DOI: 10.1002/ejic.200500640

Tetra- and Decanuclear Iron(II) Complexes of Thiacalixarene Macrocycles: Synthesis, Structure, Mössbauer Spectroscopy and Magnetic Properties

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Keywords: Calixarenes / Hydrothermal synthesis / Iron / Magnetic properties / Mössbauer spectroscopy

Two iron(II) complexes, namely $[Fe_4(L)_2]{\cdot}H_2O$ (**1**) and $[Fe_{10}(L)_4Cl_4]{\cdot}2H_2O$ (**2**), have been synthesised under solvothermal conditions by treating *p*-*tert*-butylthiacalix[4]arene (LH_4) with $FeCl_2$ in methanol. Compound **1** crystallises in the orthorhombic system (space group *Immm*) with the unit-cell parameters a = 17.8308(4), b = 19.1372(3), c = 28.8391(6) Å and V = 9840.8(3) Å^3 (Z = 2). Compound **2** crystallises in the triclinic system (space group $P\bar{1}$) with the unit-cell parameters a = 13.8036(4), b = 18.8373(4), c = 20.1978(6) Å, α = 65.772(2)°, β = 74.120(1)°, γ = 71.922(1)° and V = 4487.6(2) Å^3 (Z = 1). Compound **1** is a neutral tetranuclear complex and is best described as an iron(II) square sandwiched between two thiacalixarene macrocycles. Each iron centre is six-coordinate in a trigonal-prismatic geometry made up of four phenoxy oxygen atoms plus two sulfur atoms. Compound **2** is a neutral centrosymmetric decanuclear complex and may be viewed as a dimer of double chloro-bridged pentanuclear complexes. Mössbauer spectra of compounds **1** and **2** have been recorded at different temperatures between 80 and 298 K. Each sub-spectrum can be characterised by a quadrupolar doublet corresponding to different iron environments where all iron ions are in high-spin state (S = 2). The hyperfine parameters (quadrupole splitting, isomer shift and line width) as well as the Mössbauer spectra area-ratios are in good agreement with the crystallographic data. The two compounds exhibit magnetic behaviours indicating that antiferromagnetic interactions occur between the iron(II) centres. The simulation of the magnetic susceptibility was done in the case of compound **1** with a single exchange coupling constant (J = –4 cm^{-1} and g = 2.02) between the iron(II) ions $[H = -J(S_1S_2 + S_2S_3 + S_3S_4 + S_1S_4)]$.

Introduction

As part of our involvement in molecular magnetism[1,2] we are interested in molecular polymetallic species. One of our motivations lies in the so-called single-molecule magnets (SMMs),[3,4] which behave as single-domain magnetic particles. Their relevance as potential components of quantum computing[5] has triggered much of the recent progress in the field of molecular magnetism, as well as in those of the polynuclear complexes.[6] Many polynuclear complexes have been isolated but few exhibit SMM properties, or at temperatures that are too low for applications. Therefore, there is a real need for discovering new systems. Another motivation lies simply in the chemical point of view, where there is a general interest in finding rational routes for synthesising molecular polymetallic species in the frame of the emerging nanosciences. Up to now many clusters have been obtained serendipitously, but as more examples become available we may be expected to find some rules for predetermination.[7] The main difficulty in the formation of molecular polymetallic aggregates is to avoid the polycondensation of the metal ions, which is generally afforded by using multidentate and bulky organic capping ligands.[8]

With this in mind, we have investigated the coordination chemistry of thiacalixarene macrocycles, whose chemistry is well known by some of us.[9–12] Compared to the related calixarenes, the chemistry of thiacalixarenes is recent as the synthesis of thiacalixarenes and their sulfinyl and sulfonyl derivatives has been known only since the late 90's.[13–20] These early reports pointed out the high complexation ability of thiacalixarene macrocycles.[16,17,21,22] This was then proved by the isolation and structural characterisation of complexes of *p*-*tert*-butylthiacalix[4]arene with Co^{II},[23,24] Ni^{II},[23] Cu^{II},[25] Zn^{II},[24,26] UO$_2$,[27] Nd^{III},[28] and also with the alkali metals.[29] These complexes are either mononu-

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clear (UO_2 and Zn^{II}),[26,27] dinuclear (Co^{II} and Ni^{II}),[23] trinuclear (Co^{II} and Zn^{II})[24] or tetranuclear (Cu^{II} and Nd^{III}).[25,28] Higher nuclearities have even been found for complexes of *p-tert*-butylthiacalix[6]arene,[30,31] with examples of tetranuclear Ni^{II},[30] pentanuclear Co^{II},[30] decanuclear Cu^{II}[31] and also some pentanuclear heterometallic[30] $Ni^{II}_4M^{II}$ (M = Mn, Co, Cu) complexes. In a few cases the magnetic properties of these complexes were also reported.[24–26,31] Despite these attractive results, thiacalixarene complexes are still somewhat scarce, which may be attributed to complications when crystallising them following conventional methods.[24] In contrast, we found that, under solvothermal conditions, *p-tert*-butylthiacalix[4]arene and its sulfonyl and sulfinyl derivatives give polynuclear complexes with most d- and f-block transition-metal ions. We recently reported the synthesis, crystal structures and magnetic properties of two tetranuclear manganese(II) complexes that we synthesised under solvothermal conditions in methanol with *p-tert*-butylthiacalix[4]arene and *p-tert*-butylsulfinylthiacalix[4]arene.[32]

In this paper we describe the syntheses, crystal structures and Mössbauer and magnetic properties of a tetranuclear complex $[Fe^{II}_4(L)_2]$ (**1**) and a decanuclear complex $[Fe^{II}_{10}(L)_4Cl_4]$ (**2**), both of which were obtained with *p-tert*-butylthiacalix[4]arene (L).

Results and Discussion

Synthesis

Most previously reported thiacalixarene complexes were synthesised and crystallised under conventional conditions, that is in an open vessel and below the boiling point of the solvent.[24–31] Typical solvents are $CHCl_3$ or CH_2Cl_2, in which the thiacalixarenes are very soluble,[15] or DMF or DMSO, where they dissolve quickly upon adding a base such as triethylamine. The down side is that the resulting complexes are also generally very soluble in those solvents, which complicates the growth of single crystals. This is generally achieved with help of a second solvent in which the thiacalixarene complexes are not or sparingly soluble, such as CH_3CN, EtOH or MeOH. After trials we found that these conditions and solvents did not afford a strong control of the formation of the clusters and their crystallisation. Water or alcohol are generally better solvents as regards the solubility of the metal salts. Unfortunately, under normal conditions the thiacalixarene macrocycles are sparingly soluble in these solvents This caused us to try the solvothermal synthesis method, which is known to be particularly suited for the reaction and crystallisation of materials with poor solubility as it allows high temperatures with a large panel of solvents in a way that generally favour solubilisation.[33,34] The advantage of this method is that not only is it a way to synthesise new compounds but it is also a way to get them in a crystalline form, which is generally not an easy task under normal conditions. During the last decade this method, which has long been restricted to water (hydrothermal), has undergone a real renaissance with the increasing use of non-aqueous solvents and has also proved to be particularly efficient in coordination chemistry for the synthesis of polyoxometallates,[35,36] metal clusters[37–42] or extended compounds.[43–46]

Under standard conditions we were unable to isolate any iron(II) complexes of the thiacalixarene. In contrast, under solvothermal conditions in methanol, as described in the Experimental Section, we were able to synthesise the two iron(II) compounds (**1** and **2**) reported in this paper reproducibly, in good yields and in the form of single crystals. No base was required for the deprotonation of the phenol groups for either complex. In both cases the compounds were obtained by treating $FeCl_2$ with *p-tert*-butylthiacalix[4]arene (LH_4). The difference in the synthesis of compounds **1** and **2** lies in the use of a different thiacalixarene/Fe ratio: for ratios from 1:2 up to 1:3 only the tetranuclear complex **1** is obtained, while compound **2** is obtained only when the thiacalixarene/Fe ratio becomes greater than 1:4. Ascorbic acid was used to avoid possible oxidation of the iron(II) ions. This was particularly required for compound **2**, which is better kept under argon. Indeed, when the reaction is carried without ascorbic acid then the isolated crystals always show some dark zones due to some oxidation of the iron(II) ions. When ascorbic acid is used no oxidation occurs, as demonstrated by the Mössbauer spectra. In contrast, compound **1** is insensitive to oxygen and can be handled without any particular care.

Description of the Crystal Structures

$[Fe^{II}_4(L)_2]\cdot H_2O$ (1)

The crystal structure of compound **1** comprises two crystallographically independent entities called hereafter M1 and M2 and exemplified for M1 in Figure 1. One water molecule crystallises per $[Fe_4(L)_2]$ entity. A selection of interatomic distances and angles is given in Table 1.

The asymmetric unit of the M1 entity is built from two independent iron(II) ions (Fe1 and Fe2), two *tert*-butylphenoxy groups and two sulfur atoms (S1 and S2). These latter play the role of linker between the *p-tert*-butylphenoxy groups (four in total) to form the thiacalixarene macrocycle. The asymmetric unit of the M2 entity is built from only one crystallographically independent iron(II) ion (Fe3), two independent *p-tert*-butylphenoxy groups and one sulfur atom (S3). As above, these sulfur atoms link the phenoxy groups to form the thiacalix[4]arene macrocycle. Thus, each of the M1 and M2 entities is built from an iron square sandwiched between two *p-tert*-butylthiacalix[4]arene macrocycles. All phenoxy oxygen atoms are doubly bridging. The complex molecules are neutral. A similar molecular structure $[M^{II}_4(L)_2]$ has been reported previously for a tetranuclear copper(II) complex[24] and by us with manganese(II).[32]

In both entities (M1 and M2) the eight phenoxy oxygen atoms lie at the corner of a compressed square-based parallelepiped. The edges of the parallelepiped are nearly orthogonal [89.5(1)° and 90.0° for M1 and M2, respectively]. The

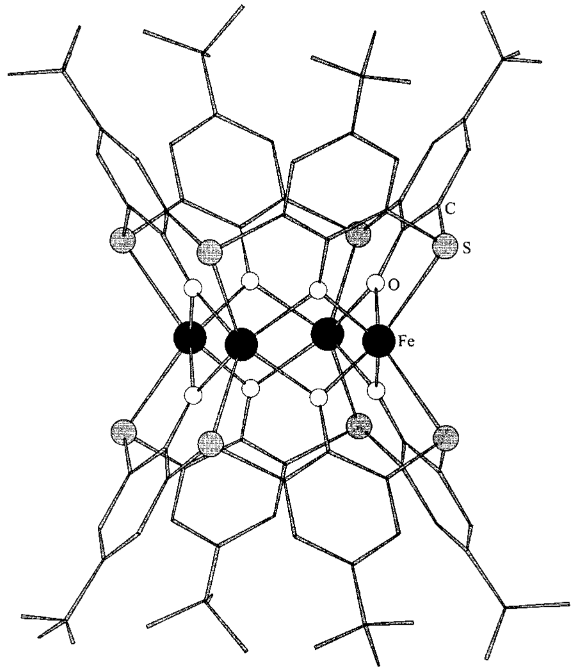

Figure 1. Molecular structure of one $[Fe_4(L)_2]$ tetranuclear iron(II) entity (M1) for compound **1**; Fe: black; S: grey; O: white.

Table 1. Selected interatomic distances [Å] and angles [°] for **1**.[a]

Fe1···Fe2	3.187(3)	Fe3···Fe3	3.192(4)
Fe1–O1	2.04(1) [×4]	Fe2–O1	2.04(1) [×4]
Fe3–O2	2.03(1) [×2]	Fe3–O3	2.04(1) [×2]
Fe1–S1	2.639(4) [×2]	Fe2–S2	2.623(4) [×2]
Fe3–S3	2.621(3) [×2]		
Fe1–O1–Fe2	102.5(6)	Fe3–O2–Fe3	103.36(6)
Fe3–O3–Fe3	103.6(8)		

[a] Numbers in square brackets indicate the number of identical bonds due to symmetry.

parallelepiped is capped above and below by the two thiacalixarene macrocycles on the square bases (Figure 1). The iron(II) ions are located in the middle and above each of the four lateral faces of the parallelepiped (Figure 1). The deviations of the iron(II) ions from the $[O_4]$ mean plane made by the four phenoxy oxygen atoms are 0.7511 (Fe1), 0.7617 (Fe2) and 0.8032 Å (Fe3).

Each iron(II) ion exhibits the same six-coordinate $[O_4S_2]$ environment (Figure 2) made by four phenoxy oxygen atoms [Fe1–O1 = 2.04(1), Fe2–O1 = 2.04(1), Fe3–O2 = 2.03(1) and Fe3–O3 = 2.04(1) Å] and two sulfur atoms [Fe1–S1 = 2.639(4), Fe2–S2 = 2.623(4) and Fe3–S3 = 2.621(3) Å]. The Fe–O bond lengths are in agreement with previously reported Fe^{II}–O(phenoxy) distances.[47–54] The Fe^{II}–S bond lengths are longer than the few previously reported for thioether complexes of high-spin iron(II) (2.20–2.29 Å).[55] This should be due to the rigidity of the macrocycle, which does not allow the sulfur atoms to come closer to the iron(II) ions. Careful analysis of the interatomic distances and angles around the iron(II) ions reveals that the coordination polyhedrons are distorted trigonal-prismatic, as shown in Figure 2. The triangular faces of the trigonal prism are defined by two phenoxy oxygen atoms and one sulfur atom belonging to the same thiacalixarene macrocycle and are equilateral. The trigonal twist angles[56] are zero but the triangular faces are not parallel and make angles of 42.16°(Fe1), 42.35°(Fe2) and 41.44°(Fe3). The four coordination polyhedra are orthogonal to each other (Figure 2). The Fe–O–Fe angles are in the range 102.5(6)–103.6(8)° (Table 1).

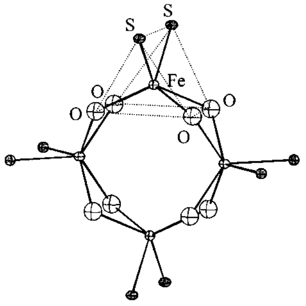

Figure 2. Representation of the iron(II) coordination polyhedra in $[Fe_4(L)_2]$ (**1**); dotted lines indicate the trigonal prism.

In the crystal the $[Fe_4(L)_2]$ entities are packed in infinite molecular chains running parallel to the *b* axis of the unit-cell in such a way that two successive molecules are rotated by 90° with respect to each.

$[Fe_{10}(L)_4Cl_4]\cdot 2H_2O$ (2)

The crystal structure of compound **2** is made up of neutral, centrosymmetrical decanuclear iron(II) moieties which are dimers of two pentanuclear $[Fe^{II}_5(L)_2Cl_2]$ units linked by a bis-chloro bridge, as shown in Figure 3. A selection of interatomic distances and angles is given in Table 2.

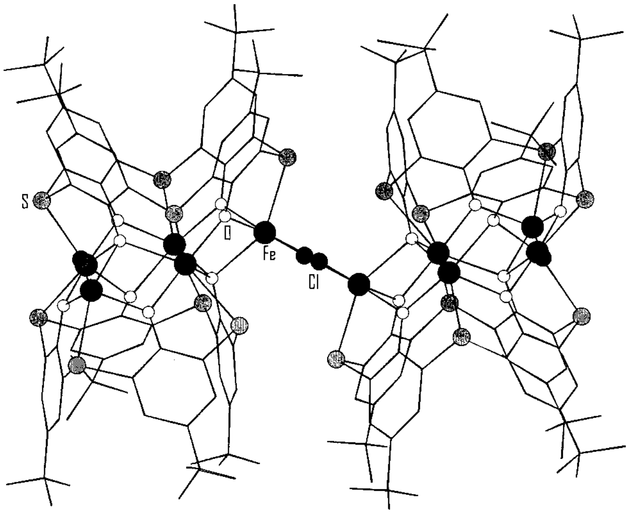

Figure 3. Molecular structure of the $[Fe_{10}(L)_4Cl_4]$ decanuclear iron(II) entities in compound **2**; Fe: black; Cl: dark grey; S: grey; O: white.

Each asymmetric $[Fe^{II}_5(L)_2Cl_2]$ unit comprises five iron(II) ions sandwiched between two thiacalixarene macrocycles. The coordination scheme is drastically different from that found for compound **1**, where the two thiacalixarene

Table 2. Selected interatomic distances [Å] and angles [°] for **2**.[a]

Fe1–O7	2.079(7)	Fe1–O8	2.087(7)
Fe1–O1	2.231(6)	Fe2–O4	2.005(7)
Fe2–O3	2.034(7)	Fe2–O5	2.287(7)
Fe3–O8	2.012(7)	Fe3–O4	2.045(6)
Fe3–O1	2.218(7)	Fe3–O5	2.230(7)
Fe4–O3	2.032(6)	Fe4–O6	2.058(7)
Fe4–O2	2.064(7)	Fe4–O5	2.202(7)
Fe5–O7	1.996(7)	Fe5–O6	2.009(7)
Fe5–O2	2.213(7)	Fe5–O1	2.223(7)
Fe1–S7	2.520(3)	Fe2–S4	2.492(3)
Fe3–S6	2.633(3)	Fe3–S3	2.648(3)
Fe4–S5	2.532(3)	Fe4–S1	2.688(3)
Fe5–S2	2.502(3)	Fe5–S8	2.782(3)
Fe1–Cl2	2.409(3)	Fe1–Cl2#1	2.442(3)
Fe2–Cl1	2.225(4)		
Fe1···Fe5	3.310(2)	Fe1···Fe3	3.353(2)
Fe1···Fe1	3.488(3)	Fe2···Fe4	3.254(2)
Fe2···Fe3	3.308(2)	Fe3···Fe5	3.608(2)
Fe3···Fe4	3.752(2)	Fe4···Fe5	3.258(2)
Cl2–Fe1–Cl2#1	88.10(1)	Fe1–Cl2–Fe1#1	91.9(1)
Fe3–O1–Fe5	108.7(3)	Fe4–O5–Fe3	115.7(3)
Fe3–O1–Fe1	97.8(3)	Fe4–O5–Fe2	92.9(3)
Fe5–O1–Fe1	96.0(2)	Fe3–O5–Fe2	94.2(3)
Fe5–O2–Fe4	99.2(3)	Fe4–O6–Fe5	106.5(3)
Fe2–O3–Fe4	106.3(3)	Fe1–O7–Fe5	108.6(3)
Fe3–O4–Fe2	109.5(3)	Fe1–O8–Fe3	109.8(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z$.

macrocycles bring eight μ_2-oxygen phenoxy atoms and eight sulfur atoms equally shared between the four iron(II) ions. This is sufficient to provide the charge and coordination number required by the four iron(II) centres with an identical environment. The situation is completely different for compound **2**. As in **1** there are two thiacalixarenes but they have to accommodate five iron(II) ions. The eight sulfur atoms and the eight phenoxy oxygens are not sufficient to fulfil both electro-neutrality and the iron(II) coordination. So in this case this is assumed by two extra chloride ions (Cl1 and Cl2) coordinated to Fe2 and Fe1, respectively, and by μ_3-phenoxy oxygen atoms. What may seem messy at first glance, however, does show some symmetry (Figure 4). Let us consider only the asymmetric $[Fe^{II}_5(L)_2Cl_2]$ unit (Figure 4). Fe1 and Fe2 have practically the same environment of three phenoxy oxygen atoms, one sulfur atom and one chloro ligand. The difference between the two is that in the case of Fe1 the chloride ion is bridging a symmetric Fe1 ion such that Fe1 is six-coordinate with a distorted octahedral polyhedron. In the case of the Fe2 ion, however, the chloro ligand is not bridging and the Fe2 ion is only five-coordinate. It may seem surprising that Cl1 is bridging but Cl2 is not, therefore the structure was checked for possible links to neighbouring iron(II) centres; none was found. The five-coordinate geometry of Fe2 was determined by means of the geometric parameter $\tau = (\beta - \alpha)/60$, where β and α are the two largest ligand–metal–ligand bond angles and $\beta > \alpha$.[57] In the case of Fe2 β is 149.3(2)° (O5–Fe2–S4 angle) and α is 144.1(2)° (O3–Fe2–Cl1), which gives a τ parameter of 0.09, in agreement with a square-pyramidal geometry. The Fe4 and Fe5 ions are both six-coordinate to two sulfur atoms, three phenoxy μ_2-oxygen atoms and one phenoxy μ_3-oxygen atom. The Fe3 ion is also six-coordinate but is bound to two sulfur atoms, two μ_2-oxo phenoxy atoms and two μ_3-oxo phenoxy atoms (Figure 4). The six-coordinate geometry around Fe5 and Fe4 is a distorted octahedron. Fe3 is connected through the phenoxy oxygen atoms to the four other iron(II) ions (Fe1, Fe2, Fe4, Fe5). Fe3 and Fe1 and Fe3 and Fe2 are μ_2-O and μ_3-O bridged, respectively, while Fe3 and Fe4 and Fe3 and Fe5 are μ_3-O bridged. Fe1 and Fe5 and Fe2 and Fe4 are μ_2-O and μ_3-O bridged, respectively, while Fe4 and Fe5 are doubly μ_2-O bridged. Fe1 and Fe1# are doubly μ_2-Cl bridged.

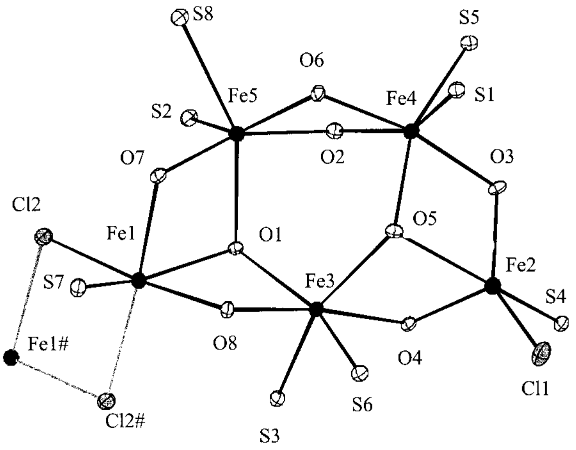

Figure 4. Representation of the coordination environment in compound **2**.

The mean value for the Fe–O(μ_2) bond length [2.11(10) Å] in **2** is slightly longer than that for **1** [2.04(1) Å] (Tables 1 and 2). The Fe–O(μ_3) bond length [2.202(7)–2.287(7) Å] and Fe–O–Fe bond angles [92.9(3)–115.7(3)°] are in the range of those previously reported.[51]

Mössbauer Spectroscopy

$[Fe^{II}_4(L)_2]\cdot H_2O$ (1)

Mössbauer spectra of compound **1** recorded at 80 and 293 K are shown in Figure 5. The Mössbauer parameters are given in Table 3. The spectra exhibit one quadrupolar doublet with characteristics of an iron(II) species in a high-spin state ($S = 2$). The four crystallographically slightly different iron centres (identical microenvironments: four oxygen and two sulfur donor atoms) are not distinguishable. The high value of the quadrupole splitting corresponding to a singlet orbital level (2.83 mm s^{-1} at 80 K) can be well explained by the trigonal-prismatic geometry of these sites, which represents a very low symmetry compared to the highest, octahedral one. In addition, the relative independence of the quadrupole splitting with the temperature suggests that the ground state is well isolated.

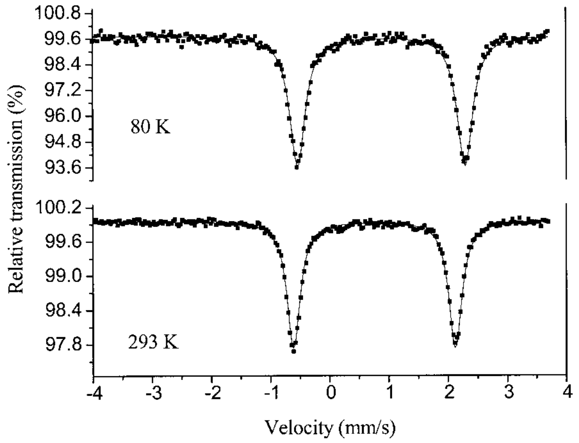

Figure 5. Mössbauer spectra of compound **1** at 80 and 293 K.

Table 3. Mössbauer parameters for compound **1**.

T [K]	δ[a] [mm s^{-1}]	Δ[b] [mm s^{-1}]	Γ[c] [mm s^{-1}]
80	0.877(1)	2.829(3)	0.321(4)
293	0.7568(7)	2.733(2)	0.271(2)

[a] Isomer shift relative to natural iron at room temperature. [b] Quadrupole splitting. [c] Full line width at half maximum.

[Fe$_{10}$(L)$_4$Cl$_4$]·2H$_2$O (2)

Mössbauer spectra of compound **2**, shown in Figure 6, were recorded at 80, 150 and 298 K. The Mössbauer parameters are given in Table 4. The shape of these spectra could indicate some texture effect (asymmetrical spectra). In order to clarify this point, another measurement was carried out at 80 K after thoroughly grinding the sample. The resulting spectrum (not shown) revealed no difference compared to the previous one. The most evident fit of these spectra would be two doublets referring to the sites with five- and sixfold coordination. Possible reasons for this behaviour are as follows: 1) a large difference in their isomer shift, 2) a large difference in their quadrupole splitting, and 3) a quadrupole splitting distribution (if the isomer shifts are the same). However, none of these hypotheses describes the global spectra properly, therefore either the molar ratio of the different sites is not in good agreement with the crystallographic data or the hyperfine parameters cannot be correlated with the X-ray structure. Fitting by three Lorentzian functions was found to describe the spectra reasonably well. The preliminary assumptions for finding the best fits were the following:

the sub-spectrum corresponding to the iron centre with fivefold coordination shows the largest quadrupole splitting;[58]

the molar ratios of the different iron microenvironments Fe1, Fe2 and (Fe3, Fe4, Fe5), as given from the X-ray structure (Figure 4), are 20, 20 and 60%;

the sub-spectrum representing three different iron centres at the same time (Fe3, Fe4 and Fe5; Figure 4) has the largest line-width because of the slight differences between these sites.

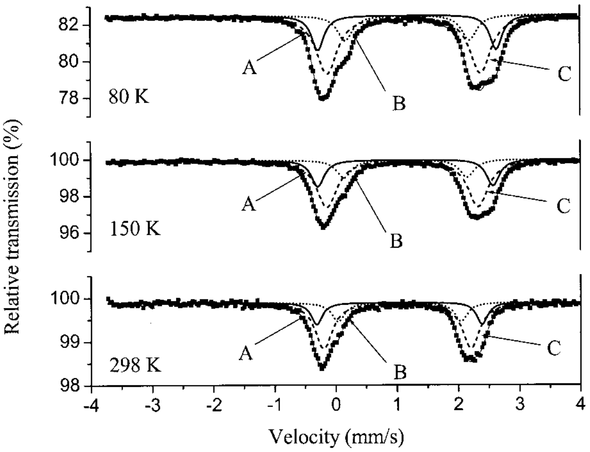

Figure 6. Mössbauer spectra of compound **2** at 80, 150 and 298 K. The sub-spectra A (solid lines), sub-spectra B (dotted lines) and sub-spectra C (dashed lines) hold for the fit of the data as explained in the text.

Table 4. Mössbauer parameters for compound **2** (fixed parameters for the fit are shown in italics).

T [K]	Fe[a]	A/A_{tot}[b] [%]	δ[c] [mm s^{-1}]	Δ[d] [mm s^{-1}]	Γ[e] [mm s^{-1}]
80	1	18.74(4)	1.180(2)	2.02(7)	0.30(1)
	2	21.21	1.177(2)	2.909(4)	0.247(3)
	3, 4, 5	60.05(5)	1.121(1)	2.503(5)	0.419(6)
150	1	16.69(2)	1.145(3)	2.004(8)	0.29
	2	21.95	1.142(2)	2.856(5)	0.258(5)
	3, 4, 5	61.36(3)	1.093(1)	2.466(6)	0.405(7)
298	1	19.13	1.042(5)	2.00(1)	0.26(1)
	2	19.13	1.038(4)	2.70(1)	0.22(1)
	3, 4, 5	61.73(1)	1.004(2)	2.401(7)	0.34(1)

[a] Iron site(s) in compound **2** (see Figure 4). [b] A/A_{tot}: Mössbauer spectrum area ratio. [c] Isomer shift relative to natural iron at room temperature. [d] Quadrupole splitting. [e] Full line width at half maximum.

The temperature dependence of the isomer shift of every sub-spectrum representing different iron microenvironments must be linear, following the second-order Doppler shift.[59]

The best fit is displayed in Figure 6. Each doublet represents iron(II) species in a high-spin state ($S = 2$). Sub-spectra A represent the Fe2 iron centre within a fivefold coordination (Figure 4) because it displays the largest quadrupole splitting, sub-spectra B represent the Fe1 iron centre (Figure 4) with the apparently low molar ratio (Table 4) and sub-spectra C represent the Fe3, Fe4 and Fe5 (Figure 4) iron centres, which have the same neighbouring atoms in the ligand sphere (four oxygen and two sulfur atoms). The Mössbauer parameters of these sub-spectra should be different because of the slight differences in the crystallographic environments, although these are not resolved in the spectra. However, this doublet has a higher line-width than the other doublets (see Table 4). The isomer shift of each doublet is relatively low despite the high electronegativity of the coordinating atoms. This is due to the bridging oxygen atoms, which are coordinated to three (O1, O5) or to two (O2, O3, O4, O6, O7 and O8) different iron centres at the same time, and therefore the donated electron density decreases. The relative independence of the quadrupole splitting with the temperature suggests that the electronic excited states are not populated at 298 K.

Magnetic Properties

The results are displayed in the form of the product of the magnetic susceptibility and the temperature (χT) in Figures 7 and 8. For both compounds, all features of the curves were reproducible with different samples and no loss of water occurred during the measurements (see Experimental Section).

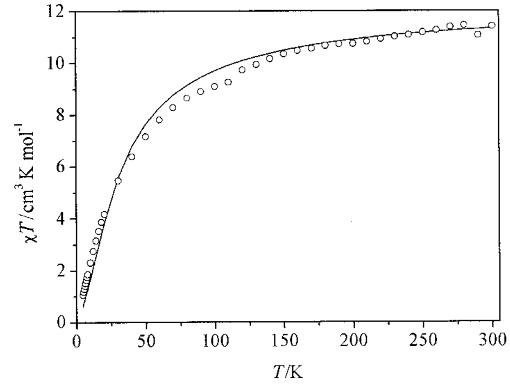

Figure 7. Temperature dependence of the product of the molar magnetic susceptibility (χ) with temperature (χT) for compound **1** (circles). The solid line shows the best fit of the data.

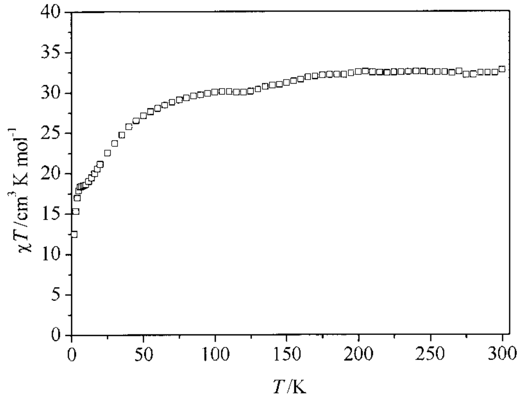

Figure 8. Temperature dependence of the product of the molar magnetic susceptibility (χ) with temperature (χT) for compound **2** (squares).

$[Fe^{II}_4(L)_2]\cdot H_2O$ (1)

At 300 K the χT product is 11.4 cm^3 K mol^{-1} for **1** (Figure 7). This value is close to that expected for four uncoupled iron(II) ions (12.0 cm^3 K mol^{-1}). Upon cooling the χT product decreases continuously down to zero while the magnetic susceptibility (χ) shows a maximum at 5 K. Linearisation of the $1/\chi$ vs. T curve in the range 100–300 K shows Curie–Weiss regimes with a Curie constant, C, of 12.9 cm^3 mol^{-1}, which is also close to the value expected for four uncoupled iron(II) ions (12.0 cm^3 K mol^{-1}). This behaviour indicates that antiferromagnetic interactions occur between the iron(II) ions. Intermolecular interactions can be ruled out because the tetranuclear cores are well separated from each other due to screening by the bulky thiacalixarene ligands. The shortest intermolecular Fe–Fe distances are longer than 16.95(3) Å.

As shown in the structural section, the four iron centres, independently of the entities M1 and M2, have identical environments, which is also in agreement with the Mössbauer study. Moreover, the Fe–O(phenoxy) bond length and the Fe–O–Fe bond angles, which are relevant to magnetic exchange couplings, do not show any striking differences. Accordingly, the magnetic data of compound **1** were analysed by considering one iron(II) square with the four exchange couplings on the edges as equal (i.e. $J = J_{12} = J_{13} = J_{34} = J_{14}$) and no diagonal interactions ($J_{13} = J_{24} = 0$), based on the Heisenberg Hamiltonian $H = -J(S_1S_2 + S_2S_3 + S_3S_4 + S_1S_4)$.

The energy levels of this Hamiltonian can be expressed as $E = -J[S(S + 1) - S_{13}(S_{13} + 1) - S_{24}(S_{24} + 1)]$, where S is the total spin and S_{13} and S_{24} are the intermediate spins. The S_{13} and S_{24} values vary from 0 to 4, and for each pair of intermediate spins the total spin takes values from $|S_{13} - S_{24}|$ to $S_{13} + S_{24}$.

The best least-square fitting of the χT vs. T data with the van Vleck equation based on the above energy levels gives a poor fit, with $J = -4$ cm^{-1} and $g = 2.02$. However, the value of the exchange coupling is in the range of those previously reported for other Fe^{II}–O–Fe^{II} systems.[47,48,60–62] The discrepancy between the fit with the experimental data at low temperatures is due to the fact that no zero-field splitting terms were taken into account. The apparent plateau between 100 and 120 K, which is not accounted for by the calculated curve, cannot yet be explained.

$[Fe_{10}(L)_4Cl_4]\cdot 2H_2O$ (2)

The χT product for this complex is 32.8 cm^3 K mol^{-1}. This value is slightly larger than that expected for ten uncoupled iron(II) ions (spin only 30.0 cm^3 K mol^{-1}) as is normally observed for high-spin iron(II) complexes. Upon cooling, χT decreases slowly while the magnetic susceptibility (χ) increases continuously without any maximum in the temperature range 300–2 K. At 9 K there is a small shoulder on the χT curve (with a value of 18.4 cm^3 K mol^{-1}), then χT decreases rapidly. Linearisation of the $1/\chi$ vs. T curve in the range 100–300 K shows Curie–Weiss regimes with a Curie constant of 34 cm^3 mol^{-1}. This behaviour indicates that antiferromagnetic interactions also occur between the iron(II) ions in **2** that are weaker than in compound **1**. One explanation for the shoulder at 9 K is that the magnetic interaction (Fe1···Fe1#) through the bis-chloro bridge is weaker than those within the pentanuclear moieties through the phenoxy and oxo bridges. Therefore, the antiferromagnetic coupling of the Fe^{II} ions within each pentanuclear moiety leads to a non-zero resultant spin, which explains the shoulder; the decrease at lower temperatures is due to the coupling through the bis-chloro bridge. We did not try to fit the magnetic data owing to the large number of magnetic interactions between the iron(II) centres in **2**. Indeed, the fitting of such a system by matrix-diagonalizing techniques is very complicated due to the high nuclearity of the cluster and its low symmetry. The Monte Carlo technique has previously been used for the magnetic data analysis of a decanuclear iron(III) cluster,[63] but the corresponding Heisenberg Hamiltonian contained only three parameters. In our case we have at least five exchange parameters to take into account and a zero-field splitting parameter must probably also be added.

Concluding Remarks

The two iron(II) complexes reported here, which were obtained by a solvothermal route, confirm the high coordination ability of the thiacalixarene macrocycles. They are among the very few iron(II) polynuclear complexes of high nuclearities. Indeed, there are less than ten Fe^{II}_4 clusters[51,64–68] and, to the best of our knowledge, compound **2** is the first iron(II) decanuclear complex. It should be noted that compound **1** is particularly stable as it appears to be insensitive to oxidation by air. Both compounds exhibit weak Fe···Fe intramolecular antiferromagnetic exchange couplings. We are now engaged in a program to synthesise clusters of higher nuclearities with mixed-valence or different metals.

Experimental Section

All chemicals and solvents were used as received; all preparations and manipulations were performed under aerobic conditions. The *p-tert*-butylthiacalix[4]arene ligand was synthesised by the published procedures.[13,14]

Synthesis of $[Fe^{II}_4(L)_2]\cdot H_2O$ (1): Compound **1** was isolated in the form of pale-yellow, needle-shaped crystals from the reaction of *p-tert*-butylthiacalix[4]arene (LH_4; 0.15 g, 0.2 mmol) with $FeCl_2$ (0.050 g, 0.4 mmol), ascorbic acid (0.07 g, 0.4 mmol) and methanol (23 mL) in a 43-mL, Teflon-lined autoclave under autogenous pressure at 170 °C for 3 d. The crystals were isolated by filtration then washed with methanol and dried in vacuo. Compound **1** is stable in air and is insoluble in common organic solvents. Yield: 66%. $C_{80}H_{90}Fe_4O_9S_8$ (1675.5): calcd. C 57.34, H 5.41, Fe 13.33, S 15.32; found C 57.77, H 5.4, Fe 13.05, S 15.6.

Synthesis of $[Fe_{10}(L)_4Cl_4]\cdot 2H_2O$ (2): Compound **2** was obtained in the form of pale-yellow, irregular, parallelepiped-shaped crystals from the reaction of *p-tert*-butylthiacalix[4]arene (LH_4; 0.15 g, 0.2 mmol) with $FeCl_2$ (0.10 g, 0.8 mmol), ascorbic acid (0.07 g, 0.4 mmol) and methanol (23 mL) in a 43-mL, Teflon-lined autoclave under autogenous pressure at 170 °C for 3 d. The crystals were isolated by filtration then washed with methanol and dried in vacuo. Compound **2** is best kept under argon and was found to be soluble in most common organic solvents ($CHCl_3$, CH_2Cl_2, etc.). Yield: 52%. $C_{160}H_{180}Cl_4Fe_{10}O_{18}S_{16}$ (3604.4): C 53.31, H 5.03, Cl 3.93, Fe 15.50, S 14.23; found C 53.03, H 4.87, Cl 4.05, Fe 16.05, S 14.57.

X-ray Crystallography

Data Collection: Experimental details for $[Fe_4(L)_2]\cdot H_2O$ (**1**) and $[Fe_{10}(L)_4Cl_4]\cdot 2H_2O$ (**2**) are given in Table 5. Data processing was performed with the KappaCCD analysis software[69] and the lattice constants were refined by a least-squares refinement using 6303 reflections ($1.0° < \theta < 27.9°$) and 12035 reflections ($1.0° < \theta < 27.5°$) for **1** and **2**, respectively.

Structure Solution and Refinement: $[Fe^{II}_4(L)_2]\cdot H_2O$ (**1**) crystallises in the orthorhombic system. According to the observed systematic extinctions, the structure was solved in the *Immm* space group (no. 71). $[Fe^{II}_{10}(L)_4Cl_4]\cdot 2H_2O$ (**2**) crystallises in the triclinic system and the structure was solved in the $P\bar{1}$ space group (no. 2). The unit-cell parameters, crystal system, space group and refinement details for both of them are summarised in Table 5. Both structures were

Table 5. Crystal data and structure-refinement parameters for compounds **1** and **2**.

	$[Fe^{II}_4(L)_2]\cdot H_2O$ (**1**)	$[Fe_{10}(L)_4Cl_4]\cdot 2H_2O$ (**2**)
Formula	$C_{80}H_{90}Fe_4O_9S_8$	$Fe_{10}C_{160}H_{180}Cl_4S_{16}O_{18}$
Fw ($g mol^{-1}$)	1675.5	3604.4
T [K]	293	293
λ(Mo-$K\alpha$) [Å]	0.71069	0.71069
Crystal system	orthorhombic	triclinic
Space group	*Immm* (no. 71)	$P\bar{1}$ (no. 2)
a [Å]	17.8308(4)	13.8036(4)
b [Å]	19.1372(3)	18.8373(4)
c [Å]	28.8391(6)	20.1978(6)
α [°]	90	65.772(2)
β [°]	90	74.120(1)
γ [°]	90	71.922(1)
V [$Å^3$]	9840.8(3)	4487.6(2)
Z	2	1
D [$g cm^{-3}$]	1.130	1.320
μ [mm^{-1}]	0.680	1.083
Crystal size [mm]	0.015 × 0.015 × 0.025	0.015 × 0.020 × 0.060
Reflections collected	11680	26194
Independent reflections	6353	15841
Goodness of fit on F	1.06	1.20
$R^{[a]}$ [$I > 3\sigma(I_o)$]	0.1114	0.0578
$R_w^{[b]}$	0.1206	0.0665
Res. electron density [$e Å^{-3}$]	–0.98, 2.24	–0.66, 1.09

[a] $R = \Sigma(|F_o - F_c|)/\Sigma|F_o|$. [b] $R_w = \{\Sigma[w(|F_o - F_c|)^2]/\Sigma[w|F_o|^2]\}^{½}$.

solved by direct methods using SIR97[70] in combination with Fourier difference syntheses and then refined against *F* using reflections with $[I > 3\sigma(I)]$ with the CRYSTALS program.[71] Hydrogen atoms were not refined and were placed either theoretically or found in the Fourier difference maps. All the thermal atomic displacements for non-hydrogen atoms and non-oxygen atoms from water molecules were successfully refined anisotropically.

CCDC-278036 (for **1**) and -278037 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic Measurements: The magnetic susceptibilities were measured on bulk polycrystalline samples placed in a Teflon-capped basket, in the range 2–300 K, with a Quantum Design MPMS SQUID magnetometer operating at a field strength of 0.5 T. The data were corrected for the sample holder, the diamagnetism of the previously measured thiacalixarene macrocycle and the diamagnetism of other constituent atoms using Pascal's constants. As the compounds described in the paper contain water of crystallisation, which may be lost during the measurements, every sample was weighed before and after measurement and did not show any lost of weight. For both compounds, the magnetic measurements were also performed on several samples from different preparations.

Mössbauer Spectroscopy: Mössbauer spectra were recorded using a constant acceleration type spectrometer equipped with a ^{57}Co source (15 mCi). The spectra of compounds **1** and **2** were recorded at 80 and 293 K and at 80, 150 and 298 K, respectively. Mössbauer isomer shifts are given relative to natural iron at room temperature. Least-squares fitting of the Mössbauer spectra was carried out with the assumption of a Lorentzian line-shape using MossWinn 3.0.[72]

Supporting Information (see footnote on the first page of this article): Figure S1. Representation of the two asymmetric moieties (M1 and M2) in compound **1**.

Acknowledgments

The "Région Rhône-Alpes" is gratefully acknowledged for financial support and a postdoctoral fellowship to C.D. Support for magnetic measurements was provided by the "Commissariat à l'Energie Atomique" (CEA) through a "Laboratoire de Recherche Conventioné" (LRC no. DSM-03-31).

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Received: July 19, 2005