourier transformation.

Results and Discussion

The crystals of [**3**]ClO_4 are monoclinic[12] and isomorphous with those of [**1**]$Cl \cdot CHCl_3 \cdot 12CH_3OH$;[7] a complete X-ray diffraction study on [**3**]PF_6, which crystallizes in trigonal space group $R\bar{3}$, evidenced substantial structural differences between the cores of **1**−**2** and **3** (Figure 1). A comparison is best carried out between **2** and **3**, both of which have a crystallographically-imposed S_6 symmetry (Table 2). Upon substitution of sodium with lithium, the M−O1 separation decreases from 2.352(1) Å in **2** to 2.199(3) Å in **3**. However, the Fe−O*i* and Fe-O*i*^{a} (i = 1, 2) distances do not vary within error, showing that the encapsulation of the central alkali metal ion is due to essentially noncovalent interactions. While the planarity of the hexairon moiety is retained, as shown by the Fe···Fe^a···Fe^b angles, the nearest-neighbor Fe···Fe separation decreases considerably, being 3.2152(5) Å in **2** and 3.140(1) Å in **3**. Correspondingly, the diameter of the ring, as defined by the Fe···Fe^c distance, decreases from 6.425(1) to 6.272(3) Å. Furthermore, the Fe−O1−Fe^e and Fe−O2−Fe^e angles are significantly more acute in **3** [101.3(1) and 103.8(2)°, respectively] than in **2** [104.6(2) and 106.5(2)°, respectively]. Therefore, the shorter ionic radius of Li (0.68 Å) with respect to that of Na (0.97 Å) leads to a decrease in the “size” of the metal ring and to a more regular topology of the oxygen atoms with respect to an idealized closest-packing CdI_2-type arrangement.[7,8,13]

The solid-state magnetic behavior of [**3**]X was investigated in the temperature range 2.6−300 K with an applied field of 1 T. The experimental χ *vs* T curves for [**1**]Cl and [**3**]ClO_4 are reported in Figure 2 for comparison. The lower value of χ for [**1**]Cl suggests a stronger antiferromagnetic coupling. The temperature dependence of χ confirms this view, with the maximum observed at about 90 K for **3** and 130 K for **1**. Since the temperature of the maximum is expected to scale linearly with the coupling constant j, this is a clear indication of a large variation of j in the two compounds. A quantitative analysis of the magnetic susceptibility of [**3**]X was carried out by means of Heisenberg Hamiltonian:[8]

$$\mathbf{H} = j\sum_{i=1}^{5}\mathbf{S}_i\cdot\mathbf{S}_{i+1} + j\mathbf{S}_6\cdot\mathbf{S}_1$$

The best-fit parameters with g fixed at 2.00 are j = 14.30(2) and 14.68(4) cm^{-1} for X = ClO_4^- and PF_6^-, respectively. These values are to be compared with those obtained for [**1**]Cl (20.4 cm^{-1}) and [**2**]ClO_4 (19.9 cm^{-1}).[8,14]

In order to establish a possible functional analogy between iron(III) rings and crown ethers, we investigated the solution behavior of **1** and **3**. NMR experiments on the trapped heteronuclei proved to be extremely useful, since the encapsulated alkali metal ions in **1** and **3** reside in highly-paramagnetic environments and produce characteristic signals. The ^{23}Na

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(12) Unit cell parameters for [**3**]$ClO_4 \cdot xCHCl_3 \cdot yCH_3OH$ at 298 K: mC, a = 28.830(3) Å, b = 17.565(2) Å, c = 28.588(5) Å, β = 118.06°, V =12775(4) Å^3, Z = 4.

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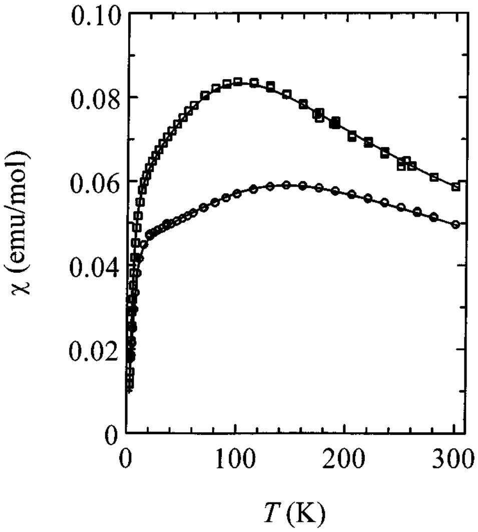

Figure 2. Magnetic susceptibility of powdered samples of [**1**]Cl (○) and [**3**]ClO_4 (□) at 1 T as a function of temperature. The solid lines represent the best-fit curves, as described in the text.

spectrum of **1** in $CDCl_3$ has been already reported,[8] while the room-temperature ^7Li spectrum of [**3**]ClO_4 in $CDCl_3$ is shown in Figure 3a. It is characterized by a very broad, downfield-shifted singlet at about 440 ppm. A much narrower peak at ∼0 ppm is observed after the addition of a soluble lithium salt to the solution (not shown). This strongly suggests that the signal at low field arises from encapsulated lithium ions and that the cyclic structure of **3** is fully retained in solution. Furthermore, since free and encapsulated lithium ions give rise to distinct signals, the exchange reaction

$$[\mathrm{LiFe_6(OCH_3)_{12}(dbm)_6}]^+ + \underline{\mathrm{Li}}^+ \rightleftarrows \mathrm{Li}^+ + [\underline{\mathrm{Li}}\mathrm{Fe_6(OCH_3)_{12}(dbm)_6}]^+$$

must be *slow* on the NMR time scale. The successful assignment of ^{23}Na and ^7Li NMR resonances for **1** and **3**, respectively, prompted us to investigate the selectivity of the rings for alkali metal ions. The ^{23}Na spectrum remained unchanged after the addition of $LiBPh_4$ (1 equiv) to a chloroform solution of [**1**]Cl. At the same time, the ^7Li spectrum indicated the presence of free lithium ions only. In contrast, the addition of $NaBPh_4$ (1 equiv) to a chloroform solution of [**3**]ClO_4 led to the characteristic signals of free lithium and encapsulated sodium ions (Figure 3b,c).

It can be concluded that the reaction

$$[\mathrm{LiFe_6(OCH_3)_{12}(dbm)_6}]^+ + \mathrm{Na}^+ \rightarrow \mathrm{Li}^+ + [\mathrm{NaFe_6(OCH_3)_{12}(dbm)_6}]^+$$

is favored under the adopted conditions and that the $[Fe_6(OCH_3)_{12}(dbm)_6]$ "crown" has a marked affinity for sodium ions.

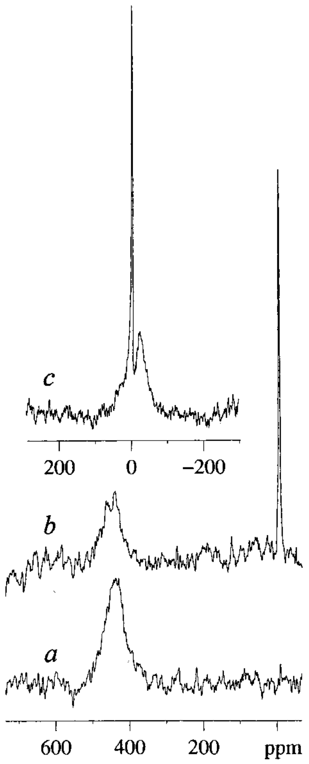

Figure 3. ^7Li spectrum of [**3**]ClO_4 in $CDCl_3$ (a) and ^7Li (b) and ^{23}Na (c) spectra recorded 16 h after the addition of $NaBPh_4$ (1 equiv). Chemical shifts are referenced to external LiCl (saturated) and NaCl (saturated) in $CDCl_3$.

Table 3. Chemical Shifts (ppm from TMS) of Aromatic *Para* and *Meta* Protons of dbm Ligands in Iron(III) Complexes ($CDCl_3$ Solution at 300 K)[a]

compound	δ *para*	δ *meta*	χ/Fe (300 K)[b]
Hdbm[c]	7.56	7.50	
$[NaFe_6(OCH_3)_{12}(dbm)_6]Cl$[c]	6.79 (−0.77)	10.74 (3.24)	0.0083
$[LiFe_6(OCH_3)_{12}(dbm)_6]ClO_4$[c]	6.64 (−0.92)	11.29 (3.79)	0.0098
$[Fe_2(OCH_3)_2(dbm)_4]$[16,c]	5.87 (−1.69)	12.19 (4.69)	0.0123
$Fe(dbm)_3$[17,c]	5.74 (−1.82)	13.88 (6.38)	0.0156

[a] The calculated paramagnetic shifts, defined as $\delta-\delta$(H*dbm*), are given in parentheses. [b] Experimental solid-state magnetic susceptibilities (emu mol^{-1}) *per iron atom* at 300 K. [c] This work.

In a further experiment, a possible reaction of **3** with potassium ions was monitored. However, the ^7Li spectrum was not affected by the addition of KPF_6 (1 equiv) to a chloroform solution of [**3**]ClO_4. These results, while proving that **1** and **3** are true inorganic analogues of crown ethers, open very interesting perspectives for the synthesis of heptanuclear clusters displaying the basic CdI_2-type structure.

Room-temperature ^1H NMR spectra of **1** and **3** in $CDCl_3$ were also recorded. The broad, paramagnetically-shifted resonances from *para* (*meta*) protons of dbm ligands are detected at 6.79 (10.74) and 6.64 (11.29) ppm in **1** and **3**, respectively. As shown in Table 3, the paramagnetic shifts of *para* and *meta* protons in **1**, **3**, $[Fe_2(OCH_3)_2(dbm)_4]$,[16] and $[Fe(dbm)_3]$[17] scale essentially as the solid-state magnetic susceptibilities *per iron atom* at 300 K (Table 3), thus pointing to prevalent contact contributions. The larger paramagnetic shifts observed in **3** with respect to those in **1** are indicative of a larger unpaired spin

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(14) The sudden change of slope around 20 K in the χ *vs* T curve of **1** cannot arise from simple Boltzmann population of spin states. A similar feature was observed in the decairon(III) cluster $[Fe_{10}(OCH_3)_{20}(O_2CCH_2Cl)_{10}]$ and attributed to the presence of magnetic impurities.[15] The susceptibility χ_0 predicted by **H** was, therefore, corrected according to the general expression $\chi = \chi_0(1-\alpha) + 6\alpha N g^2\mu_B{}^2/3k_B(T-\theta)S'(S'+1)$, where $S' = {}^5/_2$ and $g = 2.00$. The introduction of the parameter θ in the fitting of experimental susceptibility data was statistically justified for [**1**]Cl and [**3**]PF_6 only. The best-fit α and θ parameters are as follows: $\alpha = 6.2(2)\times10^{-3}$, $\theta = -7.3(4)$ K for [**1**]Cl; $\alpha = 4.3(3)\times10^{-4}$ for [**3**]ClO_4; $\alpha = 2.2(1)\times10^{-2}$, $\theta = -7.3(2)$ K for [**3**]PF_6.

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density on the metal centers and confirm that the aromatic protons of dbm ligands are sensitive magnetic probes in this class of compounds.[18]

Complexes **1**−**3**, like other polyiron(III) species studied in our laboratory, cover the low-end range of exchange-coupling interactions, for which the scatter obtained by correlating *j* with the Fe−O distance is maximum.[19] The difference in magnetism of **1**−**2** and **3**, which have identical Fe−O distances, clearly demonstrates that other factors may become important when the coupling is small. Our recent studies on a homogeneous series of weakly-coupled polyiron(III) compounds, comprising Fe_2, Fe_4, and Fe_6 species, have revealed a well-defined dependence of *j* on the Fe−O−Fe angle,[16] which is beautifully confirmed by the results reported in this paper: smaller Fe−O−Fe angles lead to weaker exchange-coupling interactions, as observed in strongly-coupled units.[20] Furthermore, the experimental trend shows that the direct overlap of metal orbitals plays a minor role, since it would enhance antiferromagnetic coupling at shorter Fe···Fe separations. Hence, it can be concluded that the encapsulated alkali metal ion in **1**−**3** has a tuning effect on the magnetism of the core: the *j* value is related to the ionic radius of the guest ion, which determines the exact geometry at the bridging methoxide ligands.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the complex [**3**]PF_6 is available on the Internet only. Access information is given on any current masthead page.

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